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EFFECT OF SHARP CONCENTRATION GRADIENT ON NUCLEATION DURING THE INTERDIFFUSION - RECONSIDERATION OF DIFFERENT MODES OF THERMODYNAMICS OF NUCLEATION.

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Abstract. Nucleation of intermediate phase during the reactive diffusion in the binary diffusion couple due to fluctuation, which takes into account the optimized redistribution of composition in the diffusion zone, is considered in details. The nucleation mode, corresponding to unlimited redistribution in the concentration gradient direction outside the newborn nucleus as well as inside, is presented. The concentration profiles corresponding to the critical nuclei of the new phase are found, as well as the nucleation barriers depending on the concentration gradient and system parameters. Analysis of transversal and polymorphous modes of nucleation in binary diffusion couple A-B has been modified with taking into account the gradient term in the free energy density. For all modified modes of nucleation formulas of dependencies of the Gibbs free energy on volume, shape and concentration gradient have been obtained.

1. Introduction

Reactive diffusion that is diffusion with nucleation and growth of intermediate phase, takes special significant part in manufacture of composite materials and protective coating. It is known that nucleation during the reactive diffusion may be considered as separation of the inhomogeneous solid solutions. Nucleus of new phase may form in diffusion zone – in the concentration gradient field changing in time. Corresponding modification of the classic nucleation theory has been partly made by research groups: Desre P. J. (France), Gusak A. M. (Ukraine). However, it still stays imperfect. The theory of critical gradient is used by different experimental groups P. Gas (France), J. Perepezko (USA), K. Barmak (USA), G. Schmitz (Germany) and others for analysis and forecasts of new phase layers appearance in binary couples: Ni-Zr, Co-Al, AL-Ni, Ag-Cu, Ti-AL, Nb-AL, Ti-Si. Thus one needs the developing of such modified method which will be generalize the nucleation theory in the changing concentration gradient field.

The recent achievements in the field of solid state reactions, especially, the tomographic atom-probe method (TAP), the different methods of solid state amorphazing reactions (SSAR) made the problem of intermediate phase nucleation in the concentration gradient field an urgent issue. The thermodynamic constraints on the nucleation are the main reasons of the phase competition and of formation of metastable phases instead of stable intermetallics. It is known that the thermodynamic and kinetic constraints on the nucleation are connected first of all with the narrow space domain of possible nucleation, with the sharp concentration gradient [1-4].

The detailed thermodynamic analysis of the nucleation in the concentration gradient has been made independently by different authors [5-10]. The above mentioned approaches were based on the different specific assumptions: frozen diffusion [5], unlimited transversal diffusion inside every slice perpendicular to the concentration gradient direction (∇C direction) [6], total mixing inside a new-born nucleus [7]. There were also different assumptions about the nucleus shape: sphere [5], cube [6], ellipsoid [9], arbitrary figure of rotation with optimized shape [9]. All [5,6,8-10] models gave the same important result - the nucleation of intermediate phase is thermodynamically forbidden if the concentration gradient exceeds certain critical value (figure 1). And nucleation barrier decreases when the concentration gradient decreases. Because of this result in these two modes we call them prohibiting modes. The theoretical estimation for real systems Ni-Zn, Ni-Al gives this value about 10^{7} -10^{9} m^{-1}.

