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Mean-field and quasi-phase-field models of nucleation and phase competition in reactive diffusion

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Two alternative models for description of phase formation and competition are suggested: (1) 3D generalization of Martin–Erdelyi–Beke model of simultaneous interdiffusion and ordering in binary diffusion couples with face-centered cubic (FCC) or body-centered cubic (BCC) coherent lattices and (2) phase-field-type model with random choice of phase variable for elementary cells with compositions within two-phase regions. Dependence of phase nucleation and phase competition on thermodynamic and kinetic factors is studied.

Keywords: reactive diffusion; binary system; ordered phases; nucleus

1. Introduction

The initial stage of phase formation in solid-state reactions (in particular, in thin film samples) has not been properly described yet. Despite numerous attempts of theoretical and computer simulation there are no definite answers to the following questions:

- (1) in which cases the emergence of a new phase begins with the formation of the nucleus followed by the growth and in which a phase layer occurs immediately during the contact?
- (2) if the phase formation begins with a two-dimensional island, what is the structure of this 2D-phase, and is it close or is it far from the eventual structure of the emerging 3D-phase?
- (3) does a new phase always appear at the interface, or it may appear at some distance from the interface inside one of the parent phases?
- (4) may we assume that the nuclei of all intermediate phases occur simultaneously, but not all survive, or rather some phases are not present even in a virtual form?
- (5) if the system contains several intermediate phases, but at first only one is formed, how to predict what phase will be first, what phase will be second and so on (most popular example is Ni–Si system).
- (6) how to determine the incubation time of each of the phases?
- (7) usually formation of a new intermediate phase means both a new type of ordering and some specific concentration range close to stoichiometric composition (most favourable for the new order). For a long time the discussion continues

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- ‘what happens first: first new composition and then new structure or the opposite?’

The attempts to answer these questions started with the works of Tammann, Wagner, Kidson, Geguzin, Van Loo, Tu and many others [1–3]. A new look at this problem has been published recently [4,5]. Its main point is an influence of external fluxes on the nucleation in open systems. To check validity of this approach at atomic scale we need some atomic-scale models. Below, we propose two alternative models for description of phase formation and competition; mean-field 3D model and phase-field-type model.

2. Mean-field model of reactive diffusion with formation of ordered phases

2.1. Fundamentals of Martin–Erdelyi–Beke’s (MEB) model

MEB model [6–9] had been used by Beke et al. to study the diffusion of asymmetric systems [7] during the last 10 years. In this section, we modify this model to three-dimensional case. Asymmetry of diffusion means, as a rule, that one of the components of diffusion couple is much more fusible and therefore all diffusion coefficients strongly depend on the concentration, varying by several orders within the allowable concentration range. Erdelyi and Beke have shown that diffusion in the initial stage is non-linear and leads to sharpening the concentration profile instead of smoothing it. Recently, Erdelyi’s introduced a model which has been used to describe the formation of ordered phases [9]. In particular, authors of [10] discovered that in highly asymmetric systems with body-centered cubic (BCC) lattice characterized by possibility of second-order transition to β -brass (B2) order, formation of intermediate ordered phase can start far beyond the equilibrium concentration range. We have applied this method to study the formation of intermediate phases for the case of the face-centered cubic (FCC) lattice. In contrast to the results of [10] here we are dealing with the first-order phase transition, rather than the second order. In particular, it is not sufficient to describe it with the MEB quasi-one-dimensional model. Therefore, we have generalized this model for three-dimensional case. What we have obtained can be called ‘the model of grey sites’ or ‘mean-field model’ (see also [10–12]).

In the original MEB model the value of concentration has been assigned to the atomic plane. Detailed balance considerations have led Martin to the following set of equations for each (i th) plane:

$$\frac{dC_i}{dt} = -Zv[C_i(1 - C_{i-1})\Gamma_{i,i-1} - (1 - C_i)C_{i-1}\Gamma_{i-1,i} + C_i(1 - C_{i+1})\Gamma_{i,i+1} - (1 - C_i)C_{i+1}\Gamma_{i+1,i}],$$

where Zv is the number of atoms in the neighbouring plane and $\Gamma_{i,i+1}$ is the jumps frequency from i th plane to $(i+1)$ th.

Pre-exponential factor is assumed to be independent on local composition:

$$\Gamma_{i,i+1} = v \exp\left(-\frac{E_0 - \bar{E}_{i,i+1}}{kT}\right),$$

where $\bar{E}_{i,j}$ is the energy of the system before atom jump in the mean-field surrounding and E_0 is the energy of saddle configuration. The simplest assumption about the saddle point which had been initially proposed by Martin was to take all saddle points with the same energy – for example, zero energy. In our model we use this old assumption.

