Phase-Field Modeling of Phase Transformations in Platinum-Based Alloy Nanoparticles

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A phase-field model that describes the phase decomposition and phase transformations inside platinum-based alloy nanoparticles is developed to elucidate the effects of particle size, alloy composition, and heat-treatment temperature on the microstructure formation. FePt, CoPt, NiPt, CuPt and IrPt binary alloy nanoparticles with diameters of less than 10 nm are investigated. The calculation results clearly show that surface segregation and atomic ordering are sensitive to the alloy components and particle size, and that the equilibrium nanostructure obtained varies according to the balance between the surface energy and chemical interaction between atomic components. Platinum-based alloy nanoparticles are expected to find applications as electrocatalysts in polymer electrolyte fuel cells. Thus, the proposed phase-field approach demonstrates its usefulness for the control of the radial distributions of each alloying component within a nanoparticle, leading to improvements in the activity and durability of the catalyst and reducing the required amount of platinum loading.

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1. Introduction

For many years, intensive effort has been focused on developing platinum-based alloy nanoparticles for applications as electrocatalysts in polymer electrolyte fuel cells.¹ The alloying technique is expected to improve the oxygen reduction reaction in the cathode layers of fuel cells and reduce the required amount of platinum loading through the replacement of some platinum with less expensive metals. During the nanoparticle fabrication process, a compositional difference between the bulk and surface of an alloy may be induced by differences in the surface energies of the alloying elements and changes in the interaction energies between them. This compositional difference is known as surface segregation,² and it influences the catalytic activities of alloys.³ On the other hand, the diameter of the current pure platinum catalyst is less than approximately 10 nm so as to ensure that it provides an extensive surface area for the electrochemical reaction.⁴ On the scale of a few nanometers, the influence of the surface energy on the thermodynamic equilibrium is inversely proportional to the particle size; this tendency causes degradation because of Ostwald ripening.⁵ Therefore, the particle size is also expected to affect the surface segregation. To overcome these obstacles for the design and fabrication of a binary alloy nanoparticle, we believe that it is necessary to understand the fundamental effects of particle size, alloy composition, and heat-treatment temperature on the microstructure formation.

Computational modeling studies are useful for elucidating driving forces and predicting resultant surface structures. Thus far, various methodologies have been proposed for the investigation of the surface structure of platinum-based binary alloys, such as those based on the thermodynamic model,⁶ the Monte Carlo simulation model with embedded-atom method (EAM) potential,⁶–¹⁴ and first-principles methods.¹⁵ We think that a thermodynamic model based on the knowledge of the thermodynamic parameters of the bulk, rather than those observed on the nanoscale, is useful for understanding the general trend in surface segregation that is common to a number of alloy systems. The previously proposed thermodynamic method estimated the surface atom fraction on the basis of pure element vaporization enthalpies and alloy solution activity coefficients.⁵ The alloy particle-size dependence of the surface composition has also been discussed. However, the combined influences of the particle size and phase transformations on the degree of surface segregation were not well described.

The phase-field method¹⁶ has recently attracted more attention as a numerical simulation method for the prediction of nanascale phenomena. This method was applied to investigate the size dependence of the ordering of FePt nanoparticles,¹⁷,¹⁸ the results clearly showed that the disordered phase induced by the FePt particle surface becomes dominant as the particle size decreases. On the other hand, the phase-field model simulating the temporal evolution of the platinum density profile successfully represented the formation process of platinum nanoparticles on a carbon substrate.¹⁹ These application results thus legitimate the phase-field model used to discuss the thermodynamic equilibrium in the case of a high surface-area-to-volume ratio. In the present study, we concentrate on achieving the description of the surface segregation in consideration of the phase transformations of the internal particles. Recent methodological progress in the phase-field technique has enabled simultaneous evaluation of the conservative temporal evolution of the atomic concentration and the nonconservative temporal evolution of the phase transformation through solution of the Cahn–Hilliard²⁰ and Allen–Cahn²¹ equations, respectively.

