Materials Science Forum Vols. 539-543 (2007) pp 2395-2400
online at http://www.scientific.net

Free Energy Calculations of Precipitate Nucleation

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Keywords: first principles calculation, activation barrier, Fe-Cu

Abstract. Our recently proposed calculating method reliably predicts the nucleation free energy barrier of the homogeneous and coherent precipitations. Helmholtz free energy change is clearly defined and calculated by the purely enthalpic and entropic contributions between the initial state of the isolated solute atoms scattering around the matrix and the final state of the cluster of size *n* traveling around the matrix. The enthalpic term is calculated by the reliable first principles method and the entropic term is estimated by the ideal solution model. The vibrational free energy is also included by the quasi-harmonic approximation. The model calculation was performed on bcc Cu precipitations in the Fe-Cu system. The predicted values of the critical number of 12 atoms and the critical free energy barrier of 0.6eV show good agreement with the experimentally estimated ones for the annealing temperature of 773K and the initial concentration of 1.4at%Cu.

Introduction

The activation energy barrier for the nucleation is the one of the key values for controlling the microstructures of materials. The driving force and the interface energy are necessary to estimate the free energy change for the cluster formation during the precipitations. For the reliable estimations of the free energy differences between two phases, which is the driving force, have been performed by the first principles calculations for these two decades. The reliable estimation of the interface energies of the small clusters, however, has not been established yet.

The newly proposed calculating method for predicting the free energy of the precipitate nucleation avoids this difficulty[1-3]. The reconstruction of the configurational free energy change between the initial and final states of the precipitation phenomena makes the calculations purely enthalpic and entropic separately. Very recently the vibrational contributions was also included on this method based on the quasi harmonic approximation[4].

In the present paper, the idea of the reconstruction of the free energy is shown. The additional effects of the vibrational free energy is also examined on bcc Cu precipitations in the Fe-Cu system.

Basic idea of the activation energy

Free energy is the state quantity, which means that the value is determined by the difference between those of the initial and the final states. The free energy change can be constructed by the sum of the configurational, vibrational, namely,

$$\Delta F = \Delta F_{\text{config}} + \Delta F_{\text{vib}} \quad (1)$$

Because the volume change due to the thermal expansion affects very small on the free energy, we can neglect it for the simplicity[4]. The first term, the configurational contributions, will be examined, and the second term on the next section.

For the precipitation process, we will take the following assumptions, which are valid for the initial stage of bcc Cu precipitations in the Fe-Cu system.

1. The solute atoms are one species and substitutionals not interstitials.
2. The lattice structure does not change before and after the precipitation. The small deviations around the fixed sites are allowed for the relaxations.
3. The precipitated clusters show coherent interfaces to the matrix and distributed homogeneously.

The current model of the precipitation process is illustrated in Fig.1.

At the very beginning of the precipitation treatment, the system is held at the higher temperature than the solidus line, where is the solid solution region. Thus the initial atomic configuration of the system is the equilibrium state not at the annealing temperature but at the quenching temperature. Thus in the initial state, the solute atoms are randomly distributed in the solvent atoms.

At the annealing temperature, the solute atoms get together and make clusters below the solidus line, where is the phase separating region. The interface is taken to be coherent as assumed before.

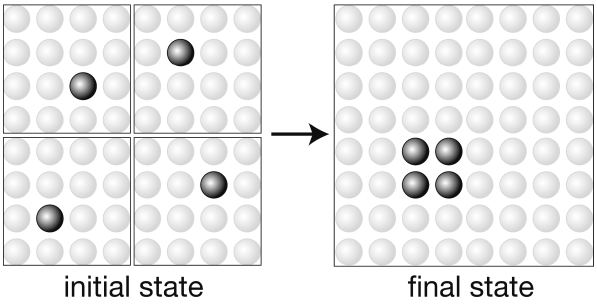

Fig. 1 Schematic illustration of the precipitation process.

