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MODELING OF CONCENTRATION AND TEMPERATURE DEPENDENCIES OF INCUBATION TIME AT DECOMPOSITION OF SOLID SOLUTION BY MONTE CARLO METHOD*

The article presents the application of Monte Carlo method to the kinetics of nucleation at the decomposition of a binary solid solution with a face-centered cubic lattice. We built a phase diagram of a binary solid solution by Monte Carlo method and found the dependence of incubation time on supersaturation of solid solution at different reduced temperatures in metastable regions. Obtained results of the computer experiment are compared with the classical nucleation theory, in which the nucleus is born at once with almost optimal composition, and then just grows.

Keywords: nucleation, Monte Carlo method, solid solution, binodal, spinodal, supersaturation.

1. Introduction

Origin of the research problem. For a long time, nucleation as the initial stage of decomposition of metastable solid solution is a subject of intense theoretical and experimental researches [1-6]. However, now the whole range of fundamental questions remain without answers. In particular, it is still not clear which evolution path the metastable alloy chooses for successful nucleation: a large fluctuation of concentration in a small volume, and then the expansion of the volume of this fluctuation, or rather the growth of volume with a small change of concentration, and then growth of concentration in this volume. This problem is related to another question - is it possible to assume that the surface tension between the nucleus and the parent phase is constant, or it

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should be taken into account that it depends on the difference of concentrations in parent phase and nucleus and changes in the process of nucleation. Experimental data for such nanoobjects as "near-critical" nuclei are still ambiguous. Thus, an atomic Monte Carlo and mean field methods play an important role in the understanding of the nucleation phenomenon. In our opinion, they are more "honest" in comparison with the generally accepted solution of the Fokker-Planck equations [4] in size space. Therefore, the application and comparative analysis of Monte Carlo and mean field methods are an **actual problem**.

In this paper, we present the results of computer modeling of nucleation in a supersaturated solid solution with face-centered cubic lattice by the Monte Carlo method [7]. Also, we compare our results with the classical nucleation theory [8]. The properties of nucleation are being investigated in parallel with recently developed alternative method SKMF [9-12].

The aim of the paper is to investigate by Monte Carlo method the kinetics of homogeneous nucleation at the initial stage of decomposition of a binary solid solution, depending on supersaturation and temperature.

Tasks:

1. Construction of the phase diagram of a binary solid solution by the Monte Carlo method, taking into account that this method automatically includes the short-range order, unlike the mean-field model.

2. Formulation of the nucleation criterion, providing almost irreversible growth after its achieving.

3. Computer experiment for obtaining the dependencies of the incubation time on supersaturation at different reduced temperatures $kT/Emix$. Here incubation time means the time until the first irreversible (overcritical) nucleus appearance.

4. Comparison of the computer experiment results with the classical Volmer-Becker-Doering-Zeldovich nucleation theory.

Section 2 outlines the main features of a computer model for exploring kinetics of nucleation at the decomposition of a binary solid solution by the Monte Carlo method. The same Section describes the construction of the phase diagram based on the diffusion couples method and shows that the Monte Carlo method provides a better account of the correlation effects than the mean field models. Section 3 contains the criteria for successful nucleation, which we used in this computer model. Section 4 describes the dependencies of incubation time on supersaturation at different reduced temperatures in metastable regions and presents a comparison of the obtained results with CNT.

2. Monte Carlo model

The computer model for exploring kinetics of nucleation at the decomposition of a binary solid solution by Monte Carlo method was based on:

- Exchange mechanism of diffusion.
- Approximation of the first coordination sphere for exchanges and for interaction energies.
- Metropolis algorithm.
- Periodic boundary conditions for a model sample of a binary solid solution with a face-centered lattice measuring 30x30x30 sites.

