

First-principle calculation on free energy of precipitate nucleation

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Abstract

A slight modification of the nucleation theory enables reliable calculations of cluster free energies of precipitate nucleation. This method divides the free energy into the cluster energy and entropy terms. The former, consisting of the enthalpy of driving force and the interface energy, is precisely calculated by first-principles calculations. The latter, which is entropy loss from scattered atoms condensing into a cluster, is estimated by the ideal solution model. Model calculations have been performed for an Fe-Cu alloy, Ni added Fe-Cu alloy, and vacancy behavior around Cu clusters.

Key words: first-principles calculation, nucleation, Fe-Cu, Ni addition, vacancy

1 Introduction

For accurate simulations of nucleation and growth, the utilization of the first principles technique has been attempted in some metallic systems. The main success of these trials are the kinetic simulations on the shapes of precipitates using the mixed-space cluster expansion[1]. The other way is calculating the finite-temperature interfacial thermodynamic properties by the cluster variation method[2,3]. Further combinations of those atomistic level simulations with the continuum theory predict the realistic microstructure evolutions in

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industrial, multicomponent and complex systems[4]. These methods are applied in large size precipitates in the growth stage rather than the nucleation stage, and need the cluster expansion or other extraction of the effective interactions in order to perform large scale Monte Carlo simulation or the cluster variation method.

In this paper, we will propose a different approach in which free energy change by cluster formations is accurately and directly estimated using first principles calculations. We apply this novel technique to an Fe-Cu system, where the Cu precipitate nucleation is the crucial mechanism controlling the brittleness of nuclear reactor pressure vessel steels and the ductility of ultra high strength steels. In the next section, we show the derivation of a novel expression for the free energy change of nucleation. Then we show the application of the actual method of calculation on the Fe-Cu binary system, Ni added Fe-Cu alloy, and vacancy behavior around Cu clusters.

2 Basic idea of free energy calculation

In classical nucleation theory, the free-energy change is described by the sum of negative driving force ΔF and positive interface energy H_σ . The main ambiguity of the classical nucleation theory is the assumption that the interface energy is applied to a small cluster with a spherical interface area. By dividing ΔF into two components of enthalpy change ΔH and entropy change $-T\Delta S$, and treating enthalpy change ΔH and interface energy H_σ together, the free energy change is expressed as

$$\Delta F(n) = \{\Delta H(n) + H_\sigma(n)\} - T\Delta S(n), \quad (1)$$

where n is the number of atoms in a cluster.

Figure 1 shows the schematic illustration of precipitate nucleation in the Fe-Cu system. To simplify the models, we employ the cluster comprising n Cu atoms. The initial state is described as the summation of the isolated solute atoms, and is the dilution limit of an alloy. The final state is described as one cluster moving around on the matrix. Thus the free-energy change is calculated from the enthalpy and entropy differences between the initial and final states.

The first term of eqn.(1) is the cluster energy change, which includes all the environmental changes of solute and solvent atoms. The cluster energy change is assumed to be independent of temperature and can be calculated precisely by the density functional codes. The second term of eqn.(1) is entropy change, and includes the interfacial entropy implicitly. The vibrational entropy contributions for the Fe-Cu system can be neglected due to their small differences

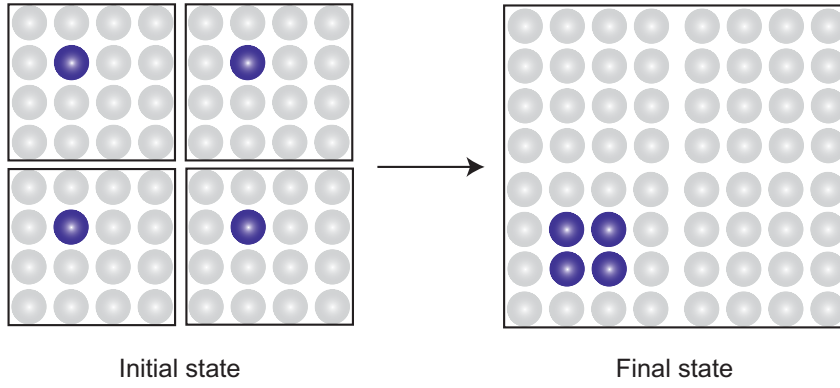


Fig. 1. Initial and final states of the precipitate nucleation process.

in atomic size, weight and bulk modulus as discussed elsewhere[5]. The rest of the entropy contribution is the configurational change between the scattered atoms and the condensed cluster, which can be estimated by the simple ideal solution model as pointed out by Kamijo and Fukutomi[6],

$$\Delta S(n) = k_B (n - 1) \ln(x), \quad (2)$$

where k_B is Boltzmann constant and x is an initial solute concentration.