The outline of this paper is as follows: In Sec. 2, formulations and implementations of the simulation method are described. The temporal evolution is calculated using the Cahn–Hilliard and Allen–Cahn equations on the basis of the free-energy function associated with surface energy and...

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internal energy including the effects of phase transformations. In Sec. 3, the results of practical applications are explained. First, to verify the accuracy of this simulation, we compare this model with experimental and other simulation results for the phase transformations in FePt nanoparticles. Next, the effects of the alloying elements on the equilibrium microstructures of FePt, CoPt, NiPt, CuPt and IrPt binary alloy nanoparticles with diameters of less than 10 nm are investigated. Unfortunately, since the radial distribution of alloy components has not yet been fully investigated experimentally, it is difficult to evaluate the accuracy of our model in this regard. On the other hand, theoretical prediction of the microstructure formation of the nanoparticle has been made by using Monte Carlo simulations. Therefore, the validity of our simulation results is discussed mainly through comparisons with previously reported atomistic simulation results. The conclusions are given in Sec. 4.

### 2. Calculation Methods

#### 2.1 Formulation

We introduced three types of field variables related to the atomic concentration, c, long-range crystallographic ordering, s, and phase transition, θ, between solid and liquid. A condensed-matter phase is distinguished from a surrounding vapor phase by the vacancy concentration. The temporal evolutions of the radial distributions of each atomic concentration within a nanoparticle are calculated by using the ternary Cahn–Hilliard equation,22,23 as expressed in the following conservative form:

\[
\frac{\partial c_i}{\partial t} = \nabla \cdot \left[ M_i \nabla \left( \frac{\delta G_{\text{sys}}}{\delta c_i} \right) - M_{ij} \nabla \left( \frac{\delta G_{\text{sys}}}{\delta c_j} \right) \right],
\]

\(i = \text{Pt}, \text{TM}; j = \text{Pt}, \text{TM}; i \neq j,\)

\(c_{\text{Pt}} + c_{\text{TM}} + c_{\text{Va}} = 1,\)  

where \(c_i\) is the local atomic concentration of component \(i\) as a function of the radial coordinate, \(r\), and the time variable, \(t\), and its value is normalized with respect to the maximum concentration so that it is a dimensionless value between 0 and 1; the subscripts TM and Va indicate the transition-metal element alloyed with platinum and the vacancy, respectively; and \(M_{ij}\) is the mobility of component \(i\) due to the gradient of the functional derivative of \(G_{\text{sys}}\) with respect to the concentration of component \(i\). \(M_i\) and \(M_{ij}\) are expressed as \(M_i = c_i(1 - c_i)D/R T\) and \(M_{ij} = c_i c_j D/R T\), respectively, when all species have the same diffusion coefficient, \(D.\) Here, \(R\) and \(T\) are the gas constant and absolute temperature, respectively.

The equilibrium radial distributions of the ordered–disordered phase and the solid–liquid phase within a nanoparticle were calculated using the Allen–Cahn equation,21 expressed in the following nonconservative form:

\[
\frac{\partial s}{\partial t} = -L_s \frac{\delta G_{\text{sys}}}{\delta s},
\]

\[
\frac{\partial \theta}{\partial t} = -L_\theta \frac{\delta G_{\text{sys}}}{\delta \theta},
\]

where \(s\) is defined as the long-range order parameter so that \(s\) values of 0 and 1 correspond to disordered and ordered phases, respectively; \(\theta\) is defined as the phase-field parameter so that \(\theta\) values of 0 and 1 correspond to liquid and solid phases, respectively; and \(L_s\) and \(L_\theta\) denote the mobility of the ordered–disordered and solid–liquid phase interfaces, respectively. As a consequence of temporal evolution, quasi-stationary microstructures corresponding to the minimum free energy are obtained.

