First-Principles Calculations of Phase Equilibria and Transformation Dynamics of Fe-Based Alloys

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Theoretical procedures of first-principles calculations of phase stability and phase equilibria are summarized. The present scheme is shown to be able to reproduce the transition temperatures with surprisingly high accuracy for Fe-Pd and Fe-Pt systems. The main emphasis of the present report is placed on the extension of the first-principles calculation to transition dynamics calculations. This is performed by combining the cluster variation method with the phase-field method via a coarse graining operation. The time evolution process of antiphase boundaries associated with $L1_0$ ordering for Fe-Pd system is demonstrated.

1. Introduction

Recent progress in first-principles calculations of phase diagrams has been remarkable, and for certain systems, the transition temperatures are obtained with surprisingly high accuracy.[1-5] Although several approaches to first-principles phase diagram calculations are available, main schemes based on a combination of electronic structure total energy calculations with statistical mechanics methods such as the cluster variation method[6] or Monte Carlo simulations are well established.

Remaining problems in the future direction of the first-principles calculations of phase stability and phase equilibria can be summarized as (a) extension to a multicomponent systems, (b) application to a low symmetry structures, and (c) separate introduction of chemical interaction and other interactions, such as magnetic interactions. Extension to multicomponent systems is a requirement for practical purposes, but applying a brute force first-principles calculation to a multicomponent system is a questionable approach. In particular, in view of excellent tools of the CALPHAD-type software packages supported by powerful databases, one needs to focus on the well-tuned problems for which only first-principles calculation can provide answers.

The second subject of the low-symmetry structure, in a sense, shares the common background with the first subject. Most of the first-principles calculations performed so far have centered around a high-symmetry structure, such as a cubic structure. In order for the first-principles calculation to be a versatile tool for a wide class of alloy systems, it is desirable that a calculation procedure be established at least for tetragonal and hexagonal structures. Note that symmetry does not necessarily refer to the Bravais lattice. The lowest energy state of a given alloy system is realized by local atomic displacement at each lattice point, which breaks the global symmetry of the entire lattice. Hence, even if the global lattice symmetry is characterized in terms of the Bravais lattice, local structure is generally topologically disordered and atomistic calculations need to incorporate such a low symmetry in the calculations. Recent development in the Continuous Displacement Cluster Variation Method (CDCVM)[7-12] had made it a potential theoretical tool, and further development is urged.

The settlement of the third subject is a sheer necessity in connection with the current study on Fe-based alloy systems. As has been reported in the authors' recent articles,[1-5] magnetism plays an essential role in the phase stability of Fe-Ni, Fe-Pd, and Fe-Pt alloy systems. Although spin-polarized electronic structure calculations reveal the significance of magnetism, the separation of the atomic interaction energies into chemical and magnetic energy contributions have not been attempted. It is plausible that a number of unsettled subjects in the Fe-based phase diagram calculations originate from the neglect of the separate treatment of the two contributions. Among such problems is the significant deviation of the congruent composition of $L1_0$ ordered phase found in the Fe-Pd phase diagram.[13] Despite various attempts, the authors have not been able to reproduce the shifting of the congruent composition from 1:1 stoichiometry. The double-Ising type formulation is believed to be necessary for introducing interaction energies of different origins.

Apart from the settlement of these subjects in the phase diagram calculations, the other direction in which the first-

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principles calculations can be extended is the transition *kinetics* and transition *dynamics*, which are time-dependent phenomena. The clear distinction between kinetics and dynamics has not been well drawn, and in the current study 'kinetics" is defined as the temporal evolution of atomistic phenomena, while "dynamics" includes morphological/microstructural evolution and devolution processes. One may believe that kinetics is easier to deal with, but the accurate calculation of configurational kinetics[14-24] is quite difficult. This is mainly due to the difficulty of estimating the saddle-point energy of an atomic migration by electronic structure calculations. The absolute value of the saddle-point energy is not a formidably small value; however, it is very sensitive to the local environment, and it is not an easy task to derive such a dependence with reasonable accuracy. In view of this, the authors' attention has been directed toward *first-principles dynamics calculations*. Because the outline of the calculation procedure and the main results have already been reported in a previous article,[25] the main focus of the current study is placed on the statistical mechanics behind the first-principles dynamics calculations.