2.2. 3D modification of MEB model

The main generalization of our model: we prescribe the concentration to a particular site (instead of particular plane). This makes it possible to construct three-dimensional grid of ‘grey’ sites.

Rate of change of concentration in each site ‘ i ’ of the three-dimensional grid is defined according to matter conservation and corresponding local flux balance at each site:

$$\begin{aligned} \frac{dC_i}{dt} &= - \sum_{j=1}^Z [C_i(1 - C_j)\Gamma_{i,j} - (1 - C_i)C_j\Gamma_{j,i}] \\ &= -C_i \sum_{j=1}^Z (1 - C_j)\Gamma_{i,j} + (1 - C_i) \sum_{j=1}^Z C_j\Gamma_{j,i}, \end{aligned}$$

where C_i is the concentration of A at this site (molar fraction), C_j is the concentration in the j th neighbouring site with the total number of nearest neighbours Z , $C_i(1 - C_j)$ is the probability that the i th site is occupied by A atom and the neighbouring j th site is occupied by B atom, i.e. the exchange of atoms possible and $\Gamma_{i,j}$ is the probability of such an exchange per unit time, i.e. the jump rate of A atoms from this site to the j th neighbouring site (and backward jumps of B atoms), which is determined by:

$$\Gamma_{i,j} = v \exp\left(\frac{-Q_{i,j}}{kT}\right),$$

where $Q_{i,j} = E_0 - \bar{E}_{i,j}$, E_0 is taken the same for all jumps, $\bar{E}_{i,j} = E_i^A + E_j^B$, $E_i^A = V_{AA} \sum_{j=1}^Z C_j + V_{AB} \sum_{j=1}^Z (1 - C_j)$, $E_i^B = V_{AB} \sum_{j=1}^Z C_j + V_{BB} \sum_{j=1}^Z (1 - C_j)$, E_i^A and E_i^B – interaction energies of the A or B atom in the i th site with its neighbours. Thus, the jump frequencies can be expressed directly via the atomic energy in the site:

$$\Gamma_{i,j} = v' \exp\left(\frac{\bar{E}_{i,j}}{kT}\right), \text{ where } v' = v \exp\left(\frac{-E_0}{kT}\right)$$

The main objective of our model is to investigate the incubation and/or suppression times of various phases depending on the size and asymmetry of the initial noise of concentration. Modelling has been conducted for the FCC lattice with the initial distribution of concentration in a diffusion couple A – B . Component B has higher melting point than the component A , and, respectively, the lower diffusivities.

2.3. Distinguishing ordered phases

It is important in our model to distinguish two disordered solutions and three ordered intermediate phases. For this, we introduced the two local order parameters. To distinguish phases A3B1 and A1B3, we use parameter \tilde{S}_n :

$$\tilde{S}_n = (SX_n \times SY_n \times SZ_n),$$

where

$$SX_n = \frac{1}{8} \sum_{i=1}^{63} k_i \times \cos(\pi \times (l_n - l_i)) \times C(l_n, p_n, m_n),$$

$$SY_n = \frac{1}{8} \sum_{i=1}^{63} k_i \times \cos(\pi \times (p_n - p_i)) \times C(l_n, p_n, m_n),$$

$$SZ_n = \frac{1}{8} \sum_{i=1}^{63} k_i \times \cos(\pi \times (m_n - m_i)) \times C(l_n, p_n, m_n),$$

n – index of the site of simple cubic lattice (with lattice parameter $\frac{a}{2}$) with coordinates $x_n = l_n \times \frac{a}{2}$, $y_n = p_n \times \frac{a}{2}$, $z_n = m_n \times \frac{a}{2}$. Real FCC lattice (with lattice parameter a) contains only sites with coordinates satisfying constraint $l_n + p_n + m_n = \text{even number}$. In total, summation is taken over 63 sites – one central site and 62 neighbouring sites belonging to five coordination shells. k_i is a weight factor depending on the coordination shell: $k_i = 1$ for the first coordination shell and for the central site, $1/2$ for the second and third coordination shell, $1/4$ for the fourth coordination shell and $1/8$ for the fifth coordination shell.

One can easily check that for strictly stoichiometric and ideally ordered phases A3B1 and A1B3 values of \tilde{S}_n are equal to -1 and 1 , respectively, for a strictly stoichiometric and ideally ordered phase A1B1, as well as for random alloy of arbitrary composition – $\tilde{S}_n = 0$. We prescribe site to the phase A1B3 if $\tilde{S}_n > 0.25$ and to phase A3B1 if $\tilde{S}_n < -0.25$.