We defined \(G_{\text{sys}}\) as the volume integral of the local chemical free energy and the gradient energy term over the entire volume, \(V\), as follows:

\[
G_{\text{sys}} = \frac{1}{V} \int \left[ h(\theta)G_{\text{chem}}^{(\text{S})} + \left( 1 - h(\theta) \right)G_{\text{chem}}^{(\text{L})} \right] + \frac{k_{\text{Pt}-\text{TM}}}{2} \left[ (\nabla c_{\text{Pt}})^2 + (\nabla c_{\text{TM}})^2 \right]
\]

\[
+ \frac{k_{\text{Va}}}{2} (\nabla c_{\text{Va}})^2 + h(c_{\text{Pt}+\text{TM}}) \kappa_s \left| \nabla s \right|^2
\]

\[
+ W(1 - \theta) + \frac{\kappa_\theta}{2} (\nabla \theta)^2 \right] \, dV,
\]

\(h(x) = x^3(6x^2 - 15x + 10), \) \(x = \theta, \quad c_{\text{Pt}+\text{TM}},\)

\(c_{\text{Pt}+\text{TM}} = c_{\text{Pt}} + c_{\text{TM}},\)  

where \(W\) is the energy barrier for the solid–liquid transition and \(\kappa\) is the gradient energy coefficient. The particle-size dependence is naturally taken into account through the atomic-concentration derivative of the gradient energy term of the phase-field model. Here, we define \(W\) and \(k_\theta\) as given in the following equations:

\[
W = \frac{c_{\text{Pt}}}{c_{\text{Pt}+\text{TM}}} W_{\text{Pt}} + \frac{c_{\text{TM}}}{c_{\text{Pt}+\text{TM}}} W_{\text{TM}},
\]

\[
k_\theta = \frac{c_{\text{Pt}}}{c_{\text{Pt}+\text{TM}}} k_{\theta,\text{Pt}} + \frac{c_{\text{TM}}}{c_{\text{Pt}+\text{TM}}} k_{\theta,\text{TM}}.
\]

Because the spatial derivative terms multiplied by \(k_{\text{Pt}+\text{TM}}\) are not zero when the spatial derivative term multiplied by \(k_{\text{Va}}\) is not zero, \(k_{\text{Va}}\) is represented by subtracting \(k_{\text{Pt}+\text{TM}}\) from a linear combination of \(k_{\text{Pt}}\) and \(k_{\text{TM}}\), as given in the following derivation:

\[
\frac{1}{2} \left[ \frac{1}{c_{\text{Pt}+\text{TM}}} \left( k_{\text{Pt}} + k_{\text{TM}} \right) \left( \nabla c_{\text{Va}} \right)^2 - \frac{k_{\text{Pt}+\text{TM}}}{2} \left( \nabla c_{\text{Pt}+\text{TM}} \right)^2 \right]
\]

\[
= \frac{1}{2} \left[ \frac{c_{\text{Pt}}}{c_{\text{Pt}+\text{TM}}} k_{\text{Pt}} + \frac{c_{\text{TM}}}{c_{\text{Pt}+\text{TM}}} k_{\text{TM}} \left( \nabla c_{\text{Va}} \right)^2 - \frac{k_{\text{Pt}+\text{TM}}}{2} \left( \nabla c_{\text{Pt}+\text{TM}} \right)^2 \right]
\]

\[
= \frac{1}{2} \left[ \frac{c_{\text{Pt}}}{c_{\text{Pt}+\text{TM}}} k_{\text{Pt}} + \frac{c_{\text{TM}}}{c_{\text{Pt}+\text{TM}}} k_{\text{TM}} - k_{\text{Pt}+\text{TM}} \right] \left( \nabla c_{\text{Va}} \right)^2
\]

\[
= \frac{1}{2} k_{\text{Va}} (\nabla c_{\text{Va}})^2,
\]

with

\[k_i = h(\theta)k_i^{(\text{S})} + \left( 1 - h(\theta) \right)k_i^{(\text{L})}, \quad i = \text{Pt}, \text{TM},\]

where \(k_i^{(\text{S})}\) and \(k_i^{(\text{L})}\) are the gradient energy coefficients of the solid–vapor and liquid–vapor interfaces, respectively, of atomic element \(i\).

