Conference Paper

Simulation of Correlation Effects in Ordering Binary Alloys

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Abstract

In this paper, computer simulation is used to study correlation effects for vacancy in the binary ordering alloys. At first we obtain a set of equilibrium states by Monte Carlo method for different temperatures and then we simulate the vacancy migration by Kinetic Monte Carlo using atomic structures of mentioned states. Correlationfactordependencies fromthe temperature and short-range order parameter are derived for the vacancy migration.

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1. Introduction

The rate of growth of new phase inclusions and the rate of degradation of the structure of two-phase materials (natural composites) are determined by diffusion processes, and primarily by diffusion near the interface of phases because in this area ordering effects that affecting the magnitude of diffusive fluxes play an important role. Correlation effects are manifested in this case both in the diffusion of vacancies and in the migration of atoms in binary and multicomponent alloys.

Vacancies that are contained in any crystal lattice, open an easy path for diffusion [1, 2]. An elementary event in diffusion by the vacancy mechanism is the exchange of a defect with an adjacent atom. If the jumps are carried out chaotically, without revealing any preferential direction, then the vacancy commits random walks. The diffusion of the vacancy in the crystal lattice of a metal can serve as an example of a process of random walks, since the correct structure of the crystal lattice makes it possible to carry out jumps of defects of only a certain length and in certain discrete directions. When considering diffusion in the random walk approximation, it is assumed that the probabilities of atomic and vacancy jumps are independent of the directions of the preceding displacements. However, in real crystals such a relationship often occurs. So vacancies in metals migrate randomly, however, the jumps of atoms already depend on the preceding jumps [1, 2], therefore successive jumps of atoms are connected, in

other words, correlate, with each other, i.e. atoms in the metal do not random walks, but correlated walks [2].

In the case of diffusion in the alloys, correlation effects are observed for both atoms and vacancies [1, 2]. Manning in his paper [2] derived equations for the calculation of correlation factors for the diffusion of atoms in disordered alloys, which include the magnitude of the correlation factor for vacancy migration. In the binary alloy, the mean frequency of the jumps in the vacancy *W* is

$$W = c_A\omega_A + c_B\omega_{B,} \tag{1}$$

where ω_A and ω_B are the exchange frequencies of atoms A and B with vacancies.

In the case of diffusion in the alloy, the successive jumps of vacancies themselves are related to each other. After the exchange of seats with atom A, the vacancy is still in the site adjacent to this atom. If ω_A is greater than *W*, then the vacancy after exchange of positions with atom A has a high probability of making a reverse jump due to a repeated exchange of places with this atom A. Similarly, there is a smaller (than in case of random walk) probability of re-exchange of places with a slowly diffusing atom B for which $\omega_B < W$. The correlation factor for vacancy diffusion in a disordered binary alloy will be [2]:

$$f = \frac{\omega_A N_A f_v^A + \omega_B N_B f_v^B}{\omega_A N_A + \omega_B N_B}, \tag{2}$$

Here f_v^A and f_v^B are partial correlation factors for the process of exchange of vacancies by places, respectively, with atoms A and B.

The model considered above refers to a disordered alloy in which there is no connection of vacancies with any atoms. The frequencies of jumps of vacancies when exchanging places with labeled atoms A and B are considered equal to ω_A and ω_B irrespective of surrounding atoms, whereas exchange with other atoms is characterized, by assumption, by one frequency W. This is a very simplified model. It is not applicable to the description of diffusion in alloys, where the indicated connection can play an important role, and in particular for ordering alloys, where much stronger correlation effects are observed. In a number of papers [3-14], the assumptions of the Manning model are analyzed and variants for its improvement are proposed. And in most of them, diffusion in disordered alloys is studied. In theoretical approaches, the correlation factor for the vacancy diffusion enters into the expressions for the correlation factors for the diffusion of atoms. The definition of the latter presents a certain complexity both in disordered and in ordering alloys (i.e. in alloys with a certain degree of short-range order characterizing the equilibrium states of the alloy for a given temperature).