Since \tilde{S}_n has the same value in two absolutely different cases, one needs one more order parameter. Namely, for distinguishing phase A1B1, we introduce parameter related to anisotropy of this type of ordering (sequence of planes A and B along X or Y or Z axes):

$$S_n = \max(SX_n^2, SY_n^2, SZ_n^2) - 1,$$

where $\max(SX_n^2, SY_n^2, SZ_n^2)$ is a maximal value among SX_n^2, SY_n^2, SZ_n^2 . One can easily check that for ideally ordered stoichiometric A3B1 and A1B3 when one gets $S_n = 0$ for random alloy $S_n = -1$ and for ideally ordered stoichiometric phase A1B1 – $S_n = 3$. Below we choose condition $S_n > 1$ as a criterion for phase A1B1.

2.4. Results of the mean-field model

2.4.1. Time evolution of interdiffusion with ordering and phase competition

So far we studied only diffusion couples with coherent interface and with concentration gradient along direction $\langle 100 \rangle$. Results strongly depend on the asymmetry of the system. If system is thermodynamically and kinetically symmetric ($|V_{AA}| = |V_{BB}|$), then, at chosen phase criteria (see above) the first phase to form is A1B1, and then, after some incubation time, two other ordered phases A3B1 and A1B3 appear (naturally, simultaneously). See Figure 1 (So far we did not check how does this result depend on the phase criteria – say, if we decide that phase A3B1 appears if $\tilde{S}_n < -0.5$).

If system is essentially asymmetric (in our case $|V_{AA}| > |V_{BB}|$), then the phase formation sequence is changed – at first, the phases A1B1 and A1B3 are formed (phase A1B1 – a little bit earlier). And the phase with maximal content of component with high melting point (A3B1) appears last.

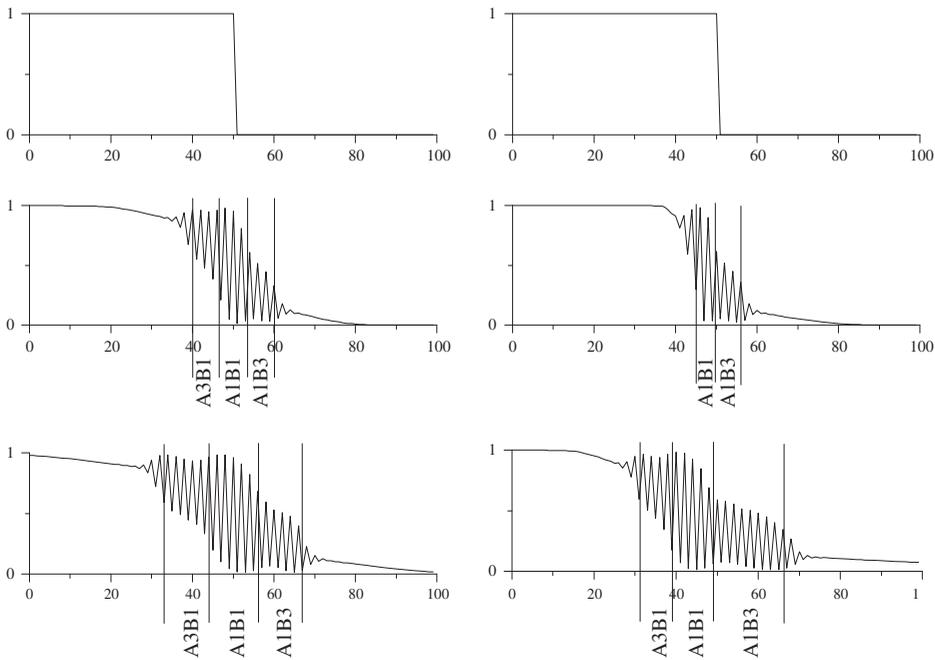


Figure 1. Growth kinetics of the ordered phases in case of symmetric (left) and asymmetric (right) diffusion. Horizontal axis – number of the plane and vertical axis – the average concentration of component A in the plane [100].

It seems that the incubation time can be a real problem only for strongly asymmetric couples.

2.4.2. Incubation period dependence on the asymmetry magnitude

We have received the incubation time dependence on the asymmetry ($M = |V_{AA} - V_{BB}|$) for the three different phases (A1B1, A1B3 and A3B1).

In our calculations, incubation time was a period till the moment when above-mentioned criterion for certain phase started to be satisfied at least for one site (to be more accurate – for cluster containing five coordination shells around this site).

It has been found (if $|V_{AA}| > |V_{BB}|$) that asymmetry for A3B1' and A1B1' phases leads to increasing of incubation time and for A1B3 phase leads to decreasing of incubation time (see Figure 2).

