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METALS

Pseudospinodal in the Monte Carlo Simulation of the Decomposition of an Alloy

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Abstract—A hypothesis about the existence of a pseudospinodal separating the homogeneous and heterogeneous nucleation regions in the phase diagram of a binary alloy has been proposed on the basis of the results obtained from the Monte Carlo simulation of the decomposition in a simple system with a short-range attractive potential of the impurity atoms.

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1. INTRODUCTION

In the theory of phase transitions in alloys [1, 2], different types of decomposition kinetics are classified according to parameters (temperature, composition) of an alloy in the phase diagram. The solubility limit (binodal) is determined by the condition of the equality of the chemical potentials of the phases, whereas the limit of stability of a homogeneous state (spinodal) is defined as the boundary of the convex portion of the concentration dependence of the free energy. Thus, there is a region of metastable states between the spinodal and the binodal in the phase diagram, where the alloy is stable with respect to small fluctuations of the composition, but undergoes decomposition into equilibrium phases in the case of the formation of critical nuclei. The physical reason for the existence of this region in the phase diagram is the fact that there is a contribution from the configurational entropy of the atoms to the free energy of the alloy.

At present, it is considered to be established [3, 4] that the spinodal is only a theoretical concept. It exists in the limit of infinitely long-range interactions [5–7], but, in systems with a short-range potential, thermal fluctuations provide a smooth transition from the absolute instability to the regime of nucleation and growth, so that it is impossible to determine the line separating these two kinetic regimes. This is evidenced by the experimental data [8, 9] and the results of the computer simulation [10, 11].

The process of nucleation near the binodal has been investigated to a lesser extent. In a number of research papers, the authors discussed the necessity to separate the region of metastable states into two subregions. In particular, Binder [5] constructed a schematic phase diagram that included the "classical nucleation" region (immediately below the binodal) and the "spinodal nucleation" region (immediately above the spinodal), even though the transition between these regions was assumed to be smooth. Earlier [8, 12], the idea of two nucleation regimes was used to explain the experiments on the scattering of light in binary liquid mixtures. Patashinskii and Shumilo [13] theoretically predicted that there is a third region between the metastable region and the region of unstable states in the phase diagram, where the initial homogeneous state is stable with respect to infinitesimal long-wavelength fluctuations, but transforms into a heterophase state under the influence of finite thermal fluctuations. The line bounding from above this region was called the physical spinodal. Kiselev and Kostyukova [14] obtained a similar line for a single-component gas in the vicinity of the critical point. It was noted that this line lies closer to the binodal than to the theoretical spinodal. Wang and Wood [3, 15] predicted the existence of a "pseudospinodal" in binary polymer mixtures, which was experimentally confirmed by Lefebvre et al. [16] (it should be noted, however, that we are dealing here with single experiments). The pseudospinodal coincides with the mean-field spinodal in the limit of infinite molecular weight, which is mathematically equivalent to the transition to a long-range potential. The theory proposed by Wang [3] is valid for a sufficiently large (even though finite) molecular weight and cannot be extended to alloys with a short-range potential. The interpretation of the pseudospinodal is debatable. Wang [3] put forward the hypothesis that the pseudospinodal separates regions of physically accessible (observable) and inaccessible (unobservable) metastable states, because, usually, the decomposition occurs very rapidly. It remains unclear

whether the pseudospinodal exists in real alloys with a short-range interaction. There are no results obtained from the simulation using the Monte Carlo technique that would confirm the existence of a pseudospinodal in any system.

In this paper, based on the results obtained from the Monte Carlo simulation of the decomposition of an alloy with a short-range potential, it has been shown that the hypothesis of the existence of a pseudospinodal in the alloy is justified. The criterion for the achievement of the pseudospinodal line is the fact that the incubation period for the formation of a critical nucleus tends to infinity, which apparently occurs below the binodal. Therefore, the pseudospinodal separates the region of possible homogeneous nucleation and the region of possible heterogeneous nucleation.