\(G_{\text{chem}}^{(\text{S})}\) and \(G_{\text{chem}}^{(\text{L})}\) denote the changes in the chemical free energies between the solid and vapor phases and between the liquid and vapor phases, respectively. The chemical free energies are evaluated along with the approximation of the regular solution model expressed as follows:
Here, the diffusive transition region from very low to very high vacancy concentration, which depends on the alloy components. In the case of the condensed-matter–vapor interface with a one-dimensional gradient, the following relationship (22) exists between the surface energy, $\gamma_i^{(j)}$, interfacial thickness, $\Delta d_i^{(j)}$, and gradient energy coefficient, $\kappa_i^{(j)}$:

$$\gamma_i^{(j)} = \frac{\kappa_i^{(j)}}{\sqrt{V_i^{(j)}}} \int_{c_i=0}^{c_i=1} \sqrt{2 \Delta G(c) dc}$$

$$\Delta d_i^{(j)} = (c_s - c_v) \sqrt{\frac{\kappa_i^{(j)}}{2 \Delta G(c = 0.5)}}$$

where the subscript $i$ indicates the alloy component (Pt, Fe, Co, Ni, Cu, or Ir); $c_s$ and $c_v$ are the atomic concentrations of the condensed and vapor phases, respectively; $\gamma_i^{(j)}$ is the molar volume; and $\Delta G$ is the free-energy change across the interface, which correlates with $L_i^{(j)}$. In our calculations, $L_i^{(j)}$ and $\kappa_i^{(j)}$ were determined to reproduce the $\gamma_i^{(j)}$ and $\Delta d_i^{(j)}$ values. The $\Delta d_i^{(j)}$ value for the solid phase was set at $3.0 \times 10^{-10}$ m by adjusting the mono-vacancy formation energy, $\Delta H_i^{(j)}$, which led to a change in the $L_i^{(j)}$ values. Here, we employed the values obtained for the solid surface energy, $\gamma_i^{(j)}$, of the (111) surfaces of Pt, Fe and Co from first-principles calculations (30) and of Ni, Cu and Ir evaluated from embedded-atom calculations. (34) Since there is a discrepancy between the Pt surface energies in Refs. (33) and (34), the values in Ref. (34) were scaled to fit the Pt value in Ref. (34) to the Pt value in Ref. (33). Table 1 shows the surface energy including the temperature correction. The temperature correction was made by using the following equation:

$$\gamma_i^{(j)}(T) = \gamma_i^{(j)}(0) - RT/A,$$

where $A$ is the surface area per mole of surface atoms, as defined in the following equation:

$$A = 1.612N^{1/3}V^{2/3},$$

where $N$ is Avogadro’s number and $V$ is the molar volume. The liquid surface energy, $\gamma_i^{(L)}$, was estimated from $\gamma_i^{(L)} = \gamma_i^{(j)}/1.18^{(35)}$. For representation of the differences in the bond strengths in solids and liquids, $\Delta H_i^{(j)}$ was assumed to be expressed as a relative value of $\Delta H_i^{(j)}$, as defined by the following equation:

$$\Delta H_i^{(j)} = \frac{\Delta H_{m,i,j} + \Delta H_{e,i,j}}{\Delta H_{m,i,j}} \Delta H_i^{(S)},$$