The organization of the present report is as follows. In the following section, first-principles calculations of phase stability and phase equilibria are summarized for Fe-based binary alloy systems, Fe-X with X = Ni, Pd, and Pt. In the third section, a hybrid scheme of phase-field methods and cluster variation methods, the core of the present theoretical approach, is introduced. The essential ingredients behind the present scheme owe much to coarse graining operations,[26-28] and general theory is discussed briefly. Finally, the results of the first-principles dynamics calculation on the evolution process of antiphase boundary of FePd L1$_0$ ordered phase is demonstrated.

2. First-Principles Calculation of Phase Stability and Phase Equilibria

In general, the free energy of a phase n can be written as[29]:

$$F^{(n)}(r,T) = E_{el}^{(n)}(r) + E_{vib}^{(n)}(r,T) - T \cdot S_{vib}^{(n)}(r,T) \qquad \text{(Eq 1)}$$

where $E_{el}^{(n)}$ is the electronic contribution to the internal energy and $E_{vib}^{(n)}$ and $S_{vib}^{(n)}$ are, respectively, the vibrational energy and entropy, which are also given as:

$$E_{vib}^{(n)}(r,T) = \frac{9}{8} k_B \cdot \Theta_D^{(n)} + 3k_B \cdot T \cdot D\left(\frac{\Theta_D^{(n)}}{T}\right) \qquad \text{(Eq 2)}$$

and

$$S_{vib}^{(n)}(r,T) = 3k_B \cdot \left[\frac{4}{3} D\left(\frac{\Theta_D^{(n)}}{T}\right) - \ln\left\{ 1 - \exp\left(-\frac{\Theta_D^{(n)}}{T}\right) \right\} \right] \qquad \text{(Eq 3)}$$

within the Debye-Gruneisen quasi-harmonic approximation. Generally, the electronic contribution $E_{el}^{(n)}$ is calculated

at several lattice constants r by employing FLAPW[30] within GGA.[31] This yields a binding energy curve, $E_{el}^{(n)}(r)$. The key ingredient of the whole procedure is that the binding curve $E_{el}^{(n)}(r)$ at the ground state provides the Debye temperature $\Theta_D^{(n)}$, which determines the vibrational contributions in Eq 2 and 3.

A common practice to perform a first-principles calculation of phase stability and phase equilibria starts by deriving the free energy $F^{(n)}(r,T)$ for five kinds of ordered compounds including pure metals; Fe ($n = 1$) and X ($n = 5$) with fcc structure, Fe$_3$X ($n = 2$) and FeX$_3$ ($n = 4$) with L1$_2$ structure, and FeX ($n = 3$) with L1$_0$ structure, where X indicates one of Ni, Pd, or Pt. In view of the fact that the ground state of Fe is not fcc but is bcc, the vibrational free energy for bcc-Fe was also calculated. Then, the free energy of formation is obtained through:

$$\Delta F^{(n)}(r,T) = F^{(n)}(r,T) - \frac{4-n}{4} F^{bcc-Fe}(r_{bcc},T) - \frac{n}{4} F^{(5)}(r_X,T)$$

$$\text{(Eq 4)}$$

Note that the energy reference state assumed in the equation above is the segregation limit at each temperature.

Then, by operating the cluster expansion method (CEM),[32] effective interaction energies are extracted via:

$$v_i(r,T) = \sum_m \{\xi_i^m\}^{-1} \cdot \Delta F^{(m)}(r,T) \qquad \text{(Eq 5)}$$

where i indicates a cluster and $\xi_i^{(n)}$ is a correlation function,[33,34] defined as the ensemble average of a spin variable σ_p, which takes values of either $+1$ or -1 depending upon A or B atoms on the lattice point p, and conveys the information of atomic arrangements on the cluster i in the phase m. The details of the correlation functions and actual operation of the CEM have been amply demonstrated in the previous articles.[1-5] It is noted that $\Delta F^{(m)}(r,T)$ in Eq 5 forms a 5×1 vector, hence with a 5×5 matrix of correlation functions, one obtains five effective cluster interaction energies. This is explicitly represented by a vector-matrix notation given as:

$$\begin{pmatrix} v_0 \\ v_1 \\ v_2 \\ v_3 \\ v_4 \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1/2 & 0 & -1/2 & -1 \\ 1 & 0 & -1/3 & 0 & 1 \\ 1 & -1/2 & 0 & 1/2 & -1 \\ 1 & -1 & 1 & -1 & 1 \end{pmatrix}^{-1} \cdot \begin{pmatrix} \Delta F^{Fe} \\ \Delta F^{Fe_3X} \\ \Delta F^{FeX} \\ \Delta F^{FeX_3} \\ \Delta F^{X} \end{pmatrix}$$

$$\text{(Eq 6)}$$

where the values of correlation functions are explicitly indicated. It is noted that i in v_i starts with null. This is because the first term obtained by a conventional CEM provides the energy for a null cluster, which is equivalent to the energy of a completely random solid solution at 50

at.%.[35] Other ν_i correspond to a nearest-neighbor i-point cluster.

It has been demonstrated that the spin-polarized calculation is indispensable for $E_{\mathrm{el}}^{(n)}(r)$ because magnetism plays a crucial role in the stability of each ordered phase. In fact, the nonpolarized calculation predicts that all of the ordered compounds (n = 2-4) have positive heats of formation and are never stabilized for all the three Fe-based alloys, which is in serious contradiction with the experimental phase diagrams. It is, on the other hand, confirmed that the correct tendency of the stabilities are properly reproduced by the spin-polarized calculations.[1-5]

The extracted effective cluster interaction energies suggest that the dominant contribution arises from the nearest neighbor pair interaction energy ν_2 for all the three systems and multibody interactions such as ν_3 and ν_4 are quite small for the entire range of lattice constants.[1-5] This is a characteristic feature of cubic metallic alloy systems of which cohesive properties are mainly dominated by central forces. By including additional ordered compounds in the CEM, further distant pair interactions and irregular three- and four-body interaction energies can be obtained. The details have been reported in previous articles,[3-5] but it is emphasized that the best agreement with experimental values are obtained by the present scheme given by Eqs 1 to 6.

The cluster variation method (CVM) has been recognized as one of the most reliable theoretical tools in calculating the configurational entropy, and the tetrahedron approximation[36] is used in the current study. The entropy formulas for the disordered and $L1_0$ ordered phases, which are the main concern of the current study, are given as:

$$S = k_{\mathrm{B}} \cdot \ln \frac{\prod_{i,j} \{Ny_{ij}!\}^6 \cdot \{N!\}}{\prod_{i} \{Nx_i!\}^5 \cdot \prod_{i,j,k,l} \{Nw_{ijkl}!\}^2} \qquad \text{(Eq 7)}$$

and

$$S^{L1_0} = k_{\mathrm{B}}$$

$$\cdot \ln \left[\frac{\left\{ \prod_{i,j} (Ny_{ij}^{\alpha\alpha})! \right\} \left\{ \prod_{i,j} (Ny_{ij}^{\alpha\beta})! \right\}^4 \left\{ \prod_{i,j} (Ny_{ij}^{\beta\beta})! \right\} N!}{\left\{ \prod_{i} (Nx_i^{\alpha})! \right\}^{5/2} \left\{ \prod_{i} (Nx_i^{\beta})! \right\}^{5/2} \left\{ \prod_{i,j,k,l} (Nw_{ijkl}^{\alpha\alpha\beta\beta})! \right\}} \right]$$

$$\text{(Eq 8)}$$

respectively, where x_i, y_{ij}, and w_{ijkl} are cluster probabilities of finding the atomic arrangements specified by subscript(s) on point, pair, and tetrahedron clusters, N is the total number of lattice points, and k_{B} is the Boltzmann constant. Note that the superscript(s) of the cluster probabilities in the $L1_0$ ordered phase indicates the sublattice(s) that are diminished in the disordered state.

Hence, together with the internal energy terms, the final form of the free energies for disordered and $L1_0$ ordered phases are, respectively, given as:

$$\Delta F^{\mathrm{dis}} = \sum_{m=0}^{4} v_m(r,T) \cdot \xi_m$$

$$- T \cdot k_{\mathrm{B}} \cdot \ln \frac{\left\{ \prod_{i,j} (Ny_{ij})! \right\}^6 \cdot (N!)}{\left\{ \prod_{i} (Nx_i)! \right\}^5 \cdot \left\{ \prod_{i,j,k,l} (Nw_{ijkl})! \right\}^2} \qquad \text{(Eq 9)}$$