The enthalpic energy of the system can be calculated precisely by the usual first principles methods. The total energy of the final state includes unlike pairs at the interface, which is the origin of the interface energy. The configurations of clusters with the specific size, say four, can show various shapes such as line, plane, or tetrahedron. The lowest energy among these shapes should be taken due to the enough time for the internal relaxations or from the concept of the most preferred state. The entropic contributions could be derived by Bragg-Williams approximation[2]. The final form of the entropy change between the initial and final states of the precipitation is identical with the simpler model of the ideal solution, which is first proposed by Kamijo and Fukutomi[5],

$$\Delta S = (n-1)k_\mathrm{B} \ln x \tag{2}$$

where n is the size of the cluster and x is the initial concentration of the solute.

Figs.2 illustrate the reconstruction of the enthalpic and entropic terms, from the classical droplet model (a) to newly proposed method (c). The volume driving force ΔF_v is proportional to the cluster size n, and the interface energy H_σ is proportional to $n^{2/3}$. The former could be divided into the enthalpic ΔH_v and the entropic $-T\Delta S_\mathrm{v}$ contributions formally (Fig.2(b)). The purely enthalpic contribution is derived by adding this enthalpic contribution of the driving force and the interface energy as shown in Fig.2(c). This is just the reconstruction of each contribution, but the final grouping makes the calculation easy due to the separation of purely enthalpic and entropic calculations. The enthalpic contribution automatically includes the interface energy. By these reconstructions, complicated effects of the interface areas and orientations of small clusters are automatically avoided.

Vibrational effect

By the quasi harmonic approximation, the vibrational free energy f_i for i-site is given by

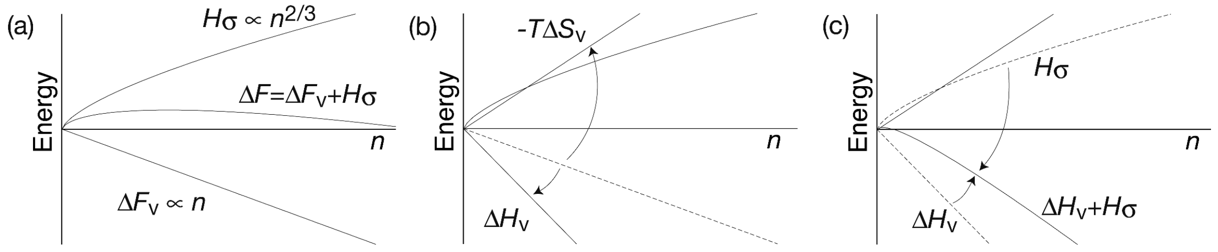

Fig. 2 Reconstruction of driving force and surface energy of nucleation free energy change. See the text in detail.

$$f_i = k_B T \ln \frac{1}{1-\exp(-\hbar\omega_i/k_B T)} + \frac{3}{2}\hbar\omega_i , \qquad (3)$$

where k_B is the Boltzmann constant, and T is the temperature. ω_i is the vibration frequency obtained by

$$\omega_i = \sqrt{\frac{K_i}{m_i}} \qquad (4)$$

where m_i is the mass and K_i is the spring constant. The latter is reasonably assumed by the local bulk modulus of atom *i*, and is obtained by the diagonal elements of the dynamical matrix.

Under the quasi harmonic approximation, the vibrational free energy change is controlled only by the frequency. When we express the vibrational free energy at the *i*-site f_i and the small change of its frequency $\delta\omega_i$, the total free energy change ΔF will be expressed by Taylor expansion

$$\Delta F_{\text{vib}} = \sum_i \{f(\omega_i + \delta\omega_i) - f(\omega_i)\} \simeq \sum_i f'(\omega_i)\delta\omega_i \simeq f'(\omega_i)\sum_i \delta\omega_i . \qquad (5)$$

The last modification is only valid when the first derivative of the atomic free energy is independent on spring constant. For the normal range of the vibrational frequency of the metallic system, below a few THz, their frequence dependency shows very small at the higher temperatures[6,7].

Fig.3 shows the total bulk modulus for the Fe-Cu 128 atoms (4x4x4 unit cells), including clusters of the shown shapes[4]. First principles calculations were performed by VASP code with PAW potentials[8-11]. This value represents the average behavior of the bond stiffness of the systems. If the spring constants of the like and unlike pairs shows the average behavior, the bulk modulus should be located on the average line between pure Fe and pure Cu as shown as the dashed one.