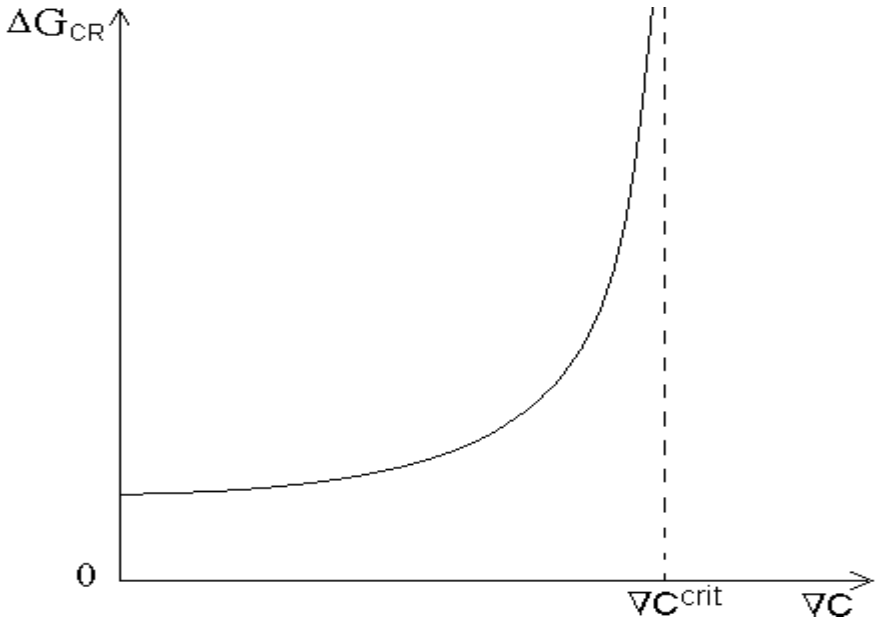

Fig. 1. Qualitative dependence of the nucleation barrier value ΔG_{CR} on concentration gradient ∇C in the parent phase for prohibiting transversal and polymorphous modes. ∇C^{crit} – critical value of the concentration gradient.

In paper [11] we showed that, strictly speaking, this result is not true. To verify this we considered one more nucleation mode - unlimited redistribution (in the ∇C - direction). It means that there is no diffusion constraints on nucleation in this direction. The principal supposition has been made in [11] by considering the unlimited redistribution in the ∇C - direction outside the new-born nucleus as well as inside it. This assumption is close to consideration of the similar total mixing mode [7], where the diffusion is taken into account only inside a new-born nucleus. We will show that the account of redistribution both inside and outside will give another result. More over we will take into account the gradient (Cahn J. W. - Hilliard J. E.) terms in the free energy density making impossible the abrupt changes of concentration at the interfaces. In mathematical sense we will generalize the Khachaturyan's approach to the nucleation [12], on the case of concentration gradient in the parent metastable phase.

In section 2 the fundamentals of the new model are considered. The variation problem for the saddle point of the Gibbs free energy surface is formulated and reduced to the system of Euler-equations for the concentration dependence outside and inside the critical nucleus. The solution of above mentioned problem is presented and results of such approach are analyzed.

In section 3 we will consider the polymorphous mode and transversal diffusion approach to present model. We will modify these two modes with taking into account the gradient term in the free energy density. For all modified modes of nucleation formulas of dependencies of the Gibbs free energy changing from volume, form and concentration gradient will be obtained.

In section 4 some conclusions about all three modes will be discussed.

2. Allowing longitudinal nucleation mode.

As an example let's consider the diffusion couple Al-Ni. TAM of the initial stages of reactive diffusion due to high spatial resolution (≈3 angstrom in the concentration gradient direction) shows that in Al-Ni system there exists very thin (≈2 нм) metastable phase of 60 at. % Al which disappears on a later stage of nucleation [4]. Hereby one makes consecutive annealing of diffusion couple Al/Ni at 200˚C, 250˚C and 400˚C during the different times (5, 30 min). The significant result of this experiment is that the later from the metastable Al_3Ni_2 phase of the inhomogeneous solution the new intermediate phase (more advantageous but metastable as well) is educed. And preliminary smoothing out of the concentration profile no one observed. It means that the sharp initial concentration gradient in these two cases of

nucleation of the new phases may stimulate the nucleation contrary to results of theoretical works [5,6,9].

We are sure that during the transformation one must account the possibility of redistribution of a component in the all alloys and significant influence of the gradient on the initial stage of reactive diffusion.

On the one side, from the beginning the parent phase is spatial inhomogeneous so that one needs to determine the nucleus parameters with taking into account inhomogeneity of the concentration profile and nonsymmetrical form of the nucleus, which in turn affect driving force of transformation.

On the other side, if there exists the concentration inhomogeneities in the solution then the density of Gibbs free energy in any spatial point depends on not only the concentration value C(r) and on spatial derivatives of C(r) characterizing the nonlocal interaction of concentration inhomogeneities (Cahn J. W. and Hilliard J. E. method) [11].