The paper is devoted to the simulation of the vacancy migration in disordered and in ordering structures. The work consists of two parts. In the first part of the work a set of equilibrium states of the system was obtained based on the Monte Carlo method (Metropolis algorithm) over a wide range of temperatures and the thermodynamic characteristics of the system and, in particular, the short-range order parameter are calculated. In the second part, the obtained states are used to simulate the migration of vacancies by the Kinetic Monte Carlo method and determine the diffusion coefficient in such a binary system in two cases: for a completely disordered system and a system, the short-range order in the arrangement of the atoms corresponds to a given temperature.

2. Simulation of the equilibrium states in the binary system

To correctly model the diffusion of a vacancy in a binary alloy at different temperatures, a set of equilibrium states of the system is required for the corresponding temperatures. Such states in this study are obtained using the Metropolis algorithm. The model takes into account the interaction of the nearest neighbors. The parameters of the system are: the system has 2,000 atoms; BCC lattice; concentration of atoms A and B kinds are equal $c_A = c_B = 0.5$; $\varepsilon_{AA} = 0.35ev$эВ, $\varepsilon_{BB} = 0.37ev$, $\varepsilon_{AB} = 0.40$ev are taken with the negative sign of the energy of interaction of pairs of atoms A-A, B-B, A-B; on the average for each of the atoms there are 200 exchanges to achieve thermodynamic equilibrium. The dependence of the energy of obtained systems on temperature is shown in **Fig.** 1.

The temperature T = 1460 K is a point of the order-disorder phase transition, below which there is a sharp increase in the short-range order parameter (Fig. 2), which was calculated by the formula:

$$\sigma = \frac{(N_{AB} - N^R_{AB})}{(N^P_{AB} - N^R_{AB})} \tag{3}$$

where $N^R{}_{AB}$– the number of pairs of type AB with a random arrangement of atoms along the lattice sites, and it equals to:

$$N^R_{AB} = zNc(1-c), \tag{4}$$

where $N^P{}_{AB}$ is the number of pairs of type AB when atoms are arranged along the lattice sites for an ideal order and is equal to:

$$N^R_{AB} = zNc, \tag{5}$$

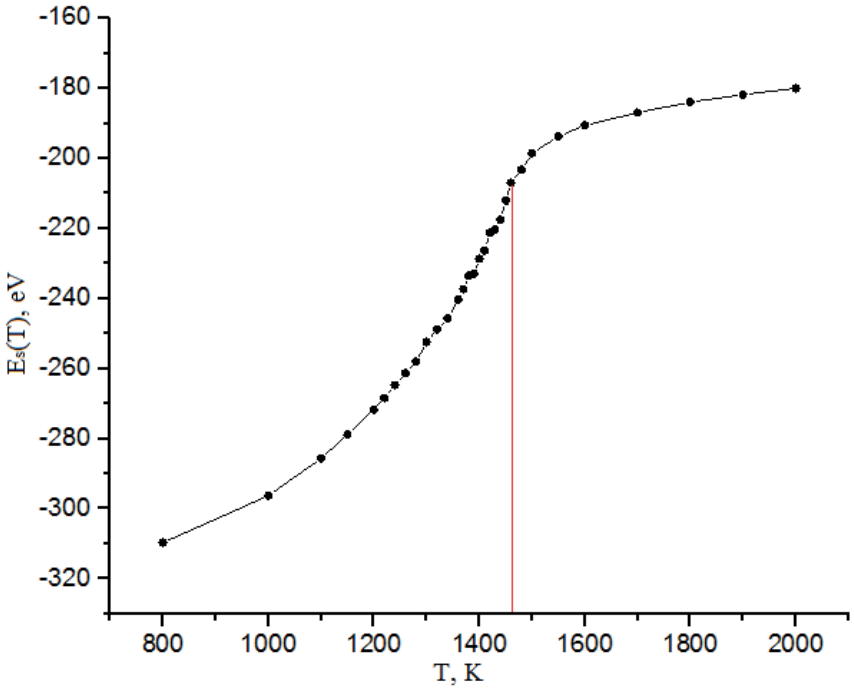

Figure 1: Dependence of system energy on temperature.

where *z* is a number of nearest neighbors (coordination number) *c* is a fraction of atoms of type A.