2. SIMULATION METHOD AND RESULTS

The simulation of the decomposition of an alloy was performed using a simple scheme of the kinetic Monte Carlo technique implementing the Kawasaki dynamics [17] with direct exchange of atoms, which was tested in our previous studies [18, 19]. For the Monte Carlo simulation, we chose the effective Cu–Cu pair potential in the matrix of body-centered cubic (bcc) Fe. For simplicity, we restricted ourselves to the potential in the paramagnetic state for the first three coordination spheres {–7.4, –2.3, –0.3} mRy without taking into account the deformation, concentration, and magnetic corrections. This choice does not provide the true solubility limit of copper in bcc-Fe, but leads to a simple model that is sufficient for the purposes of the present study. The calculations were carried out for a supercell of 90 × 90 × 90 or 60 × 60 × 60 unit cells in size with periodic boundary conditions. As was done in [18, 19], the degree of decomposition $0 < S < 1$, which was achieved to a certain point of time, was calculated from the configuration of atoms according to the following rule:

$$S = \frac{1}{N}\sum_{j=1}^{N}\Theta\left(\frac{1}{Z}\sum_{k=1}^{Z}\sigma_k^{(j)} - q,\right) \qquad (1)$$

where N is the number of copper atoms in the sample, $\sigma_k^{(j)}$ are the occupation numbers for the nearest neighbors around the jth site, $Z = 8$ is the coordination number for the nearest neighbors in the bcc lattice, and $\Theta(x)$ is the Heaviside step function. According to formula (1), the copper atom is considered as belonging to a precipitate, if the local concentration of copper in the region surrounding it is no less than q. Since it is important to accurately determine the time of the onset of the decomposition of the alloy, the local copper concentration was taken to be equal to $q = 0.25$. In this case, the degree of decomposition (1) is sensitive to the formation of even small clusters.

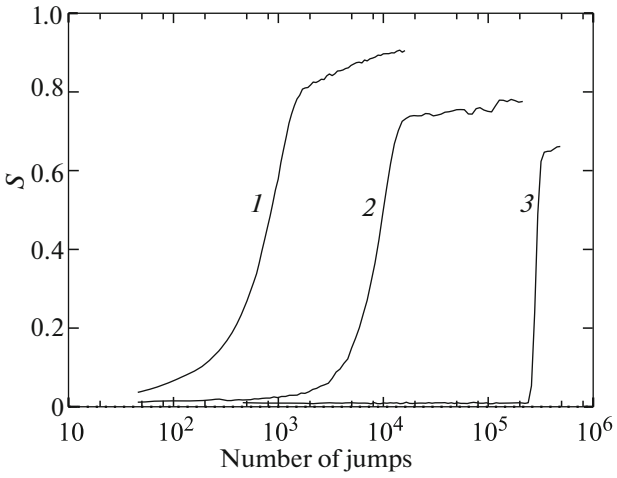

Fig. 1. Evolution of the degree of decomposition of the alloy with the concentration of impurities $c = 0.015$ at temperatures $T =$ (*1*) 800, (*2*) 1000, and (*3*) 1100 K. The time is expressed in units of the number of jumps per impurity atom.

As in the recent study [19], our calculations have demonstrated the absence of the spinodal as a physically defined line that separates the region of absolute instability from the region of nucleation and growth. With an increase in the temperature, the incubation period for the onset of the decomposition of the alloy increases monotonically from very small to very large values (Fig. 1). At the same time, it has been found out that, at technically achievable computation times, the nucleation becomes impossible in the vicinity of a particular curve in the phase diagram, which can be called the pseudospinodal (or the limit of stability of a homogeneous state) and which is significantly different from the binodal. This curve was previously calculated in [18] using the conventional procedure of the Metropolis Monte Carlo algorithm (with the rearrangement of atoms to arbitrary distances) and then was wrongly identified with the binodal. As a result, the authors of [18] came to the wrong conclusion that there is an agreement between the theory and the experiment for the solubility limit of copper in bcc-Fe. Therefore, it is necessary to perform a careful analysis of the question as to whether the limit of stability appears in our calculations for the reason that sufficiently long computation times are technically unachievable or this limit is actually a physically defined line in the phase diagram.