Incubation period dependence of the asymmetry for the A1B3 phase has a distinctly exponential character, i.e. $\tau \sim \exp(kM)$, where k – constant.

2.4.3. Concentration noise

Another important parameter in modelling of diffusion in the FCC lattice is the concentration noise. Mean-field model does not contain thermal fluctuations. From classical nucleation theory, we know that fluctuations are necessary to overcome the nucleation barrier. Therefore even for unstable phase some artificially introduced noise is needed to provide the eventual phase transition. It is important to note that the above considerations appeared to be valid only for marginal (A3B1 and A1B3) phases. 'Central' phase A1B1 appeared in our diffusion couple without any noise. It looks like that sufficiently

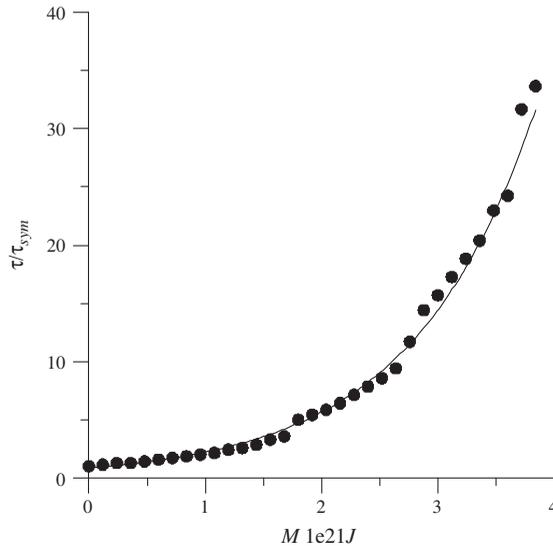


Figure 2. Ratio of incubation time τ for asymmetric case to the incubation time τ_{sym} for symmetric case dependence on the asymmetry parameter $M = |V_{AA} - V_{BB}| 10^{21} J$ for A3B1 phase.

sharp concentration gradient may *help* phase formation (see also the so-called total mixing model in the theory of nucleation in concentration gradient [13]).

Separately we studied the role of noise in ordering of *homogeneous* alloy, to exclude the possible influence of concentration gradient. Noise is set by software at the initial time moment as $C = C_0 + \alpha(2 \text{ random} - 1)$, where C_0 is the average concentration in the site and α is the initial concentration amplitude noise. Concentration noise here is introduced instead of the random transitions between states (depending on temperature) in Monte Carlo – one should have some factor assisting system to overcome the energy barrier in the first-order transition. It does not mean that initial concentration noise is equivalent to thermal noise. Neither of these factors generate real evolution of the system, they present only possible trajectories – not real ones. On the other hand, both of them are necessary to provide possibility to overcome barriers and nucleate new phases.

We expected that there should be some threshold noise amplitude α above which the transition become inevitable. To estimate this threshold amplitude, we took α which varies from 2×10^{-7} to 0.2.

Since the incubation time depends on a parameter α we were able to find the value of α , below which the initial amplitude noise does not lead to significant changes in the incubation period. It is the value $\alpha \sim 10^{-3}$. Strictly speaking, any fluctuation amplitude sooner or later should initiate phase transformation. So, in our consideration the threshold is a value below which the incubation time becomes unreasonably long.

The incubation time of the A1B1 phase logarithmically depend on α (see Figure 3), like $\tau \sim -\ln(k'\alpha)$, where k' – constant.

Using our 3D model and adjusting it to BCC lattice, we confirmed the recent result of Erdelyi et al. [10] for systems with high diffusional asymmetry – at interdiffusion in BCC diffusion couple the ordered phase A1B1 is initially formed at concentrations far

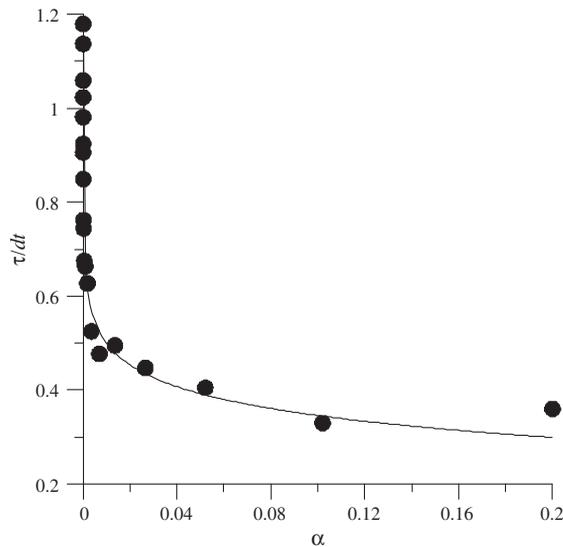


Figure 3. Reduced incubation time τ/dt dependence on amplitude of concentration noise α .

beyond the stoichiometric composition. In long-lasting discussion ‘first new composition and then new structure or the opposite’, we obtained important argument: at least in case of strong diffusional asymmetry initially a new (partial) ordering appears (due to local diffusion at atomic scale), and only after this the concentration becomes adjusted (due to global diffusion) to this ordering simultaneously with order perfection.