The change of system energy in the Metropolis algorithm due to A-B exchange was calculated using the following equations:

If (before exchange) site i was occupied by atom A, and site j – by atom B, then

$$\Delta E = 2E_{mix}(S_A(i) - S_A(j) + 1). \quad (1)$$

If (before exchange) site i was occupied by atom B, and site j – by atom A, then

$$\Delta E = 2E_{mix}(S_A(j) - S_A(i) + 1). \quad (2)$$

Here $S_A(i)$ – the number of atoms A around site i; $S_A(j)$ – the number of atoms A around site j; E_{mix} – mixing energy.

Using the described algorithm we built the binodal curve. We found the equilibrium solubilities of A in B and of B in A at various temperatures (at various mixing energies) using the method of diffusion couples. At the beginning of the computer experiment model sample consisted of two parts. One part of length $L < C_A >$ was filled with atoms A, another part of length $L < C_B >$ was filled with atoms B (here $< C_A >$ – average concentration of component A throughout the whole couple). Accordingly, after a while, the system came to an equilibrium two-phase state in the form of two regions (plateau) with different concentrations that were not changing. These concentrations are two equilibrium concentrations on both sides of the binodal at the fixed temperature.

In our case (30 atomic planes along X axe) we defined the magnitude of equilibrium concentrations as the time-averaged concentration of atoms A in seventh and twenty-second atomic planes C_7 and C_{22}. Resulting binodal coordinates are presented in Table 1 and Fig. 1, where C_{bin}^{MC} – equilibrium concentration determined by Monte Carlo model; C_{bin}^{reg} – equilibrium concentration found from the regular solid solution model.

3. Criterion of nucleation

The theory of nucleation always has a problem with determining of criterion for reaching a critical nucleus size. From the point of view of thermodynamics, the critical size corresponds to the saddle point on the surface of the Gibbs potential as a function of the nucleus composition and size. However, there are additional problems in determining the critical nucleus in kinetic methods. Firstly, if the system is open, then the critical nucleus can be overcritical in terms of thermodynamics, but subcritical in terms of kinetics [13]. Secondly, Zeldovich also took into account the possibility of dissolving the overcritical nucleus and the possibility of further growth of the subcritical nucleus as a result of a random walk in the size space (Zeldovich factor [8]). Thus, when we were formulating the criterion, we tried to define it with "overcritical guarantee".

Table 1

Dependence of binodal points on reduced temperature -comparison of Monte Carlo results with regular solid solution model.

kT/E_{mix}	2.5	2.86	3.03	3.33	3.7	3.85	4	4.35
C_{bin}^{MC}(left), %	0.96	1.85	2.32	3.91	6.24	7.71	9.21	15.31
C_{bin}^{MC}(right), %	99.06	98.13	97.58	96.09	93.55	92.48	90.71	84.78
C_{bin}^{reg}(left), %	0.89	1.71	2.22	3.35	5.18	6.08	7.07	9.83
C_{bin}^{reg}(right), %	99.91	98.29	97.78	96.65	94.82	93.92	92.93	90.17