3 Calculation results and discussions

The cluster energy, $\Delta H(n) + H_\sigma(n)$, is obtained by the usual density functional codes. The spin-polarized calculations have been performed using the Vienna Ab Initio Simulation Package (VASP)[7,8] with the GGA Perdew-Wang 91 exchange-correlation functional[9], ultrasoft pseudopotentials[10], the plane wave basis set and a cut-off energy of 237.5 eV.

For the precipitates in Fe-rich Fe-Cu alloys, many experimental efforts revealed that Cu-rich clusters precipitate with the metastable bcc structure from the supersaturated bcc-Fe alloys at the early stage of nucleation, and later transform to the fcc structure upon reaching a critical size[11–13]. It was also shown that small Cu clusters with the bcc lattice possess spherical and coherent interfaces.

The calculated equilibrium lattice constants of bcc ferromagnetic Fe and bcc Cu are 2.87 Å, and 2.90 Å, respectively. Because there are small size differences, the strain energy can be neglected in a first approximation. The vibrational contribution can be also ignored under the quasiharmonic approximation due to the almost perfect cancellation between the initial and final states[5]. The cluster energy has been calculated with 54 atoms ($3 \times 3 \times 3$

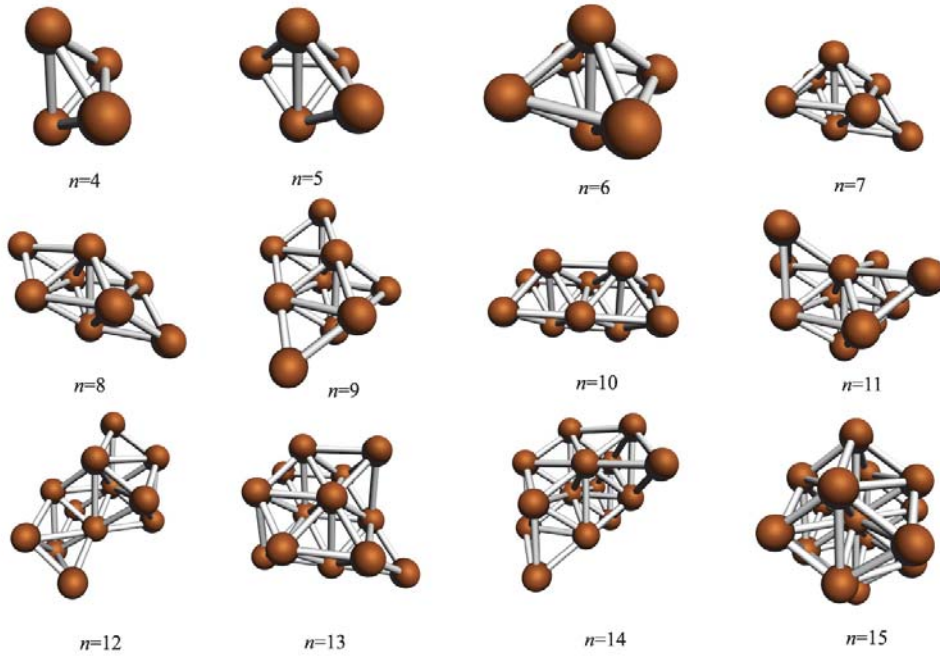


Fig. 2. Atomic configurations of the cluster for the minimum energy at a specific cluster size n .

unit cells) for clusters smaller than or equal to 5, and 128 atoms ($4 \times 4 \times 4$ unit cells) for other larger clusters, under the nonrelaxed condition of the equilibrium lattice constant of Fe. Cluster models were constructed by replacing some sites with Cu atoms.

