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FIRST PRINCIPLE CALCULATIONS OF NUCLEATION FREE ENERGY CHANGE FOR BCC CU PRECIPITATES IN FE-CU SYSTEM

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Abstract

A slight but crucial modification of the droplet model enables the first principles calculations of free energy change of precipitate nucleation. New treatment divides the free energy into cluster energy and entropy terms. The former, including the internal enthalpy change and the interface energy, is accurately calculated by ab initio methods. The latter is simply estimated by the ideal solution model. Model calculations have been performed for bcc Cu clusters precipitated in bcc Fe matrix, and give reliable predictions of the free energies of small sizes around the critical radius.

Introduction

'Droplet model' is the most primitive picture for the nucleation process. Since the proposal of Becker and Döring [1], kinetic theories for the nucleation process have been investigated by many researchers [2, 3], and are still examined in detail. Although equilibrium Helmholtz free energy change of cluster formation is the underlying assumption for these theories, its method of calculation of the canonical ensemble is still under discussion.

For the accurate estimation, 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 [4]. The other way is calculating the finite-temperature interfacial thermodynamic properties by the cluster variation method [5, 6]. Further combinations of those atomistic level simulations with the continuum theory predict the realistic microstructure evolutions in industrial, multicomponent and complex systems [7]. These methods are applied in large size precipitates in the growth stage rather than 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. Any direct, fast, and easy prediction of critical nucleation size and barrier by first principles methods, however, has not been reported.

In this paper, we will propose a different approach in which free energy change by the cluster formations is accurately and directly estimated using first principles calculations. Model calculations have been performed for bcc Cu clusters precipitated in bcc Fe matrix, which is the key issue of the steels in nuclear reactor pressure vessels and Cu added ultra high strengthened steels [8]. The results give reasonable predictions of the critical radius and the activation energy barrier.

Theory

The simplest droplet model of precipitate nucleation assumes clusters to have regular shapes, which are taken to be spheres, associated with a size-independent precipitate/matrix interfacial free energy σ. Then the free energy change for a cluster of size n is calculated by

$$\Delta F(n) = nV\Delta F_{\mathrm{v}} + (4\pi)^{1/3}(3V)^{2/3}n^{2/3}\sigma \ , \tag{1}$$

where V is atomic volume, and ΔF_{v} is thermodynamical driving force per unit volume. The elastic contribution, the strain energy arising from the cluster/matrix misfit, in what follows is reasonably ignored in the case of the Fe-Cu system as shown later. Furthermore, in this system due to the same lattice structure and similar bulk moduli of their constituent elemental atoms, the cancellation of vibrational entropies between pure elemental metals and alloys are reasonably expected from simple Einstein model [9, 10].

The main ambiguity of the classical nucleation theory is the assumption that the interfacial free energy σ is applied to a small cluster and spherical interface area. For precipitate clusters from metallic solid solutions, this difficulty can be easily avoided by using the following modifications of the nucleation theory.

The proposed treatment of the nucleation calculation divides the free energy in a slightly different manner. The basic idea is the same as the model first proposed by Kamijo and Fukutomi[11]. The bulk term of the free energy is divided into two contributions of enthalpy change ΔH_{v} and entropy change $-T\Delta S_{\mathrm{v}}$. When we bring enthalpy change and interface energy together, the free energy change is expressed as follows:

$$\Delta F(n) = (\Delta H_{\mathrm{v}} + H_{\sigma}) - T\Delta S_{\mathrm{v}}(n) \ , \tag{2}$$

where ΔH_{v} and ΔS_{v} are calculated per cluster size n, and H_{σ} is the contribution of the cluster/matrix interface.

This modification of the nucleation free energy is schematically drawn in Figure 1. The upper panel (a) illustrates the classical treatment of the nucleation theory. The volume driving force ΔF_{v} is proportional to the cluster size n. The middle panel (b) represents the dividing of the free energy to the volume enthalpy ΔH_{v} and entropy $-T\Delta S_{\mathrm{v}}$ terms. Noticing that the driving force is opposite to the free energy change, the positive entropy and negative enthalpy contributions, which are proportional to n, should be expected from the regular solution model of the phase separation system. The lower panel (c) illustrates the cluster energy change which is produced by the addition of volume enthalpy change and interface energy. The identical total free energy change as that in Figure 1 (a) is produced by the addition of the cluster energy and the entropy change.