In FCC diffusion couples (with three intermediate ordered phases) similar effect is not pronounced. Most probably, since ordering on a BCC lattice is a second-order transition, even small profit of ordering in non-stoichiometric region is favourable. In FCC lattice (with first-order transitions), concentration range of ordering is narrower and ordering outside stoichiometry is much more difficult.

3. ‘Quasi-phase-field’ model

In the previous Section, we discussed rather rare case when all three intermediate phases have the same lattice (FCC) structure, but different ways of ordering. In many real cases, the growing intermediate phases have structure different from those of parent phases as well as from other intermediate phases. To the best of our knowledge, so far there is no general recipes of choosing the appropriate reaction coordinates describing the transition from one structure to another. Therefore, in our present section, we will put aside our attempts to describe the continuous evolution of order parameters in the frame of mean-field model. Instead, we introduce the discrete phase parameters which can change only in a ‘quantum manner’ but randomly. Of course, such approach can be used only for first-order transitions characterized by nucleation barriers. On the other hand, our model should describe the phase changes at atomic scale. Therefore, we will prescribe ‘quantum’ phase states to practically atomic size cells of the system. It is important not to confuse the introduced ‘cells’ with real structure cells, because in our description the structure is changed from phase to phase but the array of cells with varying structure remains unchanged. To the best of our knowledge, the first attempts to introduce discrete change of phase in small cells during diffusion were introduced in [14,15].

We call our new model ‘quasi-phase-field-type’ one. In this model, all material is divided into the close-packed (FCC) array of cells with h being a distance between the centres of the nearest cells. Each cell of the material is formally characterized (1) by concentration, which changes continuously and (2) by phase state, which varies discretely (‘by quantum steps’) with the Glauber algorithm:

$$P_{1,2,3} = \frac{e^{-\frac{E_{1,2,3}}{k_b T}}}{e^{-\frac{E_1}{k_b T}} + e^{-\frac{E_2}{k_b T}} + e^{-\frac{E_3}{k_b T}}}.$$

Here $E_i = g_i(c)$ is the Gibbs free energy per atom for the i th phase with additional surface term included if the cell has at least one of 12 nearest cells belonging to foreign states.

Discrete changes of phase parameter are the main difference of our model from Khachatryan’s model [11]. The possibility to change the phase of each cell occurs if the composition of the cell enters the compositional ‘zone of risk’ (In our model only

half of cells from the risk zone were permitted to try the phase change – random selection of cells was provided). The evolution of concentration in the site with time is described by the equation of fluxes balance (conservation of matter):

$$\frac{\partial c_B}{\partial t} = \frac{-\sum_1^{12} \Omega_B^{i,j,i',j'}}{h},$$

where $\Omega_B^{i,j,i',j'}$ is the flux of atoms from the site (i, j) in one of the neighbouring sites (i', j') determined by the Onsager formalism with adding convective terms (proportional to drift velocity U) providing zero total flux of all components in the frame of Darken's approach:

$$\Omega_B = \Omega_{jB} + c_B U = -L_B \nabla \mu_B + c_B (L_B \nabla \mu_B + L_A \nabla \mu_A) = -c_A L_B \nabla \mu_B + c_B L_A \nabla \mu_A,$$

where $\mu_A = -c_B \partial g / \partial c + g$, $\mu_B = c_A \partial g / \partial c + g$, μ_A, μ_B – chemical potentials, $L^{A,B} = c_{A,B} D_{A,B}^* / k_b T$, L_1^A – Onsager's coefficient for flux through the site with the phase state 1, $D_{A,B}^* = D_{A_0, B_0}^* \exp(\alpha_{A,B} c_B)$, $D_{A_0}^*, D_{B_0}^*, \alpha_A, \alpha_B$ are different for different phases.