The results of our calculations at a fixed temperature and with a variation in the average composition of the alloy are presented in Fig. 2. Curve *1* in this figure shows the incubation period for the onset of the decomposition in the homogeneous system, which is determined from the condition that the degree of decomposition of the alloy reaches the value of $S = 0.05$. Curve *2* represents the time of dissolution of a single precipitate from the two-phase state, where all

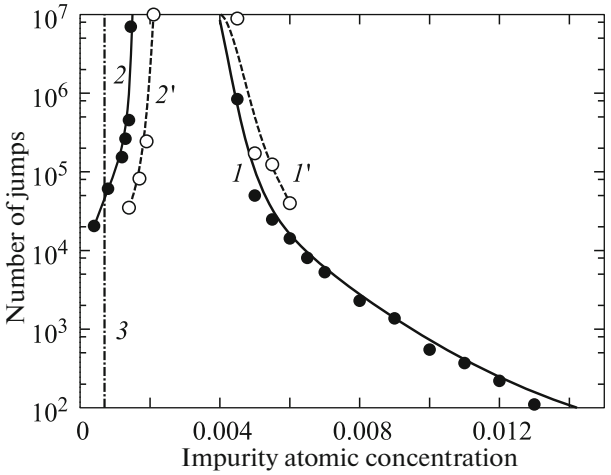

Fig. 2. (*1*, *1*') Incubation period for the onset of the decomposition of the alloy and (*2*, *2*') time of dissolution of a precipitate as a function of the average composition of the alloy at a temperature $T = 800$ K. The calculations are performed for computational regions with sizes of (*1*, *2*) 90 × 90 × 90 or (*1*', *2*') 60 × 60 × 60 unit cells. Vertical dash-dotted line *3* corresponds to the equilibrium concentration of impurities in the matrix in contact with a large-sized precipitate. The time is expressed in units of the number of elementary permutations per impurity atom.

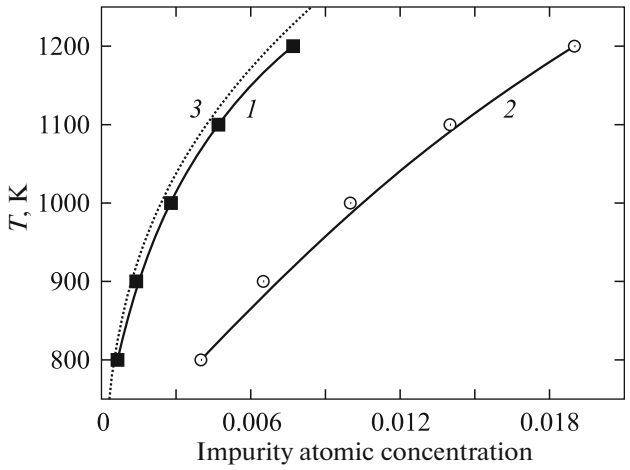

Fig. 3. (*1*) Equilibrium concentration of impurities in the matrix (binodal) and (*2*) pseudospinodal obtained from the condition that the incubation period tends to infinity. Dotted curve *3* is constructed according to the formula for the regular solution binodal [1].

impurity atoms of the system are located within one precipitate in the center of the computational region. Vertical dash-dotted line *3* indicates the equilibrium concentration of impurity atoms in the matrix (binodal). For the calculation of the binodal, a large-sized copper precipitate was placed in pure iron and allowed to stand for a sufficiently long time until the matrix reached saturation. Then, we calculated the average concentration of impurity atoms in the matrix layer located at a distance from the initial precipitate.

It can be seen from Fig. 2 that the time of dissolution of a single precipitate (curve *2*) tends to infinity in the vicinity of the equilibrium concentration of impurity atoms in the matrix (dash-dotted line *3*). The observed difference is associated with the Gibbs–Thomson effect [20, 21], because curve *2* is constructed for a small-sized precipitate, whereas dash-dotted line *3* corresponds to the equilibrium between the bulk phases. It should be noted that, in this case, the incubation period for the onset of the decomposition of the alloy (curve *1*) apparently tends to infinity at a different concentration of impurity atoms, which is several times higher than the equilibrium concentration. Taking into account the fact that the onset of the decomposition of the alloy requires the formation of a critical nucleus due to the occurrence of thermal fluctuations and also that the maximum achievable scale of fluctuations should depend on the size of the computational region, we constructed similar lines for a supercell with a decreased size of 60 × 60 × 60 unit cells (curves *1*' and *2*' in Fig. 2). It can be seen that the two curves in Fig. 2 are shifted to the right by approximately the same value. Therefore, the difference between the solubility limit and the limit of stability cannot be explained by the size effect.