where $\Delta H_{m,i,j}$ is the heat of fusion and $\Delta H_{e,i,j}$ is the heat of vaporization. The surface energy is considered to be associated with $\Delta H_i^{(j)}/A$, so $\gamma_i^{(S)}/\gamma_i^{(j)}$ is rewritten as ($\Delta H_i^{(S)}/\Delta H_i^{(j)}) \times (A_i^{(L)}/A_i^{(S)})$. In the case of platinum, $\Delta H_i^{(S)}/\Delta H_i^{(j)}$ is about 1.04 (from eq. (21)), and $A_i^{(L)}/A_i^{(S)}$ is about 1.07 (from eq. (20)). Therefore, ($\Delta H_i^{(S)}/\Delta H_i^{(j)}) \times (A_i^{(L)}/A_i^{(S)})$ is about 1.11. The derived value is approximately equal to the abovementioned value of 1.18. Therefore, we consider that the assumption of eq. (21) has a physical meaning. $\kappa_i^{(S)}$ was determined to reproduce the $\gamma_i^{(S)}$ and $\Delta H_i^{(S)}$ values. The $\Delta S_i$ value in eq. (16) approximately adopted a formulation of 1.32R, which was originally used for platinum. (30) The estimated $\Delta H_i^{(S)}$, $\kappa_i^{(S)}$, and $\kappa_i^{(S)}$ values at 973.15 K (a typical annealing temperature for the synthesis of nanoparticles) are listed in Table 1. The estimated $\Delta H_i^{(S)}$ values in Table 1 are in fairly good
agreement with the experimental values.\(^37\)\(^39\) In the case of the solid–liquid interface, the interfacial energy barrier, \(W_i\), and \(\kappa_{ij}\) values were determined by introducing the values obtained for \(\gamma_i^{S/L} (= \gamma_i^{S} - \gamma_i^{L})\) and the width of the solid–liquid interface \(\Delta d_i^{S/L}\) (which was assumed to be approximately equal to that of the solid–vapor interface) into the following equations:

\[
\gamma_i^{S/L} = \sqrt{\kappa_{ij}} \int_0^1 \frac{\sqrt{2W_i}}{V_i^{S/L}} d\theta,
\]

(22)

\[
\Delta d_i^{S/L} = \frac{\kappa_{ij}}{2W_i} \sqrt{V_i^{S/L}}.
\]

(23)

where \(V_i^{S/L}\) is introduced as

\[
V_i^{S/L} = h(\theta)V_i^{S} + [1 - h(\theta)]V_i^{L}.
\]

(24)

Equation (18) is modified slightly to the following expression\(^21\) for the estimation of the \(\kappa_i\) value for the ordered-disordered phase interface:

\[
\Delta x = 2 \sqrt{\frac{\kappa_i}{2\Delta G(s = 0)}}.
\]

(25)

where \(\Delta x\) is the width of the anti-phase boundary (APB), and \(\Delta G(s = 0)\) corresponds to the absolute value of \(\Delta G_{Pn-TM}\).

For the reproduction of the experimental results shown in Fig. 1, a \(\Delta x\) value of \(1.0 \times 10^{-9}\) m was used, which was close to the experimentally observed value of approximately \(1.38 \times 10^{-9}\) m for FePt.\(^40\) The values of \(\kappa_i\) at 973.15 K were \(1.63 \times 10^{-15}\) J m\(^2\) mol\(^{-1}\) for FePt (L\(_{10}\)), \(0.160 \times 10^{-15}\) J m\(^2\) mol\(^{-1}\) for CoPt (L\(_{10}\)), and \(0.137 \times 10^{-15}\) J m\(^2\) mol\(^{-1}\) for CuPt (L\(_{11}\)). The L\(_{10}\) phase of NiPt is unstable at 973.15 K. The \(\kappa_{Pn-TM}\) value has a meaning for binary systems with a miscibility gap, such as Ir–Pt. \(\kappa_{Pn-TM}\) for the Ir–Pt binary system in the solid phase was determined to be \(1.66 \times 10^{-15}\) J m\(^2\) mol\(^{-1}\) by assuming a value of \(1 \times 10^{-9}\) m for the width \(\Delta d\) and using the \(\Delta G\) value estimated from the CALPHAD data. The \(\kappa_{Pn-TM}\) values for the other binary systems examined in the present computational study were defined as having a negative sign according to eq. (17). However, a negative \(\kappa_{Pn-TM}\) value may induce instability during the numerical simulation. We have confirmed that when \(\kappa_{Pn-TM}\) is set to a positive value of the order of about \(10^{-17}\), such instability is avoided, and the value has a minor effect on the final concentration profile. In this study, the \(\kappa_{Pn-TM}\) values for the Fe–Pt, Co–Pt, Ni–Pt and Cu–Pt systems were set at \(5 \times 10^{-17}\) J m\(^2\) mol\(^{-1}\).