The main innovation of our model is that the local values of the Gibbs potential in solid solutions $g_I(c)$, $g_{II}(c)$ and emerging ordered phase $g_{III}(c)$ are calculated taking into account the surface energy (present if at least one neighbour belongs to other phase).

$$g_{I,II}(c) = \Phi_{BB,AA} \cdot c_{B,A} + k_b T (c_B \ln c_B + c_A \ln c_A) + N^{\text{foreign}} \frac{\gamma \Omega}{h}$$

$$\begin{aligned} g_{III}(c) &= 0.5 \{ (\varepsilon_B - \varepsilon_A) \delta c + (\varepsilon_B + \varepsilon_A) \sqrt{\delta c^2 + q^2} \} \\ &+ + kT \left\{ [\delta c + \sqrt{\delta c^2 + q^2}] \ln \frac{\delta c + \sqrt{\delta c^2 + q^2}}{2p_1} + [-\delta c + \sqrt{\delta c^2 + q^2}] \ln \frac{-\delta c + \sqrt{\delta c^2 + q^2}}{2p_2} \right\} \\ &+ g_0 + N^{\text{foreign}} \frac{\gamma \Omega}{h}, \end{aligned}$$

where $N^{\text{foreign}} \gamma \Omega / h$ – contribution of surface energy for the cell and N^{foreign} – number of neighbouring cells with the phase states different from the central cell,

$$g_0 = g_i - 0.5(\varepsilon_A + \varepsilon_B)q - k_b T \left(q \ln \frac{q}{2p_1} + q \ln \frac{q}{2p_2} \right),$$

$q = 2\sqrt{p_1 p_2} \exp(-(\varepsilon_A + \varepsilon_B) / 2k_b T)$, $\delta c = c_B - c_i$ – composition deviation from stoichiometry and $\varepsilon_B, \varepsilon_A$ – substitutional defects (antisites) formation energies. In our concrete model, the lattice of intermediate phase consists of two sublattices with site

fractions p_1 and $p_2 = 1 - p_1$ (sublattice one is filled mainly with atoms A and sublattice two is filled mainly with atoms B).

4. Results of quasi-phase-field model

According to the obtained data, we have noted that the status (undercritical, critical and overcritical) and evolution of the nucleus in the process of nucleation in open systems is determined not only by thermodynamic, but the kinetic parameters of the new and neighbouring phases.

The developed model allows to trace the behaviour of separate nucleus and of whole layer of intermediate phase 3, changing separately thermodynamic parameters (surface tension and stimulus) as well as kinetic parameters of the process (diffusion coefficients in phases).

The model allows considering homogeneous and heterogeneous nucleation (Figure 4).

4.1. The evolution of the intermediate phase layer on the interfaces

We studied influence of diffusivity inside intermediate phase and of interface tension on the phase growth kinetics (see Figures 5 and 6). At first, we considered the growth of layer of intermediate phase at the fixed value of surface tension γ and the diffusion coefficient of α and β phases, but by changing the diffusion coefficient of i th phase (nucleation kinetic control) (see Figure 5).

Kinetics of growth layer has the following two features:

- the growth process consists of the waiting periods and the rapid lateral growth of a new atomic layer and
- the coarsened time dependence of the layer thickness is close to parabolic, and the rate of growth linearly depends on the diffusion coefficient of the intermediate phase.

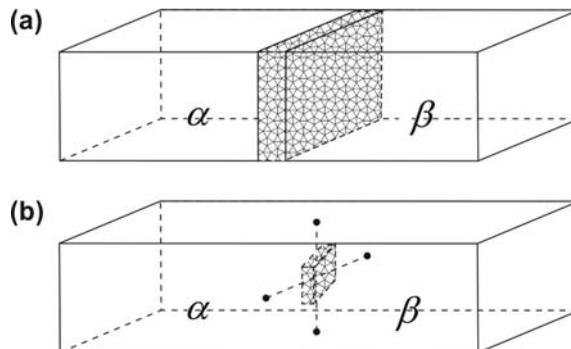


Figure 4. Initial configurations for subsections 4(a) and (b).

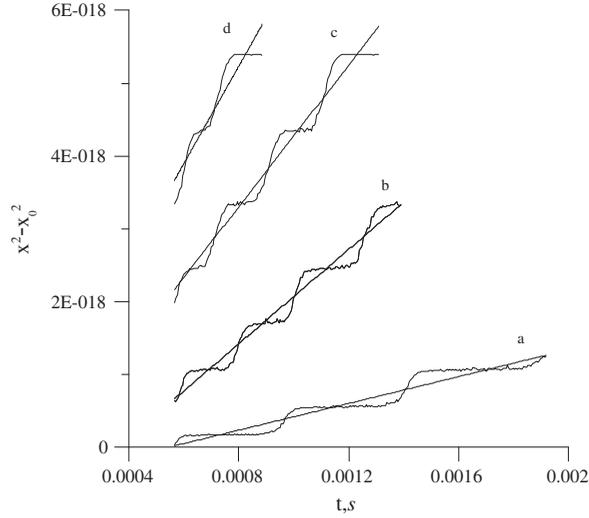


Figure 5. Time dependence of intermediate phase layer thickness (with approximation by $x^2 - x_0^2 = kt + B$) with $\gamma = 0.2 \text{ J/m}^2$: (a) $D_3 = 25 \times 10^{-16} \text{ m}^2/\text{s}$, (b) $D_3 = 50 \times 10^{-16} \text{ m}^2/\text{s}$, (c) $D_3 = 75 \times 10^{-16} \text{ m}^2/\text{s}$, and (d) $D_3 = 100 \times 10^{-16} \text{ m}^2/\text{s}$.