Figure 2 shows the atomic configuration having the minimum energy among all possible configurations. Figure 3 shows the corresponding cluster energies measured from the segregation limit of pure bcc-Fe and pure bcc-Cu. The straight line in Fig. 3 represents the extrapolated enthalpies of dilution limit, which represents the initial state illustrated in Fig. 1. The final state is represented by the closed circles, so the cluster energy changes of the system in eqn.(1) are the differences between the closed circles and straight line.

The total free energy change is obtained as the sum of this cluster energy and entropy change, as shown in Fig. 4. The entropy change is estimated at the temperature of 773 K and the concentration of 0.014 Cu for comparison with the results obtained by the classical treatment[11]. Estimated critical number n^* and activation energy F^* are 13 atoms and 0.67 eV, respectively. These are very close to the values of 13 atoms and 0.6 eV by the classical treatment. For comparing calculated free-energy with the classical treatment, we assumed interface energy being constant and spherical. Under such assumption, the cluster energy change is expressed as

$$\Delta H + H_\sigma = An + Bn^{2/3}, \quad (3)$$

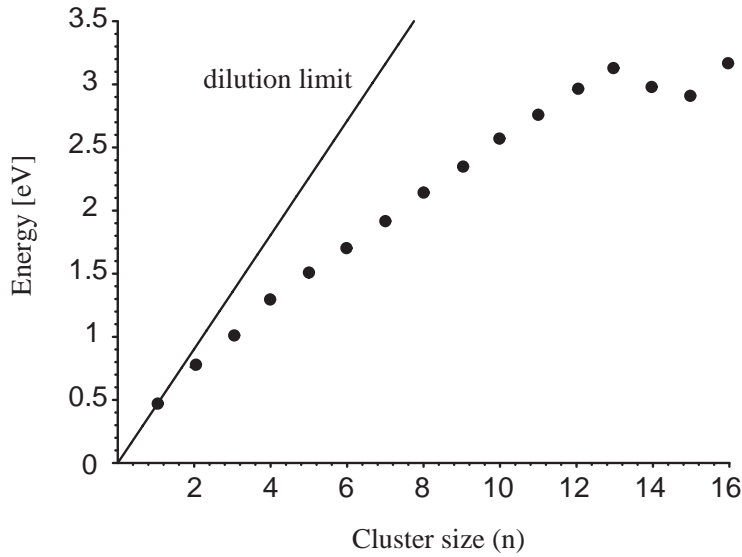


Fig. 3. Calculated cluster energies measured from segregation limit (closed circles), and extrapolated enthalpy of dilution limit (straight line).

where A and B are fitting parameters. Because the interface energy and enthalpy changes are measured from the cluster size of one, we make the simple constraint that the fitted curve should pass through the energy zero at cluster size of one, that is, B should be equal to $-A$. The remaining parameter A is fitted to the calculated data.

The fitted curve for the cluster energy and free energy are also shown in Figure 4. The interface energy estimated from the fitted curve is 0.25 J/m^2 , which is slightly smaller than the values of 0.4 J/m^2 in the classical treatment[11]. By using the first principles calculation with the slab models, the interface energies for $\{001\}$, $\{011\}$ and $\{111\}$ are calculated to be 0.60 , 0.24 , and 0.34 J/m^2 respectively. The fitted interface energy is very close to that of $\{011\}$, and this is in agreement with the interfaces of clusters being almost $\{011\}$ as shown in Figure 2.

Next we will consider ternary systems of Fe-Cu-X, where X=Ni or vacancy. The entropy contribution of the third element is derived by

$$\Delta S_V/k_B = (n-1) \ln x_{\text{Cu}} - n + \frac{3}{2} \ln n + \frac{1}{2} \ln(2\pi) + \ln x_X. \quad (4)$$

where x_X is the concentration of X[14]. When the same concentration and the cluster size, the entropy contribution is assumed to be identical. Thus the free energy is controlled only by the enthalpy difference for determining the lowest free energy. The easiest comparison of the cluster configuration is performed by the cluster consisting of 1st NN and 2nd NN atoms as $n = 15$ cluster in Fig 2, including added atom or vacancy. We considered three extreme cases:

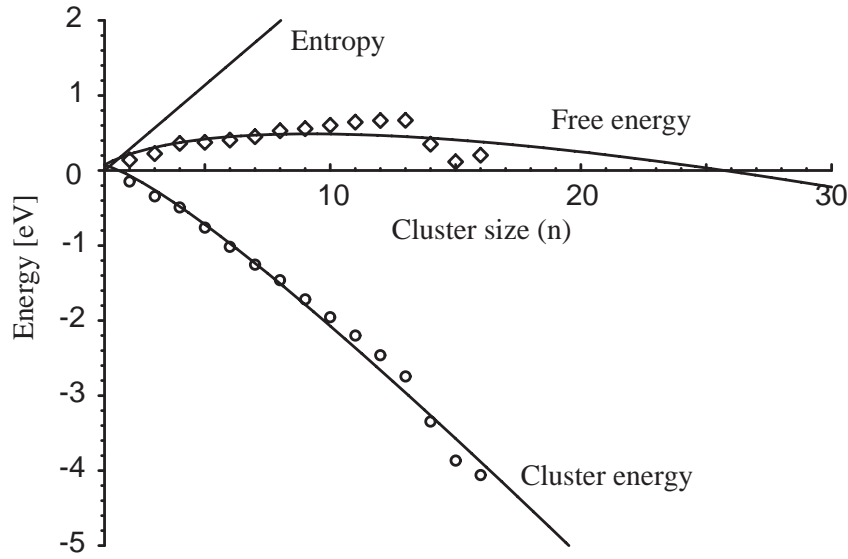


Fig. 4. Free energy change of precipitate nucleation in Fe-Cu system at the temperature of 773K and the concentration of 0.014 Cu. The curve of cluster energy is fitted to the calculation data.

one Ni atom or a vacancy is located (a) at the center of the cluster, (b) at the matrix/cluster interface, and (c) in the matrix. Table 1 shows the calculated enthalpies for Ni and vacancy added configurations.

For Ni, the enthalpy of (b) is lower than that of (a). This result suggests that Ni atom segregates at matrix/cluster interface, which is consistent with the observation of the relatively large size precipitates by atom probe - field ion microscopy[15]. Because of the enthalpy reduction shown in Tabel 1 and entropy reduction of -0.14 eV calculated by Eq. (2) and Eq. (4) from Ni scattered in matrix (c) to Ni included in cluster (b) at the temperature of 773 K and the concentrations of 0.014 Cu and 0.005 Ni, the activation barrier is reduced by Ni additions, which is consistent with the experimental observation of the acceleration of the precipitation reaction[16].

For vacancy, on the other hand, the enthalpy of (a) is lower than that of (b) for vacancy. This result suggests that vacancies shows the tendency to be surrounded by Cu atoms, which is consistent with the experimental observation by positron annihilation measurements[17] as well as the calculated results by molecular dynamics and Monte Carlo simulation[18,19]. The activation barrier is reduced by the same reason of Ni case, but the diffusion constant is also reduced by the reduction of the vacancy density due to the highly trapping ability of clusters. Thus the acceleration of the precipitate reaction due to the vacancy formation is not guaranteed by our present calculation.

Table 1

Cluster energies at size of 15 including one Ni atom or vacancy. Configurations of (a), (b) and (c) are described in the text.

	(a)	(b)	(c)
Ni	2.73	2.35	2.94
vacancy	0.77	1.22	1.69

4 Conclusions

We have shown that our novel method to calculate the free energy of precipitate nucleation is applied to an Fe-Cu system. In this treatment, the critical radius and activation energy barrier is reliably predicted because we can calculate the enthalpy of driving force and the interface energy precisely using first-principles calculation. We have also shown the application to the systems including impurities and vacancies.

In the Fe-Cu alloy, estimated critical number and activation barrier are 13 atoms and 0.67 eV, respectively, those are very close to the values obtained by the classical treatment. The simple model, based on our proposed calculating method, revealed that the added Ni prefers segregating at matrix/cluster interface, and that the vacancies prefers surrounded by Cu atoms.

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