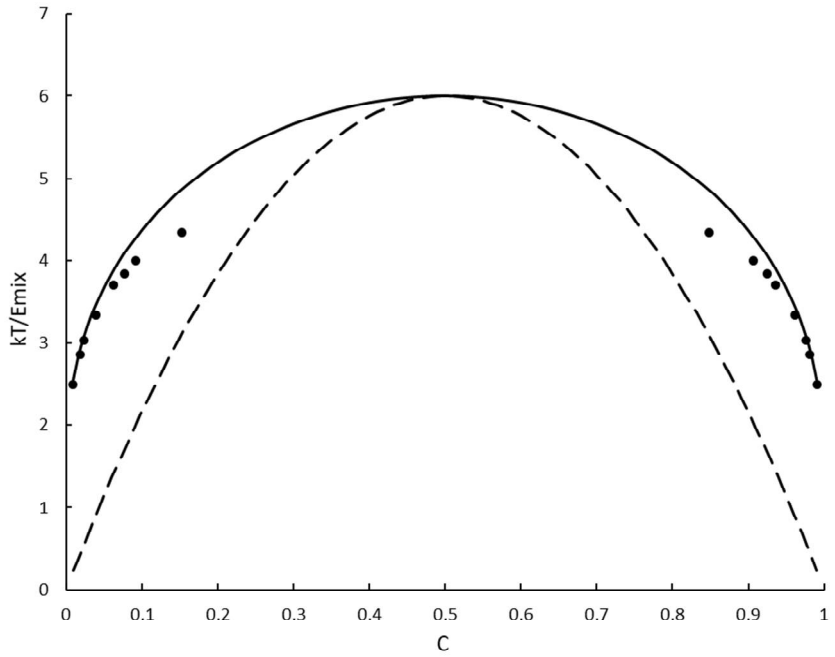

Fig. 1. Phase diagram of a solid solution. The binodal and spinodal calculated with regular solid solution model are shown with solid and dashed lines accordingly. The binodal points obtained by the Monte Carlo method are represented with dots.

Let's calculate for each site of the system the total number of atoms A in first coordinating sphere and mark it as S_A. If we are interested in the formation of the nucleus around some site (i,j,k), then calculate the average value of the parameter S_A in the first coordination sphere of this site. The magnitude $\frac{S_A(i,j,k)}{z}$ (z - the number of nearest sites, in our case z = 12) means the probability of randomly chosen neighbor site (to this site (i,j,k)) to be occupied by atom A. Let's take the sum on these probabilities on all sites of first coordination sphere and divide it by z. The obtained parameter, as we hope, gives a value of the approximate amount of the average cluster concentration. Thus, we introduce the value $s(i,j,k)$:

$$s(i,j,k) = \frac{\sum_{q=1}^{12} S_A(i_s(q),j_s(q),k_s(q))}{144}, \quad (3)$$

where i,j,k – coordinates of site for which criterion of nucleation is being checked; i_s,j_s,k_s – coordinates of neighboring site in the first coordination sphere; q – neighbor number; $S_A(i_s, j_s, k_s)$ – the number of atoms A surrounding site (i_s, j_s, k_s) in the first coordination sphere.

We fix the appearance of a viable nucleus around site (i,j,k). The "incubation time" is the number of Monte Carlo steps, after which the condition $s(i,j,k) \geq w$ is satisfied for this site. In this computer experiment, we choose $w = 0.95(1 - C_{bin})$, C_{bin} – equilibrium concentration from the Monte Carlo model. To determine the correctness of this criterion, we need to compare the calculations for different parameters w in this criterion. In particular, Fig. 2 represents a plot of the logarithm of the incubation time on supersaturation for three different values of the parameter w. We can see that for w bigger then $0.95(1 - C_{bin})$, the difference almost disappears, especially concerning the slopes.