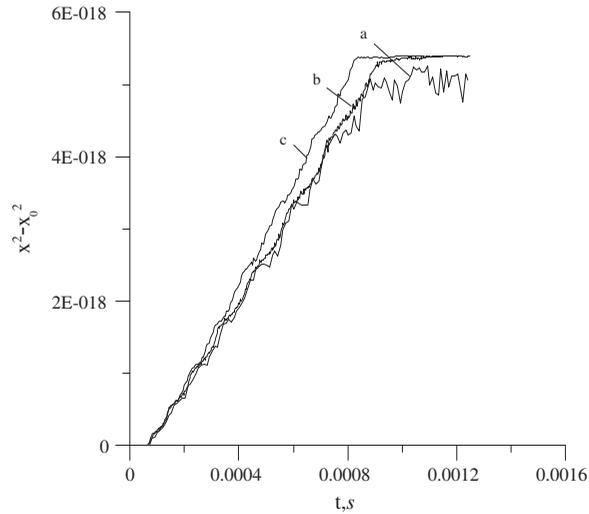


Figure 6. Time dependence of intermediate phase layer thickness with $D_3 = 50 \times 10^{-16} \text{ m}^2/\text{s}$ at various surface tensions: (a) $\gamma = 0.05 \text{ J/m}^2$, (b) $\gamma = 0.1 \text{ J/m}^2$, (c) $\gamma = 0.15 \text{ J/m}^2$.

Time dependence of the thickness of the intermediate phase (see Figure 5) can be approximated by the straight-type $x^2 - x_0^2 = kt + B$. Dependence of the linear growth rate k of the diffusion coefficient of the third phase D_3 is shown in Figure 7.

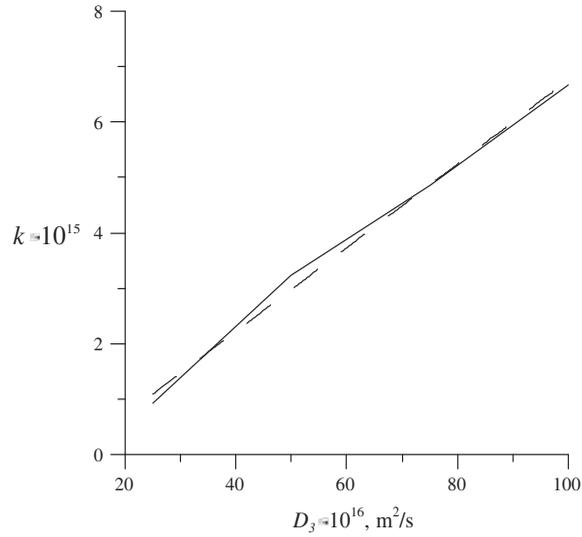


Figure 7. Growth rate coefficient k dependence on the diffusion coefficient of intermediate phase D_3 .

Kinetic coefficient k is proportional to diffusivity of the growing phase and depends also on the defect formation energy of the growing phase.

The dependence of the kinetics of intermediate phase layer growth on the surface tension γ (thermodynamic control of nucleation) at fixed diffusion coefficients of all three phases is shown in Figure 6. Thus, growth kinetics practically does not depend on surface tension. This conclusion becomes absolutely wrong for nucleation stage.

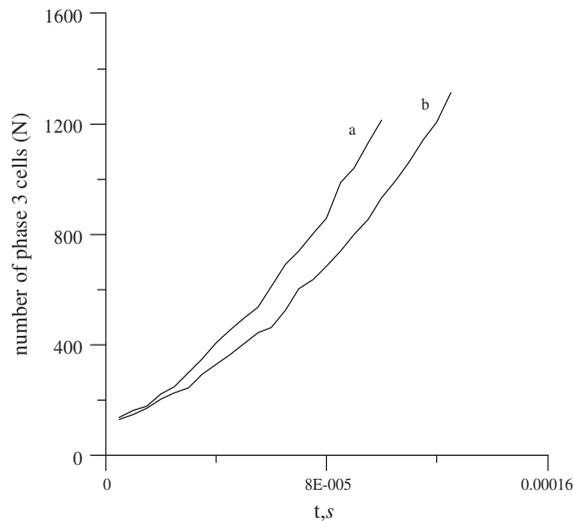


Figure 8. Time dependence of phase 3 cells number with $D_3 = 50 \times 10^{-16} \text{ m}^2/\text{s}$ and different surface strain: (a) $\gamma = 0.05 \text{ J/m}^2$ and (b) $\gamma = 0.1 \text{ J/m}^2$.