and

$$\Delta F^{L1_0} = \sum_{m=0}^{4} v_m(r,T) \cdot \xi_m^{(L1_0)} - T \cdot k_{\mathrm{B}}$$

$$\cdot \ln \left[\frac{\left\{ \prod_{i,j} (Ny_{ij}^{\alpha\alpha})! \right\} \left\{ \prod_{i,j} (Ny_{ij}^{\alpha\beta})! \right\}^4 \left\{ \prod_{i,j} (Ny_{ij}^{\beta\beta})! \right\} N!}{\left\{ \prod_{i} (Nx_i^{\alpha})! \right\}^{5/2} \left\{ \prod_{i} (Nx_i^{\beta})! \right\}^{5/2} \left\{ \prod_{i,j,k,l} (Nw_{ijkl}^{\alpha\alpha\beta\beta})! \right\}} \right]$$

$$\text{(Eq 10)}$$

Importantly, cluster probabilities and correlation functions are mutually related through linear transformations. Then, the resultant free energy is symbolically denoted in the form of $g(r,\{\xi_i^{\delta}\},T)$ where δ indicates a sublattice that is introduced only for the $L1_0$ ordered phase. The equilibrium state is determined by minimizing the free energy with respect to both correlation functions and lattice parameter:

$$\left. \frac{\partial g}{\partial \{\xi_i^{\gamma}\}} \right|_{T,r} = 0 \qquad \text{and} \qquad \left. \frac{\partial g}{\partial r} \right|_{T,\{\xi_i^{\gamma}\}} = 0 \qquad \text{(Eq 11)}$$

The common tangent construction determines the phase equilibria and the phase diagram is constructed. It has been shown that the transition temperatures of $L1_0$-disorder are reproduced for Fe-Pd and Fe-Pt systems with quite a high accuracy.[2-5] The discrepancies from the experimental values are within 10 K for both the systems. For the Fe-Ni system, the $L1_0$ ordered phase has been missing in the conventional phase diagram,[13] while previous results indicate that this phase can be stabilized below ~500 K.[5] Although the transition temperature obtained for Fe-Ni system still leaves room for further improvement, the existence of the $L1_0$ phase has been recently confirmed experimentally.[37]

3. First-Principles Calculation of Transition Dynamics

The phase-field method (PFM)[38] has attracted broad attention as a powerful tool in calculating microstructural evolution processes. Within the PFM, temporal change of the microstructure is described by the time evolution of spatial distribution of the *field variables* $\{\eta_i\}$, which constitute the free energy of the system. Field variables are classified into two categories: conservative and nonconservative variables. The concentration and long-range order (LRO) parameter are typical examples of each category, and

the time evolution process are described by the Cahn-Hilliard equation for the former variable given by:

$$\frac{\partial \eta_i}{\partial t} = -\nabla \left(-M\nabla \frac{\delta F_{\text{chem}}}{\delta \eta_i} \right) \qquad \text{(Eq 12)}$$

and time-dependent Ginzburg-Landau (TDGL) equation for the latter one written as:

$$\frac{\partial \eta_i}{\partial t} = -\sum_j L_{ij} \frac{\delta F_{\text{chem}}}{\delta \eta_j} \qquad \text{(Eq 13)}$$

where M is the mobility and L_{ij} is the relaxation constant. Only the evolution of an antiphase boundary associated with $L1_0$ ordered phase at a fixed 1:1 stoichiometry is focused upon in this study. Hence, only the TDGL equation is explicitly considered and the free energy F_{chem} is given as:

$$F_{\text{chem}} = \int (f[\{\eta_i\}] + \sum_{i=1} \kappa_i (\nabla \eta_i)^2) \cdot dV \qquad \text{(Eq 14)}$$

where $f[\{\eta_i\}]$ is the bulk chemical free energy density of the homogeneous system and the second term in the integrand indicates the interfacial energy with κ_i, the gradient energy coefficient. Unique to the PFM is the interfacial energy term that is included in the free energy of the entire system and is subject to the variational principle to obtain the minimum energy state of the entire system. Hence, an interface is not a unique entity to be separately described but is merely an inhomogeneous localization of the field variable.