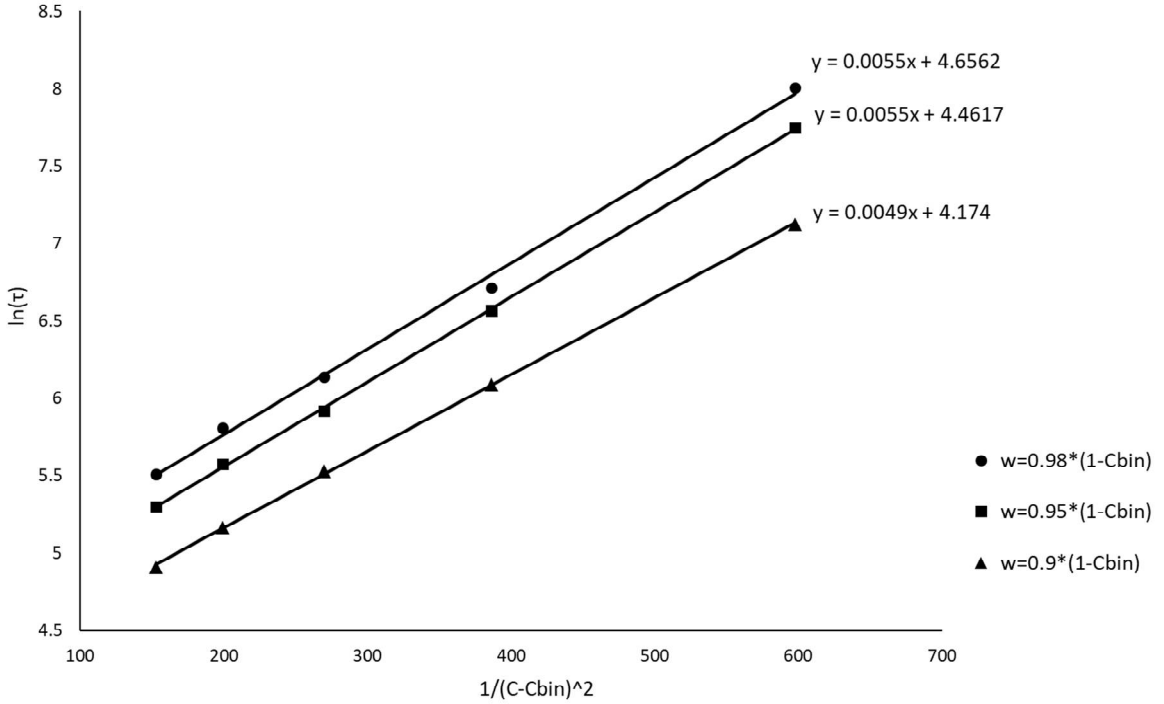

Fig. 2. Series of dependencies of the logarithm of incubation time on inverse squared supersaturation at reduced temperature $\frac{kT}{E_{min}} = 0.33$ at various values of parameter w.

4. Results of the computer experiment

A model system in computer experiment was characterized by two parameters - temperature and concentration of parent phase. Incubation time was obtained as average in the ensemble of 1000 tests with the system at same parameters. The results of the computer experiment are represented in Table 2 and Fig. 3.

We noticed that obtained dependencies correlate with the results of the classical nucleation theory. According to CNT, the incubation time should be inversely proportional to the flux of nuclei in the size space and, accordingly, proportional to the exponent of the height of the nucleation barrier divided by kT. The nucleation barrier in CNT is proportional to the cubed density of surface tension and inversely proportional to the squared bulk driving force. This driving force is determined by the rule of parallel tangents and at small supersaturation is proportional to the amount of supersaturation. Thus, CNT predicts that the logarithm of the incubation time is a linear function of the inverse squared supersaturation.

Dependencies at Fig. 3 can be approximated as

$$\ln(\tau) = \frac{\alpha}{(C-C_{bin})^2} + \beta, \tag{4}$$

where α – proportionality coefficient between $\ln(\tau)$ and $\frac{1}{(C-C_{bin})^2}$; β –constant. The value of β, in theory, should be common for all dependencies for the systems of the fixed size, but in this case, we have some deviation from the constant. However, these deviations are small.

Table 2

Dependence of incubation time on supersaturation at different reduced temperatures.

$\frac{kT}{E_{mix}}$	$\frac{1}{(C-C_{bin})^2}$	$C-C_{bin}$	τ	$\ln(\tau)$
4.35	730.46	0.037	76.902	4.34
	452.69	0.047	61.736	4.12
	307.79	0.057	49.612	3.90
	222.77	0.067	40.179	3.69
	168.66	0.077	33.886	3.52
4	696.18	0.0379	824.555	6.71
	435.84	0.0479	423.31	6.05
	298.29	0.0579	256.854	5.55
	216.90	0.0679	182.399	5.21
	164.79	0.0779	134.016	4.90
3.85	543.36	0.0429	1076.535	6.98
	357.35	0.0529	503.955	6.22
	252.75	0.0629	303.445	5.72
	188.17	0.0729	214.238	5.37
	145.51	0.0829	157.109	5.06
3.7	707.33	0.0376	4615.516	8.44
	441.35	0.0476	1193.977	7.09
	301.41	0.0576	520.454	6.25
	218.83	0.0676	322.16	5.78
	166.06	0.0776	230.108	5.44
3.33	597.80	0.0409	2312.311	7.75
	385.98	0.0509	711.359	6.57
	269.63	0.0609	372.2	5.92
	198.93	0.0709	263.055	5.57
	152.79	0.0809	200.347	5.30
3.03	456.57	0.0468	655.811	6.49
	309.96	0.0568	378.831	5.94
	224.10	0.0668	266.419	5.59
	169.54	0.0768	204.693	5.32
	132.73	0.0868	167.712	5.12
2.86	580.64	0.0415	654.626	6.48
	377.04	0.0515	359.894	5.89
	264.39	0.0615	252.258	5.53
	195.61	0.0715	198.829	5.29
	150.55	0.0815	161.379	5.08