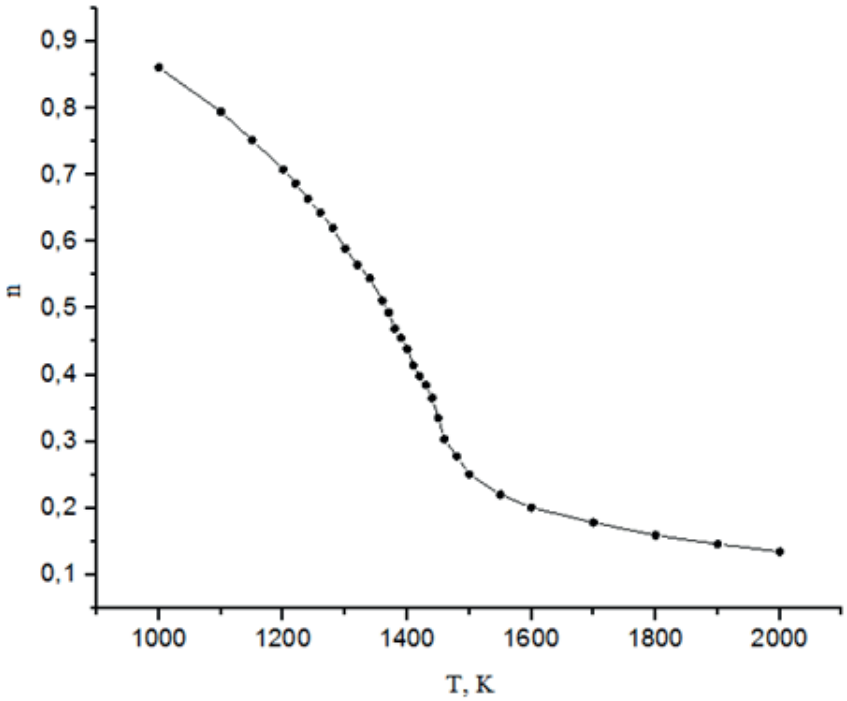

Figure 2: Dependence of short-range order of the system on temperature.

To check the consistency of the results with thermodynamic-equilibrium states, the heat capacity versus temperature is built, which is shown in Fig. 3.

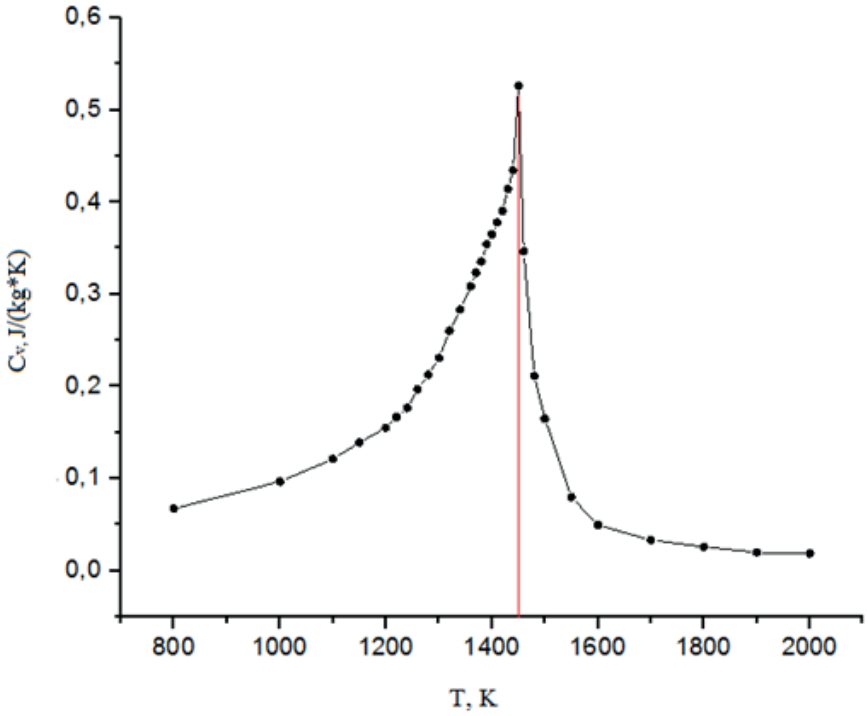

Figure 3: Dependence of heat capacity on temperature.