In the current study, CVM free energy is adopted for $f[\{\eta_i\}]$. Hence, the TDGL equation can be rewritten as:

$$\frac{\partial \xi_i}{\partial t} = -L_i \left(\frac{\partial f_{\text{CVM}}[\{\xi_i\}]}{\partial \xi_i} - \kappa_i \nabla^2 \xi_i \right) \qquad \text{(Eq 15)}$$

Note that the field variable η_i is replaced by the correlation function ξ_i. It has been amply demonstrated that five kinds of correlation function are necessary to describe the $L1_0$ ordered phase within the tetrahedron approximation of the CVM at a fixed 1:1 stoichiometric composition: ξ_1^α, $\xi_2^{\alpha\alpha}$, $\xi_2^{\alpha\beta}$, $\xi_3^{\alpha\alpha\beta}$, and $\xi_4^{\alpha\alpha\beta\beta}$, where the subscript indicates the number of the lattice point in the cluster. Among these correlation functions, the point correlation function ξ_1^α serves as the LRO parameter while the rest are short-range order (SRO) parameters.

The above scheme of implementing the CVM free energy into PFM has been termed a *hybrid* method.[39-44] Noted that such hybridization is not trivial. CVM free energy is originally defined in the discrete lattice, while PFM describes the temporal evolution in the continuum medium. Thus, the spatial scales considered in CVM and PFM are different. In order for this hybridization to be consistent, it is necessary to introduce the coarse graining operation.[26-28] Its essence is briefly summarized in the paragraphs that follow. More details are found in the authors' articles.[43,44]

We start with the microscopic configuration specified by a set of spin variable $\{\sigma_n\}$. The partition function Z of the system is then written as

$$Z = \sum_{\{\sigma_n\}} \exp \left(-\frac{H(\{\sigma_n\})}{k_B T} \right) \qquad \text{(Eq 16)}$$

where $H(\{\sigma_n\})$ indicates the Hamiltonian of the system. By dividing the system into cells with the edge size given by L, the average quantity defined as follows is introduced:

$$\phi(R) = \frac{1}{L^3} \sum_{n \in \text{cell}} \sigma_n \qquad \text{(Eq 17)}$$

where R is the spatial coordinate of the central position of a cell. The general procedure of the coarse graining operation is conducted so that the following relation is satisfied,

$$Z = \sum_{\{\sigma_n\}} \exp \left(-\frac{H(\{\sigma\})}{k_B T} \right) \cdot \delta \left(\phi(R) - L^{-1} \cdot \sum_n \sigma_n \right)$$
$$\cong \sum_{\{\phi(R)\}} \exp \left(-\frac{F_{\text{chem}}(\{\phi(R)\})}{k_B T} \right) \cong \exp \left(-\frac{V \cdot f_0(\{\phi_{\text{eq}}\})}{k_B T} \right) \qquad \text{(Eq 18)}$$

where the δ function ensures the condition given by Eq 17, $F_{\text{chem}}(\{\phi(R)\})$ is the inhomogeneous free energy of PFM, f_0 is equivalent to the homogeneous free energy f in Eq 14, and ϕ_{eq} represents $\phi(R)$ at the equilibrium state. It is noted that the last equality holds for a equilibrium state at which the entire system becomes homogeneous. The essential requirement claimed in the equation above is that the free energy of the system is not altered in the course of the operation.

The difficulty arising from the direct application of the general coarse graining procedure above is that the inhomogeneous free energy $F_{\text{chem}}(\{\phi(R)\})$ is hardly obtained in the closed form from Eq 18. To circumvent such a difficulty, the formulation of the inhomogeneous free energy based on the site-dependent CVM is employed. It is shown in the authors' previous articles[43,44] that the procedure is consistent with the conventional coarse graining operation described above. To avoid further mathematical complication, only the essential points are summarized below.

We start with describing the free energy of an inhomogeneous system by CVM:

$$F_{\text{chem}} = \sum_{n,m} f_{\text{CVM}}[R_l + r_{l'}] \qquad \text{(Eq 19)}$$

where R_l is the coordinate of l-th cell and $r_{l'}$ is the local coordinate of a lattice plane within each cell for which the origin is taken at the center of the cell and should satisfy the following relation:

$$\sum_{l'} r_{l'} = 0 \qquad \text{(Eq 20)}$$

and $f_{\text{CVM}}[R_l + r_{l'}]$ indicates the inhomogeneous CVM free energy in which correlation functions are site dependent.