Figure 2 illustrates the schematic configurations of the models. The initial state of the precipitation process is represented by the isolated solute atom, which is the dilution limit of the alloy. The final state is represented by a cluster formation of size n embedded in matrix. Free energy change is directly calculated by the enthalpy and entropy differences between the initial and final states.

The first term of eq.(2) is cluster energy change, which includes enthalpy change for solute–solute binding formations in clusters from isolated atoms and cluster/matrix interface energy. The cluster energy change is reasonably assumed to be independent of temperature and precisely calculated by first principles calculations. The second term of eq.(2) counts the entropy changes of nucleus and matrix. When we consider the clusters formed by pure solute atoms, the internal entropy of the cluster should be ignored. Thus the entropy change is mainly contributed from the entropy loss from scattered solute atoms to condensing clusters.

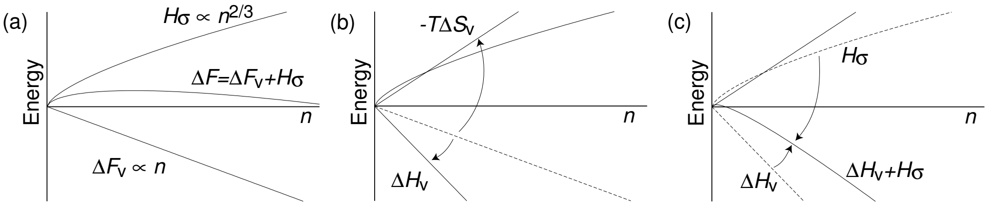

Figure 1: Modification of driving force and surface energy for the nucleation theory. (a) classical treatment where free energy ΔF is the addition of volume driving force ΔF_{v} and interface energy H_σ, (b) the division of the free energy into the volume enthalpy ΔH_{v} and entropy $-T\Delta S_{\mathrm{v}}$ changes, and (c) the cluster energy which is the addition of ΔH_{v} and H_σ.

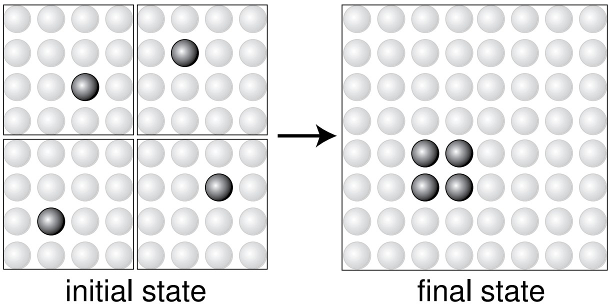

Figure 2: Schematic configurations of the initial and final states of precipitate nucleations. The initial state is represented by the isolated solute atom, and final state is represented by a cluster formation of size n embedded in matrix.

Following the simple ideal solution or Bragg–Williams approximation, the entropy change is reasonably assumed by

$$\Delta S_{\mathrm{v}} = k_{\mathrm{B}}(n-1)\ln(x) \ , \tag{3}$$

where k_{B} is the Boltzmann constant and x is the initial solute concentration [11].

Calculated results

The enthalpy change and interface energy are precisely calculated by the density functional codes. The spin-polarized calculations have been performed using Vienna Ab Initio Simulation Package (VASP) [12, 13] with GGA Perdew-Wang 91 exchange-correlation functional [14], ultra-soft pseudo potentials [15] and plane wave basis set.

Usually it is necessary to consider enormous numbers of atomic configurations even for clusters of only a few atoms. For Fe-Cu alloys, the experimental observations revealed that the small clusters possess bcc lattice [16], and spherical and coherent interfaces [17, 18]. Model clusters were constructed by replacing a few sites with Cu atoms. The calculated equilibrium lattice constants of bcc ferromagnetic Fe and bcc Cu are 2.867Å and 2.900Å respectively. The misfit energy is less than 0.02 eV/atom, which is negligibly small compared with other contributions for the first approximation. The bcc lattice energies have been calculated by the supercell method with 54 atoms (3 × 3 × 3 unit cells) for the clusters smaller than and equal to 5, and with 128 atoms (4 × 4 × 4 unit cells) for the other larger clusters, under the non-relaxed condition of the equilibrium lattice constant of Fe. The calculated results for the small clusters ($n \leq 5$) show that the system prefers spherical

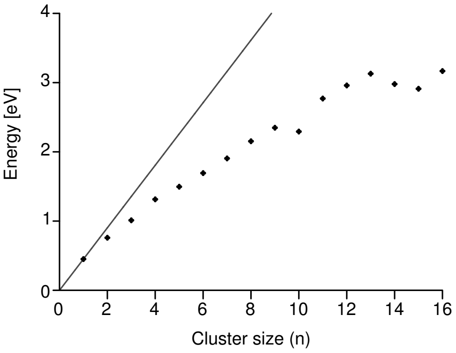

Figure 3: Cluster energy measured from segregation limit.