The data presented indicate that the obtained states of the binary system correspond to equilibrium states, which, in particular, is confirmed by the λ-shaped character of the curve.

3. Simulation of vacancy migration in a binary system

The calculated cell in which the vacancy migration occurs is constructed from 27 different equilibrium states, which were previously obtained for the corresponding temperature, and there are 54,000 atoms in it. A vacancy is placed in the center of the accounting cell, from where it begins its movement. At each step of the algorithm, neighboring atoms with respect to vacancy are considered, and the vacancy exchange rates with these atoms are calculated from the expression:

$$\Gamma_i = vexp\frac{Q_i}{kT}, \tag{6}$$

where v is a frequency factor, Q_i is the height of the potential barrier, for the vacancy to exchange with the i-th atom. This values calculated from the expression:

$$Q_i = E_i' - E_0^i, \tag{7}$$

where E_i' is energy of the atom in an activated state or saddle point energy, E_0^i is the potential energy of an atom in a given site, depending on its nearest environment. At each step it is determined by the formulas:

$$E_0^{iA} = n_A \varepsilon_{AA} + n_B \varepsilon_{AB}, \tag{8}$$

if this atom is of type A, and

$$E_0^{iB} = n_B \varepsilon_{BB} + n_A \varepsilon_{AB}, \tag{9}$$

if an atom of type B.

In the expressions (8) and (9) n_A and n_B – respectively, the number of atoms of type A and B in the first coordination sphere of the i-th atom adjacent to the vacancy; ε_{AA}, ε_{BB},ε_{AB} are taken with the opposite sign of the energy of interaction of pairs of atoms AA, BB, AB. The values of these parameters are same with those in the model for obtaining equilibrium states. We believe E_i' is the same for all jumps in order to study the contribution to the correlation factor is only due to the degree of short-range order.

The direction of the vacancy jump was determined using the standard Monte Carlo procedure. Thus, the migration trajectory of the vacancy is constructed. Then the square of the vacancy displacement is counted after a given number of steps:

$$R^2 = (x - x_0)^2 + (y - y_0)^2 + (z - z_0)^2, \tag{10}$$

where x_0, y_0,z_0 are the initial coordinates of the vacancy; x,y,z are the final coordinates of the vacancy.

The displacement square is taken for k trajectories. Then we average the squares of the vacancy displacements on the trajectories:

$$\langle R^2 \rangle = \frac{\sum_k R^2}{k}, \tag{11}$$

and calculate the diffusion coefficient from the fundamental Einstein relation:

$$D = \frac{\langle R^2 \rangle}{2nt}, \tag{12}$$

where n is a dimension of the space for which the simulation is performed, n = 3, t is the time of vacancy migration during single experiment.

Modeling of vacancy migration by the algorithm described above enables to calculate the correlation factor due to the presence of short-range order in the arrangement of atoms corresponding to a given:

$$f = \frac{D_{ord}}{D_{ran}}, \tag{13}$$

where D_{ord} is the diffusion coefficient in a system with an equilibrium degree of order, and D_{ran} is the diffusion coefficient in a system with disordered (random) arrangement of atoms along the sites of the crystal lattice.

4. Discussion of results

We calculated the vacancy diffusion coefficients in a binary alloy with a completely disordered system and with the system having a degree of short-range order corresponding to a thermodynamic system. Arrhenius charts are constructed according to these data. They are presented in Figure 4.