### 2.3 Numerical calculation

The numerical calculation of the one-dimensional problem along the radial direction of a nanoparticle was performed by using the finite volume method with the explicit Euler method. In the present calculation, the isotropic surface energy of a nanoparticle was assumed. The simulation was executed mainly at a temperature of 973.15 K. The initial grid spacing was 0.005 nm. Changes in the local molar volume depending on the changes in atomic concentrations and phase transformations were taken into account to ensure mass
conservation. Therefore, the grid spacing at each grid point was updated for each time step. The initial simulation size, \( l \), was defined as the particle radius plus 0.75 nm. The boundary conditions at \( r = 0 \) and \( r = l \) were chosen such that the spatial derivatives of the field variables were zero. In the external region of the particle, only vaporized atomic elements were present, i.e., it was an inert atmosphere. The initial concentration of platinum was equal to that of the elements were present, i.e., it was an inert atmosphere. The external region of the particle, only vaporized atomic

\[
\text{dependence of the L10 ordering in FePt particles that were}
\]

Figure 1 shows the experimentally observed particle-size dependence of the L10 ordering in FePt particles that were fabricated or annealed at 973.15 K. The degree of L10 ordering decreased as the particle size decreased. When the APB width was assumed to be 1.0 nm, in accordance with the experimental results described in Sec. 2.2, the calculated \( s \) values were in good agreement with the experimental results. This implies that the present phase-field model is sufficiently accurate to describe the order–disorder phase transition within a nanoparticle. Figure 2 shows the temperature dependence of the L10 ordering of FePt particles with diameters of 4 nm. The order–disorder phase-transition temperature decreased as the particle size decreased. This figure also shows previously reported results from Monte Carlo simulations. At first glance, the present model reproduces the general trend of the temperature dependence seen from the Monte Carlo simulations, although the simulated phase-transition temperature is slightly below that obtained from the Monte Carlo simulations. In the present simulation, the ordered–disordered phase interface has a finite width inside a particle. Therefore, the disordered phase is dominant at the particle surface. On the other hand, it is well known that the surface state from the Monte Carlo simulation result is affected significantly by the adopted surface potential. Therefore, we cannot find conclusive evidence to clarify which results are more accurate.

Another important feature is the particle-size dependence of the solid–liquid transition temperature. Figure 3 shows the equilibrium phase of the FePt nanoparticle versus the holding temperature and the particle size. When the particle diameter is on the nanometer scale, the influence of the surface tension of the particle on its chemical potential is significant. The difference in surface tension between the solid and liquid phases also leads to a difference in the equilibrium vapor pressures of those phases. Generally, the surface tension of the liquid phase is smaller than that of the solid phase, and the liquid phase is formed at a temperature lower than the melting point of the bulk to decrease the free energy. Furthermore, at temperatures higher than the complete melting temperature of the nanoparticles, it is known that a kind of core–shell structure is formed in the particle through melting only of the particle surface, which is known as surface pre-melting. In this figure, the open dots denote completely melted particles and filled dots denote partially melted particles. The simulated transition temperature of the solid–liquid phases corresponds to the interface of these dots. The temperature dependence was more remarkable in particles of less than 10 nm in diameter. Figure 3 also shows the theoretical prediction from Pawlow’s model, which yields the following equation:

\[
T_m = T_m^{\text{Bulk}} \left\{ 1 - \frac{2\sigma_s \Delta H_m}{\Delta H_m r_s} \left[ 1 - \frac{1}{\sigma_s} \left( \frac{r}{r_s} \right)^{2/3} \right] \right\}. \tag{26}
\]