Figure 3 shows the temperature dependences of the binodal and the pseudospinodal obtained on the basis of the Monte Carlo simulation data (curves *1* and *2*, respectively). Dotted curve *3* in this figure corresponds to the binodal of the regular solid solution [1], which is calculated according to the formula $kT = \nu(1 - 2c)/\ln[c/(1 - c)]$, where the energy of mixing $\nu = -38.3$ mRy is obtained from the pair potential taking into account the occupation numbers of the coordination spheres, i.e., $\nu = \left(\sum_i z_i V_i\right)/2$, $V_i = \{-7.4, -2.3, -0.3\}$ mRy, and $z_i = \{8, 6, 12\}$. It can be seen that the binodal calculated using the Monte Carlo simulation technique is very close to the binodal predicted from the model of regular solutions. The pseudospinodal in the region of small concentrations is close to a linear function, thereby exhibiting a qualitative similarity to the spinodal of the regular solid solution, which is defined by the formula $kT = -2\nu c(1 - c)$ [1]. However, this spinodal is described by numerical values of one order of magnitude lower than those of the spinodal of the regular solid solution, but, in the physical sense (the line on which the incubation period tends to infinity) is significantly different from the spinodal indicating the threshold of the absolute instability of the alloy with respect to small long-wavelength fluctuations. Note also that, in [22], it was shown that the spinodal of the cluster approximation (which is more accurate) lies much more to the left of the mean-field spinodal, while the binodal position remains unchanged.

3. DISCUSSION OF THE RESULTS

We have proposed a rough qualitative interpretation of the results obtained in this study.

In the absence of fluctuations of the alloy composition, a subcritical nucleus ($R < R_{cr}$) is dissolved. However, it can grow under the influence of fluctuations. If, in this case, the nucleus reaches a critical size ($R > R_{cr}$), it continues to grow even after the completion of the action of the fluctuations. From the energy point of view, the probability of the formation of a fluctuation with the energy ΔG obeys the law $\sim w_0 \exp(-\Delta G/kT)$. Hence, it follows, at first glance, that the critical nucleus is formed upon sufficient exposure, provided only that $w_0 \neq 0$. However, the formation of a critical nucleus is a process that develops over time, during which the nucleus size R under the influence of a fluctuation runs over all possible values from the size of a single atom to the critical size R_{cr}. Therefore, in addition to the energy factors, it is necessary to take into account the kinetic arguments. The maximum rate of supply of a new substance to the nucleus as a result of the influence of a fluctuation is limited by the average composition of the alloy with the impurity concentration c_0 and decreases with a decrease in the value of c_0. On the contrary, the intensity of dissolution of a subcritical nucleus increases as the value of c_0 approaches the binodal. The two competing processes are balanced at a certain critical size of the nuclei.

According to [23], in the absence of fluctuations, the flux at the surface of a nucleus can be represented in the form

$$j = \frac{D}{R}\left(c_0 - c_e^\infty - \frac{\sigma}{R}\right), \quad (2)$$

where D is the diffusion coefficient, σ is the renormalized surface tension, and c_e^∞ is the binodal concentration. The critical size R_{cr} of the nuclei is determined by the condition $J = 0$; i.e.,

$$R_{cr} = \sigma/(c_0 - c_e^\infty). \quad (3)$$

Let us introduce an additional contribution into expression (2), i.e., the fluctuation flux Dc_0 acting for an infinitely long time, which corresponds to the image of a maximum possible fluctuation. Then, the condition for the formation of a critical nucleus takes the form

$$R_{cr}^{fluc} = \frac{\sigma}{(c_0 - c_e^\infty) + c_0 R_{cr}^{fluc}}. \quad (4)$$

In the case of a weak supersaturation ($c_0 - c_e^\infty \gg 1$), we have

$$R_{cr}^{fluc} = \sqrt{\sigma/c_0}. \quad (5)$$

The value of the critical nucleus size R_{cr}^{fluc} remains relatively large for a sufficiently small concentration c_0. Therefore, in the case of weakly supersaturated alloys, in the vicinity of the binodal there should exist a region where subcritical nuclei are dissolved even under the conditions of the action of a maximum possible fluctuation flux. This means that the formation of a critical nucleus in this region requires an additional stimulation; i.e., only the heterogeneous nucleation takes place.

4. CONCLUSIONS

Thus, based on the results of the Monte Carlo simulation, we put forward the hypothesis that, in the phase diagram of a binary alloy, there is a pseudospinodal (or a limit of stability of a homogeneous state with respect to thermal fluctuations of the composition of the alloy). This pseudospinodal separates the homogeneous and heterogeneous nucleation regions in the phase diagram of the alloy.

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