Vacancy effect on the precipitate nucleation in Fe-Cu alloy

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ABSTRACT

The activation energy barrier height of bcc-Cu precipitates in Fe-Cu alloy has been predicted using the first principles calculations. The predicted values of the critical number of 12 atoms and the critical free energy barrier of 0.6eV show good agreements with the experimentally estimated ones for the annealing temperature of 773K and the initial concentration of 1.4at%Cu. This approach also predicted that the vacancy prefers inside not at the interface of clusters.

1. Introduction

The nucleation phenomenon is one of the main targets of the multi-scale materials modeling. The recently proposed method [1-3] predicts the fundamental but hardly obtained values of activation barrier, critical size and free energy change of the precipitate nucleation precisely using the first principles calculations. Helmholtz free energy change is apparently 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 a 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. This approach avoids the difficult calculations on the interface energy of small clusters. Firstly we will show the basic idea of the proposed method, and then the results of bcc Cu precipitation in a Fe-Cu alloy. Lastly the vacancy behavior in precipitates, which is crucial under the irradiated condition, will be discussed.

2. Calculating method

In classical nucleation theory, the free-energy change is described by the sum of negative driving force ΔF and positive interface energy $H\sigma$. 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 into two components of enthalpy change ΔH and entropy change $-T\Delta S$, and treating enthalpy change ΔH and interface energy $H\sigma$ together, the free energy change is expressed as

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

where n is the number of atoms in a cluster.

Figure 1 shows schematic illustrations of precipitate nucleation. The initial state is described as the sum of the isolated solute atoms, and is the dilution limit of an alloy. The final state is

described as one cluster constructed by n solute atoms moving around on the matrix. The free-energy change is calculated from the enthalpy and entropy differences between these initial and final states.

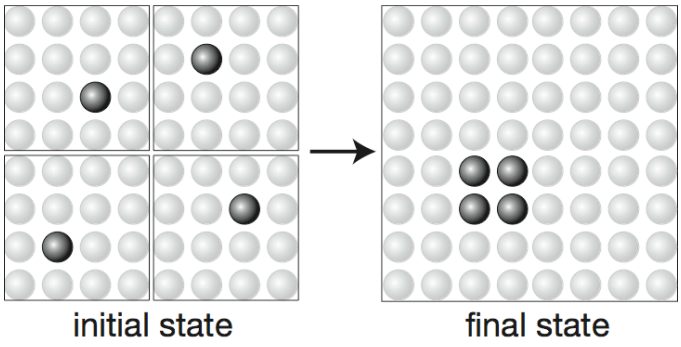

Figure 1. Schematic drawings of initial and final states of precipitation.

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 can be treated separately[3], and neglected here for the first approximation. 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[4],

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

where k_{B} is Boltzmann constant and x is an initial solute concentration.

3. 3. Calculated results

The cluster energy, $\Delta H(n)+H\sigma$, is obtained by the usual density functional codes. The spin-polarized calculations have been performed using the *Vienna Ab Initio Simulation Package* (VASP)[5,6]. For the precipitates in Fe-rich Fe-Cu alloys, many experiments revealed that Cu clusters precipitate with the metastable bcc structure from the super satuated bcc-Fe alloys at the early stage of nucleation [7]. It was also shown that small Cu clusters with the bcc lattice possess spherical and coherent interfaces. The cluster energy has been calculated with 54 atoms (3 x 3 x 3 unit cells) for clusters smaller than or equal to 5, and 128 atoms (4 x 4 x 4 unit cells) for other larger clusters, under the non-relaxed condition of the equilibrium lattice constant of Fe. Cluster models were constructed by replacing some sites with Cu atoms.

The total free energy change is obtained by the sum of this cluster energy and entropy change, as shown in Fig. 2. The entropy change is estimated at the temperature of 773 K and the concentration of 0.014 at% Cu for the comparison with the result obtained by the classical treatment [7]. Estimated critical number n^* of 13 atoms and activation energy F^* of 0.67 eV, respectively are very close to the values of 13 atoms and 0.6 eV by the classical treatment.

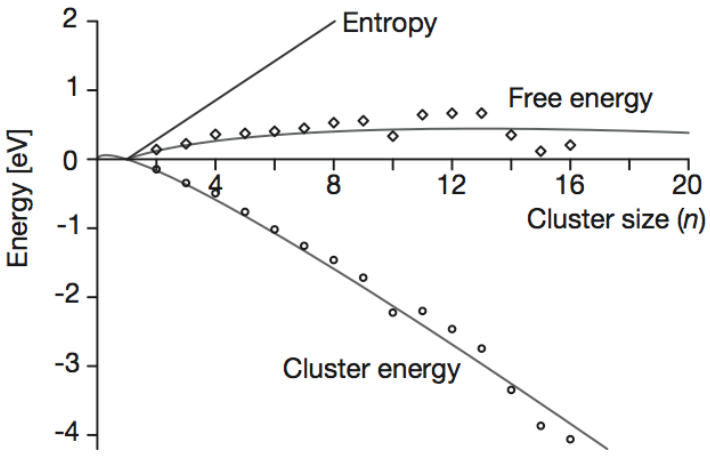

Figure 2. Activation barrier of the free energy due to the precipitate nucleation.

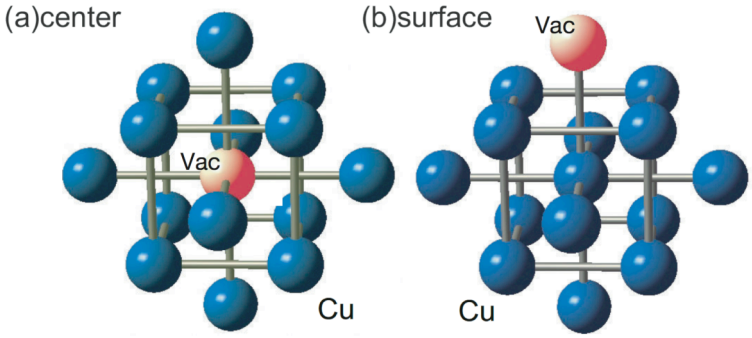

Figure 3. Atomic configurations for clusters including one vacancy and 14 Cu atoms.

Next we will see the vacancy contribution on the nucleation. The entropy change including the third element or vacancy is derived by

$$\Delta S(n)/k_{\mathrm{B}} = (n-1)\ln x_{\mathrm{M}} - n + \tfrac{3}{2}\ln n + \tfrac{1}{2}\ln(2\pi) + \ln x_{\mathrm{V}} \qquad (2)$$

where x_{M} is the major solute element and x_{V} the third element or vacancy[2]. Thus the entropy contribution is assumed to be identical at the same concentration and the cluster size. The free energy is controlled only by the enthalpy difference.

The easiest comparison of the vacancy configuration is performed by n=15 cluster as shown in Fig. 3. We considered two extreme cases: one vacancy is located (a) at the center of the cluster, and (b) at the matrix/cluster interface. The enthalpy of (a), 0.8eV, is lower than that of (b), 1.25eV. 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 [8]. This tendency is simply explained by the difference in vacancy formation energies for pure metals, 0.6 eV for bcc Cu and 2.3 eV for bcc Fe. By this enthalpic reduction, the activation barrier is reduced. At the same time, however, 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 concluded by our present calculation.

4. References

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