When the temperature is sufficiently high, the correlation functions vary smoothly, and they can be expanded around R_l. The resultant free energy is then rewritten as:

$$F_{\text{chem}} \cong \sum_{l,l'} f_{\text{CVM}}[r_{l'}, \{\phi_I[R_l]\}, \{\nabla\phi_I[R_l]\}, \{\nabla^2\phi_I[R_l]\}]$$

(Eq 21)

where ϕ_I represents an independent variable formed by a linear combination of correlation functions. By noting that the spatial gradient of the ϕ_I are assumed to be small, the free energy is further expanded around the homogeneous state, yielding:

$$F_{\text{chem}} \cong \sum_{l,l'} \left\{ f_{\text{CVM}}^0[\{\phi_I\}] + \sum_I \left.\frac{\partial f_{\text{CVM}}}{\partial(\nabla\phi_I)}\right|_0 (\nabla\phi_I) \right.$$
$$+ \sum_I \left.\frac{\partial f_{\text{CVM}}}{\partial(\nabla^2\phi_I)}\right|_0 (\nabla^2\phi_I)$$
$$\left. + \frac{1}{2}\sum_{I,I'} \left.\frac{\partial^2 f_{\text{CVM}}}{\partial(\nabla\phi_I)\partial(\nabla\phi_{I'})}\right|_0 (\nabla\phi_I)(\nabla\phi_{I'}) \right\}$$

(Eq 22)

where $f_{\text{CVM}}^0[\{\phi_I\}]$ is the homogeneous free energy, which is independent of local coordinate $r_{l'}$. The coefficient terms are uniquely calculated, and, after the sum is transformed into an integral, the final form is obtained as:

$$F_{\text{chem}} = \frac{1}{L}\int \left[f_{\text{CVM}}^0[\{\phi_I\}] + \sum_{I,I'} \kappa_{I,I'}(\nabla\phi_I)(\nabla\phi_{I'}) \right] \cdot dx$$

(Eq 23)

where $\kappa_{I,I'}$ is a generalized gradient coefficient, the detailed form of which is given elsewhere.[43,44]

The present formalism of the first principles calculation is applied to an Fe-Pd system. The phase diagram is shown in Fig. 1.[25] The transition temperature 1080 K at 50 at.% estimated without vibration effects is seen to decrease to 1030 K with the introduction of vibrational contributions. This has been explained on the basis of the lattice softening effect. In the present first-principles calculations, as mentioned in the introduction, local lattice distortion effects are not explicitly considered and only the uniform deformation is allowed. Hence, the system is still in an excited state. In particular, when the two species in different atomic size are mixed, the neglect of local distortion significantly raises the internal energy. This is more noticeable in the disordered phase, because the atomic arrangement is rather well adjusted in an ordered phase. The introduction of the lattice softening through the vibrational contributions partly relaxes such an inconvenience, and the resultant transition temperature approaches more closely the experimental value of 1023 K.

The system is then quenched at 820 K from a disordered phase. The free energy at 820 K is demonstrated as a function of LRO in Fig. 2. The existence of the free energy hump between disordered and ordered states is the indication of the nucleation-growth regime. In the nucleation-
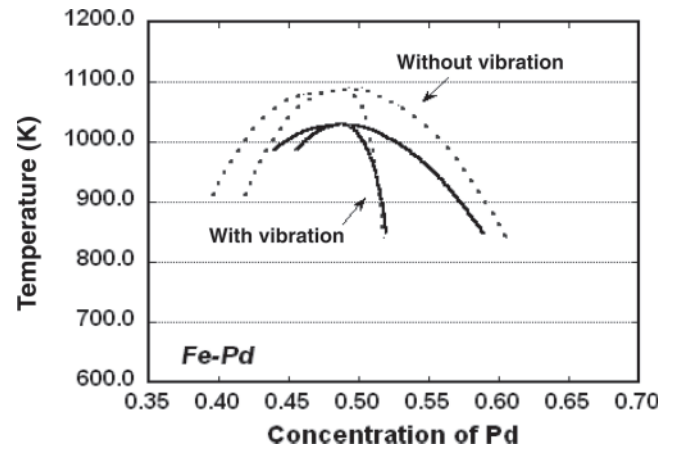