In this formula, the relationship between the melting temperature, \( T_m \), and the particle radius, \( r_s \), is estimated on
the basis of the equilibrium between solid and liquid particles. Each parameter in eq. (26) is defined as the mean of the physical constants of Pt and Fe: $T_{\text{bulk}}$, $m_{\text{C1H}}$, $v_{\text{s}}$, $v_{\text{l}}$, and the surface tensions of the solid, $\gamma_s$, and liquid, $\gamma_l$, are 1926.6 K; 16.4 kJ/mol; 8.10 $\times 10^{-6}$ and 8.97 $\times 10^{-6}$ m$^3$/mol, respectively; and the surface tensions of the solid, $\gamma_s$, and liquid, $\gamma_l$, are 1.85 and 1.57 J/m, respectively. The simulated phase boundary between the solid and liquid phases was slightly below that obtained with Pawlow’s model. It was postulated that this subtle but meaningful difference was due to surface pre-melting.46) The surface layers of the FePt particles were partially in the liquid phase, as described in the next section. This layer is expected to induce the more significant melting-temperature dependence on the particle size, as shown in Fig. 3.

3.2 Surface segregation

Figure 4 shows the radial distribution of the atomic concentrations ($c_{\text{Pt}}$, $c_{\text{TM}}$ and $c_{\text{Pt+TM}}$ values), ordered–disordered phase ($s \times c_{\text{Pt+TM}}$ value), and solid–liquid phase ($\theta \times c_{\text{Pt+TM}}$ value) of nanoparticles with diameters of 2 and 4 nm at 973.15 K. The region in which the value of $c_{\text{Pt+TM}}$ changes from 0 to 1 corresponds to the particle surface. The change of the black line corresponding to the fraction of solid phase from 0 to 1 inside the particle implies that surface pre-melting occurs. The atomic concentrations of the alloy

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**Fig. 4** Radial distribution of the mole fraction of each atom ($c_x$), the long-range ordering parameter ($s$), and the solid–liquid phase transition parameter ($\theta$) within (a) FePt, (b) CoPt, (c) NiPt, (d) CuPt and (e) IrPt nanoparticles with diameters of 2 nm (left column) and 4 nm (right column) at 973.15 K. The horizontal axis denotes the distance from the particle center. The $s$ values of 0 and 1 correspond to the disordered phase and L10 (or L11) phase, respectively.
elements were also determined. In the CuPt and IrPt particles, there was remarkable concentration decomposition, especially in the 2-nm particles. Enriched alloy element concentrations on the particle surface resulted in reduced concentrations of these elements inside the particles, as the total mass was conserved. In contrast, the FePt and CoPt particles showed no significant concentration decomposition. Figure 4 also shows that at the same temperature, the stable particles showed no significant concentration decomposition. Monte Carlo simulations with the cluster interaction energy between Fe and Pt overcame the surface energy differences. Moreover, the difference between the Ni and Pt surface energies is very small. Our simulation predicted slight Ni enrichment on the NiPt particle surface, which was in contrast to the prediction by the Monte Carlo simulation. Therefore, we suggest that in the case of a small surface energy difference, as in the NiPt particle, the actual surface can be determined by atomic size mismatch, which is not considered in this model.

4. Conclusion

We have performed phase-field simulations to investigate phase transformation and surface segregation in platinum-based alloy nanoparticles. From our results, it was evident that the surface segregation and atomic ordering were sensitive to the alloy components and particle size. The simulated equilibrium structures of nanoparticles vary according to the balance between the surface energy and chemical interaction between atomic components. So far, microscopic simulations of nanoparticles have been performed mainly by using the Monte Carlo method. Although the surface energy was accounted for through parameter values related to a flat plane surface, the proposed phase-field approach gave sufficient accuracy. This method provides a useful tool for the design of alloy nanoparticles.

REFERENCES

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