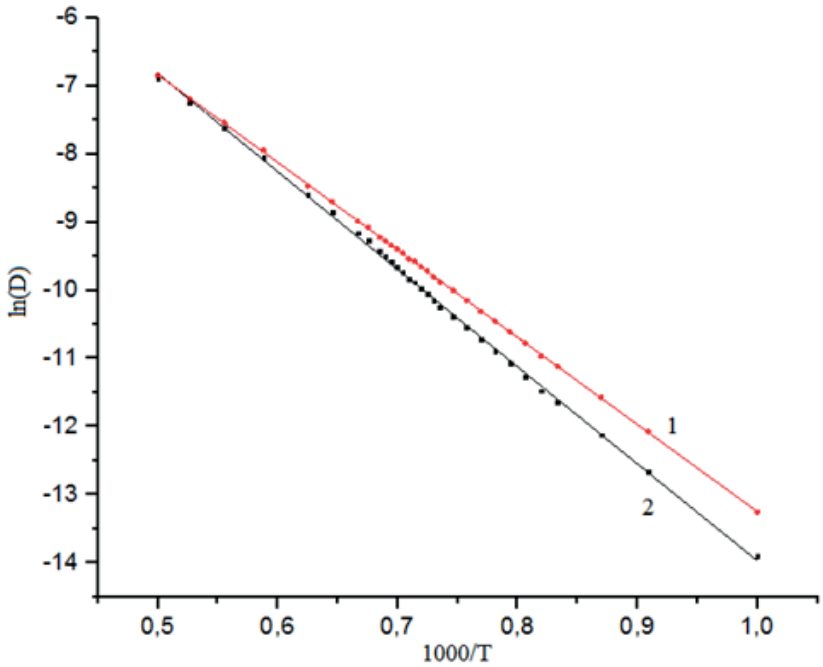

Figure 4: Arrenius dependences for vacancy migration in a binary alloy. 1 is completely disordered state of the system; 2 is the state of the system with the equilibrium value of the short-range order parameter..

In the high-temperature region, when the alloy is in an unordered state, as expected, diffusion of the vacancy occurs without manifestation of correlation effects. However, as the temperature decreases, the difference becomes more noticeable. The presence of short-range order leads to a slower diffusion of the vacancy. The correlation factor is calculated Based on simulation results and formula (13) over the entire temperature range. Dependences of the correlation factor on temperature and short-range order are shown in Figures 5 and 6.

It can be concluded on the basis of the above results that an increase in the degree of ordering of the alloy leads to a strong increase in the correlation effects and a slowing of the vacancy diffusion.

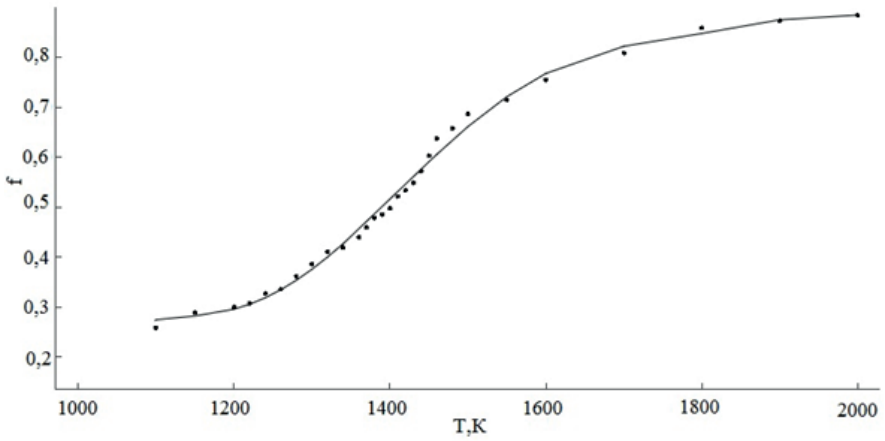

Figure 5: Dependence of the correlation factor on temperature.