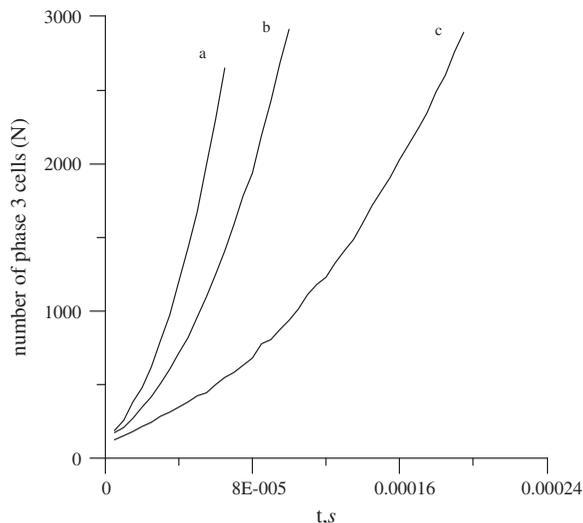


Figure 9. Time dependence of phase 3 cells number with $\gamma=0.2 \text{ J/m}^2$ and different diffusion coefficient of nucleus: (a) $D_3 = 1.5 \times 10^{-14} \text{ m}^2/\text{s}$; b) $D_3 = 1 \times 10^{-14} \text{ m}^2/\text{s}$; c) $D_3 = 5 \times 10^{-15} \text{ m}^2/\text{s}$.

4.2. The evolution of the intermediate phase nucleus on the α and β phases boundary

Similarly to the previous case, changing the thermodynamic and kinetic parameters of the process, we have analysed the evolution (growth or shrinkage) of the specially created nucleus of intermediate phase at the interface of α and β phases. This process is illustrated in Figures 8 and 9.

From the Figures 8 and 9, we can see that reducing of the surface tension γ or increasing the diffusion coefficient of intermediate phase D_3 at constant diffusion coefficient within the initial phase leads to faster growth of the nucleus.

This correlates with the thermodynamic and kinetic concepts of nucleation process: reduction of surface tension means lowering of the nucleation barrier and increase of the D_3 means lowering of the so-called ‘effective nucleation barrier’, which had been recently introduced in [1,2].

5. Conclusion

- (1) If reactive diffusion is reduced to intermixing and ordering on the fixed lattice (FCC or BCC) common for all phases then the best (economic and physically understandable) way to describe the process is the 3D extension of MEB model. If reactive diffusion leads to formation of phases with different structure the description should become more phenomenological – we believe that our quasi-phase-field model might be useful.
- (2) In our 3D extension of MEB model, we confirmed the recent result of Erdelyi et al: in strongly asymmetric diffusion couple with BCC lattice formation of ordered B2-phase starts from concentrations rise far from stoichiometry. We cannot call this process the nucleation because B2-phase formation is the second-order transition.

- (3) Application of our 3D extension of MEB model to the diffusion couple with FCC lattice allows us to study nucleation and competition of three ordered phases. Naturally, the phase containing majority of high-melting component is suppressed by two other phases. So, its absence in the diffusion zone is determined not by thermodynamic but by kinetic reasons.
- (4) Suppression time exponentially depends on asymmetry parameter $M = |V_{AA} - V_{BB}|$.
- (5) Ordering of all FCC phases starts in the vicinity of stoichiometric compositions even for asymmetric couples, contrary to BCC case. Most probably, it is because all three orderings in FCC lattice are the first-order transitions.
- (6) Formation of A1B1 phase with FCC lattice can be substantially influenced by sharp concentration gradient helping to overcome to concentration barrier.
- (7) In case of phase formation with different structures the ‘quasi-phase-field’ model confirms the main predictions of the phenomenological flux-driven nucleation theory. Nucleation can be suppressed by thermodynamic factors (large surface tension and/or small driving force) as well as by kinetic factors (small diffusivity of the new phase and/or large diffusivity of the parent phases).
- (8) Initial growth of specially constructed phase layer in our time scale appeared to be linear in average (instead of typical parabolic). Actually, this ‘linear dependence’ consists of long waiting times and fast lateral growth of new atomic planes. Thus, the phase growth at this stage is controlled by the nucleation of the new atomic layers.

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