5. Conclusions

Computer experiment using Monte Carlo method predicts the linear dependence of the logarithm of incubation time on inverse squared supersaturation at the decomposition of solid solution (equation 4).

Our results of computer modeling are consistent with the predictions of CNT, in which the nucleus is born at once with almost optimal composition, and then just grows.

The interpretation of the temperature dependence of the slope α in equation (4) will be proposed elsewhere.

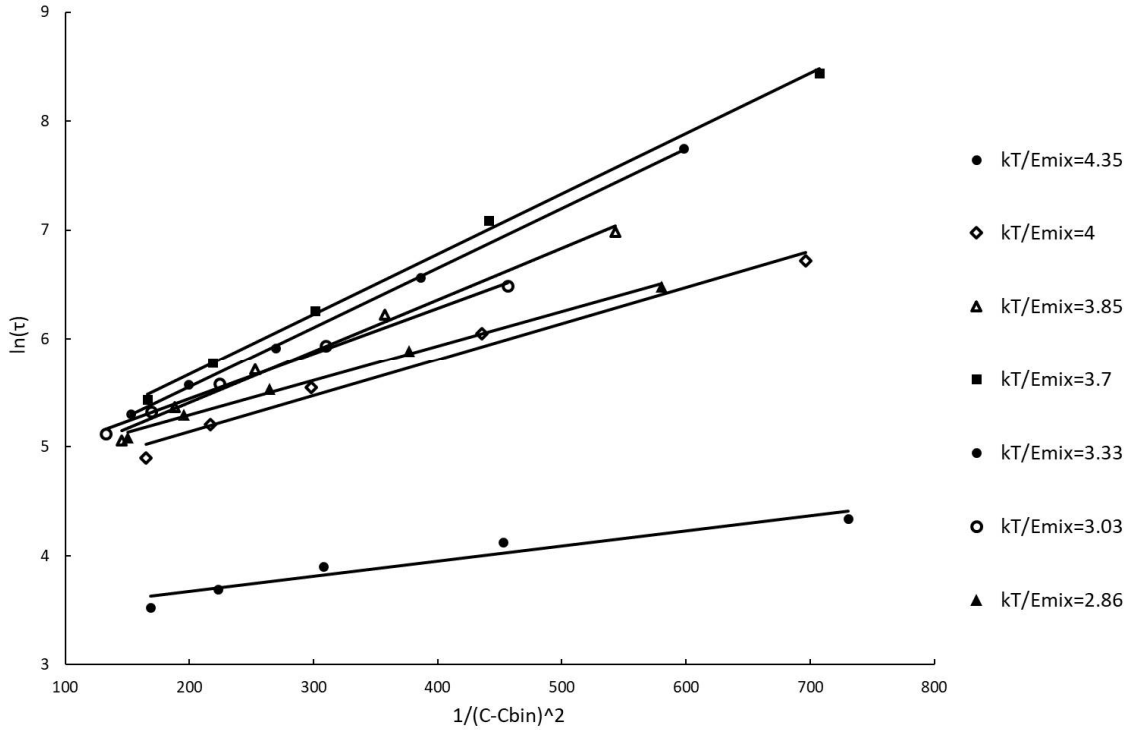

Fig. 3. Series of dependencies of the logarithm of incubation time on inverse squared supersaturation at different reduced temperatures.