Fig. 1 L1$_0$-disorder phase diagram for Fe-Pd calculated from first principles. The solid (dotted) lines are obtained with (without) lattice vibration effects. The calculated transition temperatures are 1030 K (with vibration) and 1080 K (without vibration), respectively.[4,5,25]
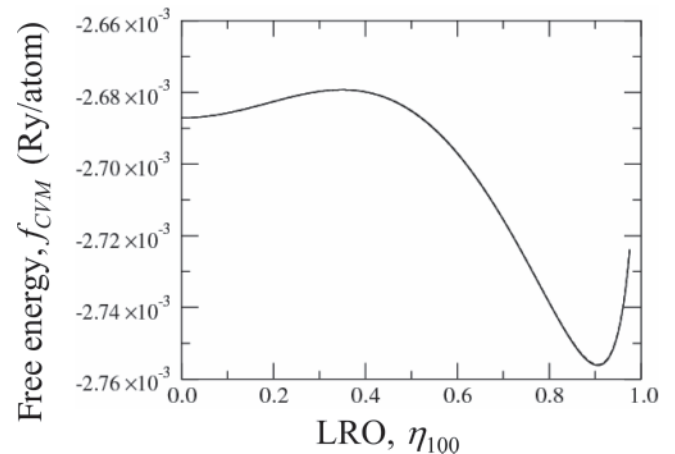

Fig. 2 CVM free energy at 820 K as a function of LRO parameter obtained by constrained minimization. A null value of the LRO indicates a disordered phase, and a finite value indicates some degree of order. The perfectly ordered state corresponds to 1, which is realized at the ground state. The free energy hump suggests that a first-order transition takes place.

growth regime, nuclei of L1$_0$ ordered phase are needed to initiate the transition, and these are assigned by generating random numbers and imposing the assumption of site saturation. The calculated results of time evolution process are demonstrated in Fig. 3.[25] Note that, with time, the characteristic microstructure of APB is formed. The length scale and crystallographic orientation are also uniquely fixed. These are indications of a proper coarse graining operation.

In the present calculation, effective pair interaction energy is limited to the nearest neighbor. A rather strong anisotropy found in the calculated APB morphology may be originating from the neglect of the second nearest-neighbor pair interaction. Use of the tetrahedron-octahedron approximation[33,34] is indispensable to incorporate the second near-
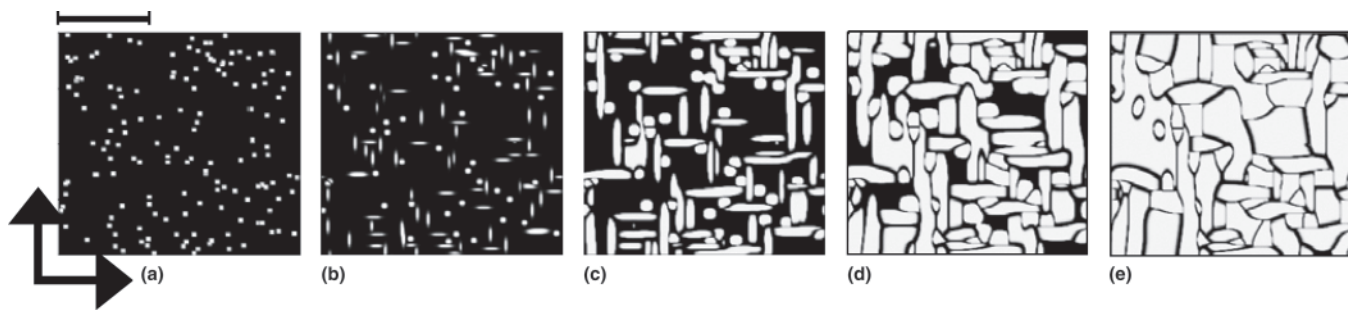
Fig. 3 First-principles calculation of APB evolution process for Fe-Pd at 50 at.% at 820 K. (a-e) correspond to time $t' = 0.01$, 0.83, 3.59, 7.04, and 16.70, respectively. The bar above panel (a) indicates a length of 100 nm, and the arrows suggest the [100] and [010] directions.[25]

est-neighbor interaction energy. The other subject to be settled in the future is the *time scale*.[45] As mentioned above, the spatial scale is properly assigned by coarse graining operation. Although the absolute time scale is not yet assigned, the time in the figure is normalized as $t' = N\nu_2 L_1^{\alpha} t$. The proper time scaling can be performed by hybridizing PFM with the path probability method (PPM), which remains a future topic of publication.[46]

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