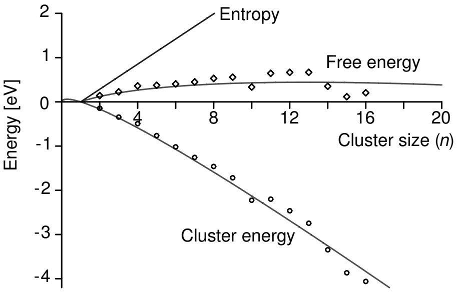

Figure 4: Cluster free energy, entropy and cluster energy changes in relation to the cluster size n. Cluster energies and free energies for specific cluster sizes are indicated by circles and diamonds, respectively. The curves of cluster free energy and cluster energy are fitted to the calculated data.

atomic configurations. However, the clusters possessing a {100} interface show very high energies compared to other planes. In particular the cluster size of 9, whose most spherical symmetry is constructed by cubic unit corner atoms with a body center atom, shows very high energy, because all the interfaces are constructed by {100} planes. Thus we set the cluster configuration as spherical as possible while avoiding {100} interfaces. The cluster configurations and energies will be reported elsewhere in detail. Figure 3 shows the lattice energies of cluster size of n measured from the segregation limit. The cluster energy changes in eq.(2) of the system are differences between those of the clusters and that of the isolated solute atom. The straight line connecting the origin to the energy value of the cluster size of one as drawn in Figure 3 represents the extrapolated enthalpy of the dilution limit. Thus the maximum energy gains from the line should be the cluster energy changes.

The total free energy change of the formation for a cluster size of n is shown in Figure 4. The entropy change is estimated at the temperature of 773K and the concentration of 0.014 (1.4%) Cu for compared with the results obtained by the classical nucleation treatment [19]. Cluster energies and free energies for specific cluster sizes are indicated by circles and diamonds, respectively. Although some points should move downward due to the relaxations, the maximum shift should be less than 0.02 eV/atom, which is the misfit energy for pure bcc Cu lattice. For comparing the results with the classical treatment, we can assume the interface energy being constant and spherical. Under such assumption, the cluster energy change should be a simple function of cluster size n, which is expressed by the classical treatment of eq.(1), namely:

$$\Delta H_{\mathrm{v}} + H_{\sigma} = A\ n + B\ n^{2/3}\ , \tag{4}$$

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

The fitted curves for the cluster energy and free energy are also shown in Figure 4. The expected deviation of the cluster energy anomaly arising from the violation of the classical assumption of constant and spherical interface energy is surprisingly small at the smaller clusters, but is notable at the medium size clusters. The fitted curve shows the critical number of about 13 atoms with the activation energy barrier of 0.44 eV, which are very close to the values of 13 atoms and 0.6 eV estimated by the classical nucleation treatment [19]. Although the interface energy estimated from the fitted curves of $0.25\mathrm{J/m}^2$ is slightly smaller than that of $0.4\mathrm{J/m}^2$ used in the classical treatment [19], the estimated critical numbers and activation energies show good agreements.

Conclusions

We have demonstrated that the newly proposed calculating method of nucleation free energy correctly predicts the critical radius and activation energy barrier of the industrially used Fe-Cu alloy. The key features of our proposed treatment are (i) avoiding the ambiguous interface energy at small sizes, (ii) using the reliable first principles calculations, and (iii) distinct definition of the initial and final states of the precipitation phenomenon. For the usage of this proposed treatment, the Fe-Cu system is the ideal alloy, where the constituent atoms are under small differences in size, weight, and bulk modulus. In such a system, we have shown that the activation energy barrier simply arises from the enthalpy gain and the configurational entropy loss between the scattered atoms and condensed clusters. The further modification of the proposed method for the ternay systems, or vacancy included system is straightforward [20, 21].

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