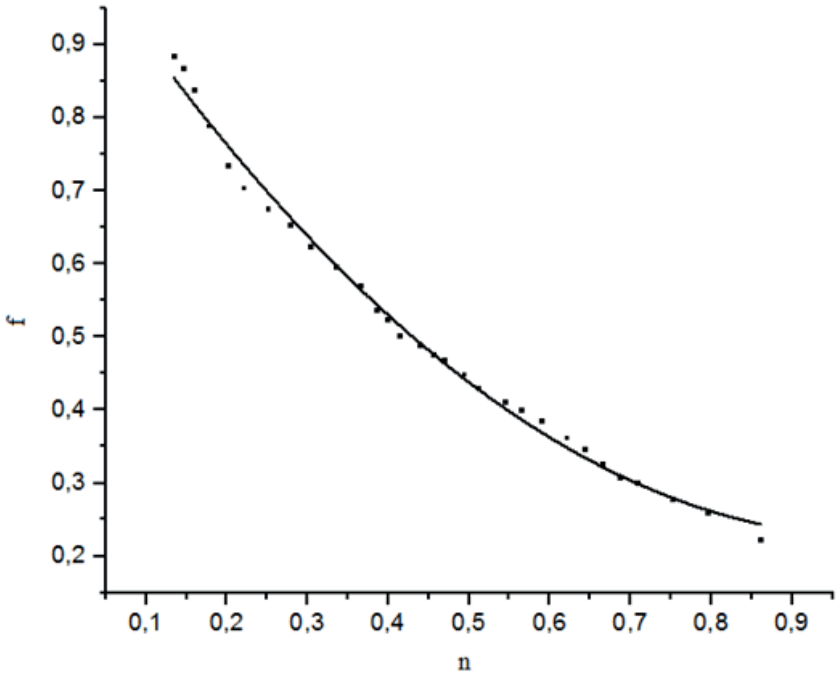

Figure 6: Dependence of the correlation factor on the degree of short-range order.

It should also be noted that the initial expression for the interdiffusion coefficient $\tilde{D}$ obtained in the alternative theory of interdiffusion [15-17] is found as one of the roots of the quadratic equation:

$$p^2 + \lambda_n^2 \left(D_V + D_A + D_B \right) p + \lambda_n^4 \left(c_A A D_B + c_B B D_A + D_A D_B \right) = 0, \tag{14}$$

$$p_2 = -\lambda_n^2 \tilde{D},$$

where

$$\tilde{D} = \frac{c_A A D_B + c_B B D_A}{D_V} g_{AB} \tag{15}$$

up to terms of higher order in the vacancy concentration.

Further, provided that the correlation effects are not taken into account and all the correlation factors are equal to unity, then

$$D_V = c_A A + c_B B, \quad D_A = D_A^* = cA, \quad D_B = D_B^* = cB, \tag{16}$$

and $\widetilde{D}$ is expressed in terms of the self-diffusion coefficients of the components of the binary alloy [16]

$$\tilde{D} = \frac{D_A^* D_B^*}{\left(c_A D_A^* + c_B D_B^*\right)} g_{AB} \tag{17}$$

where

$$g_{AB} = 1 + c_A c_B \left(\frac{\partial \ln A}{\partial c_A} + \frac{\partial \ln B}{\partial c_B} \right). \tag{18}$$

Thus, from the results of modeling and equations (14-17) it follows that correlation effects should play an important role in determining the coefficients of interdiffusion, which, as is known [1], determine the kinetics of diffusion phase transformations. This statement fully applies to the correlation effects caused by the influence of the short-range order in the atomic arrangement in the alloy. These conclusions are in agreement with the results of [17], in which the theory of interdiffusion was developed within the framework of the nearest-neighbor model, taking into account both the deviation of the concentration of vacancies from the equilibrium and ordering effects.

5. Conclusion

A set of programs for modeling the diffusion of vacancies in an ordering binary system with a bcc lattice is developed.

Modeling of equilibrium states is performed. System configurations with an equilibrium degree of order are obtained for different temperatures.

A vacancy wandering simulation was performed in a wide temperature range both in a completely disordered crystal and in a crystal with various degrees of short-range order. The diffusion coefficients are calculated and their temperature dependences are constructed.

The effect of the degree of short-range order on the diffusion mobility of vacancies in a binary alloy is analyzed. The values of the correlation factors for different temperatures are calculated. It is shown that increasing the short-range order in atomic arrangement significantly slows the vacancy diffusion.

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