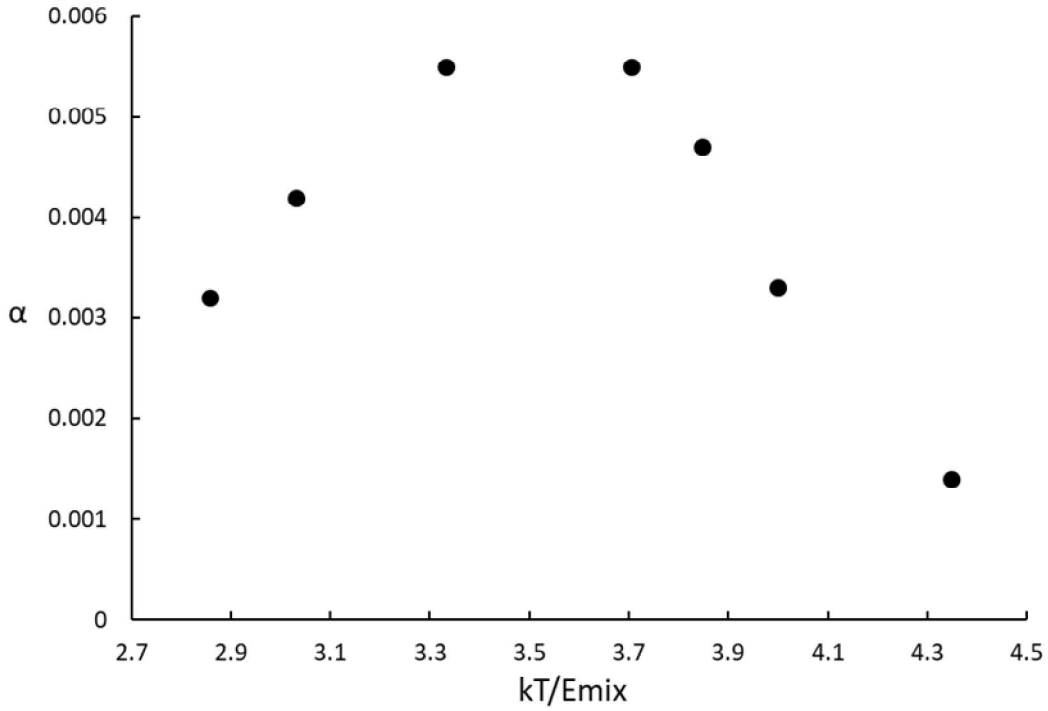

Fig. 4. Dependence of proportionality coefficient α in eq. (4) on the reduced temperature.

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МОДЕЛЮВАННЯ КОНЦЕНТРАЦІЙНОЇ ТА ТЕМПЕРАТУРНОЇ ЗАЛЕЖНОСТІ ІНКУБАЦІЙНОГО ЧАСУ ПРИ РОЗПАДІ ТВЕРДОГО РОЗЧИНУ МЕТОДОМ МОНТЕ-КАРЛО

Анотація. *У роботі представлено застосування методу Монте-Карло до моделювання кінетики нуклеації при розпаді бінарного твердого розчину в метастабільних областях. Побудовано фазову діаграму стану бінарного твердого розчину методом МК. Підібрані критерії успішного зародкоутворення, тобто ті мінімальні характеристики зародка, після досягнення яких його ріст стає практично незворотнім. Знайдені залежності інкубаційного часу від концентрації материнської фази (точніше, від пересичення, тобто від відстані концентрації розчину від бінодалі) за різних зведених температур. Обговорюється порівняння результатів комп'ютерного експерименту з класичною теорією нуклеації Фольмера-Беккера-Дьорінга-Зельдовича, в якій зародок народжується відразу майже оптимального складу, а далі просто росте.*

Ключові слова: нуклеація, Монте-Карло метод, твердий розчин, бінодаль, спінодаль, пересичення.

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