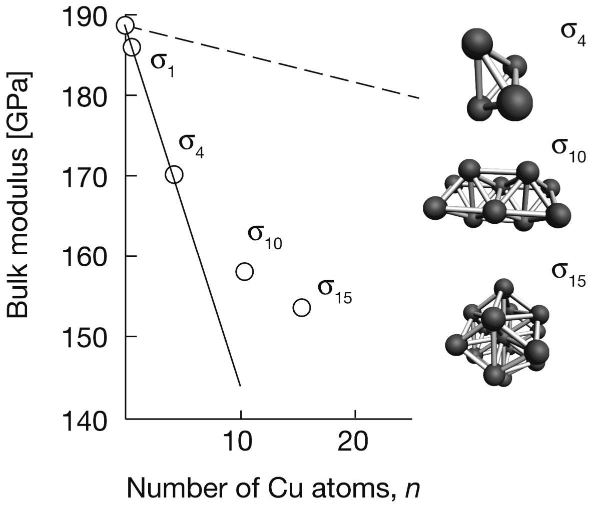

Fig.3 Bulk modulus for 128 atoms system, including a Cu atom and Cu clusters as shown in the right hand

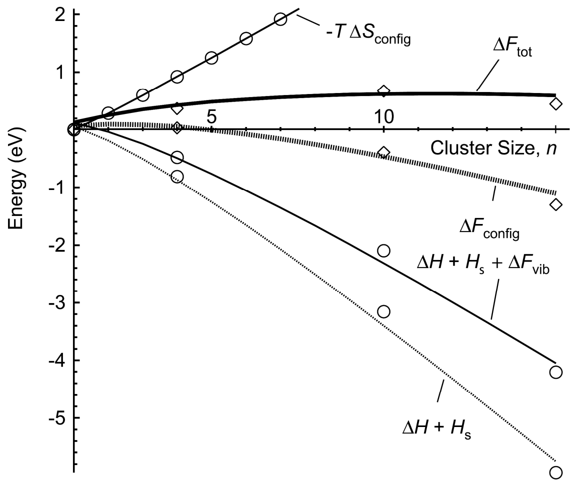

Fig.4 Calculated free energy change of bcc Cu precipitate nucleation in Fe-Cu system with and without vibrational contributions.

The subscripts of the points in Fig.3 represent the number of Cu atom replaced with Fe atoms. σ_1 is the initial state of the precipitation. The others are the final states of the precipitation, and those stable shapes are obtained by Seko et al.[2] All the values of bulk modulus were deviated from the average line. Thus the calculations of the vibrational free energy for the all sites are necessary.

Fig.4 shows the energy changes of the formation for cluster size of *n*[4]. The entropy change ($-T\Delta S_{\mathrm{config}}$) is estimated at the temperature of 773K and the initial concentration of 1.4at% Cu for compared with the results obtained by the classical nucleation treatment. The enthalpy changes are obtained by the first principles method with and without vibrational contributions. The vibrational contributions are calculated using Eq. 1. With vibrational contribution, the activation energy barrier and the critical cluster size are 0.62 eV and 12 atoms respectively, which are consistent estimations with the experimental results[12]. Without vibrational contribution, those are very small, 0.09 eV and 2 atoms respectively. The differences between with and without vibrational contributions are simply explained by the bulk modulus changes as shown in Fig.3. The bulk modulus for the final states, σ_4, σ_{10} and σ_{15} are all located above the line extrapolated from σ_1 (solid line in Fig.3). The higher bulk modulus makes the higher free energy and the smaller energy drop for the cluster energies, $\Delta H+H_s+\Delta F_{\mathrm{vib}}$ as plotted in Fig.4.

Conclusions

The combinations of configurational and vibrational free energy makes it possible to estimate the reliable activation energy barrier for Fe-Cu system. By the configurational free energy, the activation barreier arises from the enthalpy gain and the configurational entropy loss between the scattered atoms and condensed clusters. The vibrational effect also contributes the total energy significantly by the drastic change of the bond stiffness from the average values of their constituent atoms. This reliable free energy calculating method of the precipitate nucleation using the first principles methods will subscribe inevitable parameters for the microstructure controls of the material designs.

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