The aim of this chapter is generalizing the Cahn J. W. and Hilliard J. E. method on the case of intermediate phase nucleation in the existing initial concentration gradient field changing in time.

2.1. Model and method

Let's solve the rigorous variational problem for driving force of transformation as a functional of arbitrary concentration profiles C(r). The nucleus of the intermediate phase is assumed to be a cylindrical ("tablet") with the effective thickness $h=2X_R$ and radius R (figure 2).

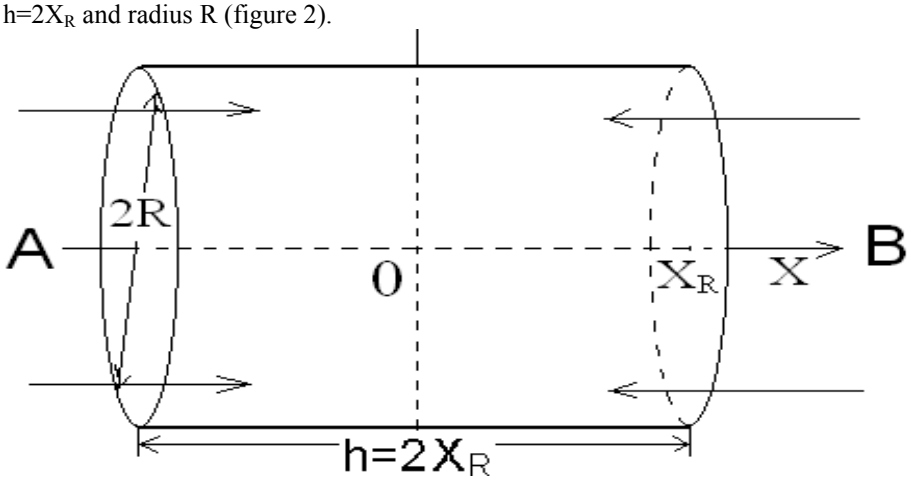

Fig.2. Scheme of the new intermediate phase nucleus form (gradient in X direction) with sharp boundary of 2R diameter across the gradient and diffuse boundary between the components A-B along the X-axis: $h=2X_R$ – effective thickness of the nucleus (height of cylinder) determining from the variation procedure [11].

The variation procedure gives the optimal concentration profile C(X) (farther else C(X,R) at fixed radius R of cylindrical nucleus) and optimal form at once.

Let's assume the fast diffusion transformation existing with unlimited redistribution in the concentration gradient direction (X-axis) at the initial stage with next reconstruction of a lattice. Such mode of nucleation in the concentration gradient with unlimited redistribution in the concentration gradient direction will be called longitudinal nucleation mode.

Consider the nucleation of intermediate phase described by parabolic free energy density dependence (figure 3):

$$g_{NEW}(C) = g_{NEW}(C_o) + \frac{\alpha_{NEW}}{2}\left(C - C_o\right)^2$$

on the basis of the metastable parent phase described by similar parabolic dependence:

$$g_{OLD}(C) = g_{OLD}(C_o) + \frac{\alpha_{OLD}}{2}\left(C - C_o\right)^2 .$$

According to the Khachaturyan approach to the problem of nucleation, there is no composition jumps at the nucleus boundaries. These very boundaries are determined as the places with compositions at which the Gibbs energy densities of the new and old phases are equal:

$$g_{NEW}\left(C_{\substack{R\\L}}(X_R)\right) = g_{OLD}\left(C_{\substack{R\\L}}(X_R)\right).$$

Thus the size of the nucleus is determined by the concentration interval (C_L, C_R), where the intermediate phase is advantageous:

$$C_{\substack{R\\L}} = C_O \pm \sqrt{\frac{2\cdot\Delta g(C_O)}{\alpha_{NEW}-\alpha_{OLD}}},$$

where $\Delta g(C_O) = g_{OLD}(C_O) - g_{NEW}(C_O)$, $\Delta g(C_O) > 0$.

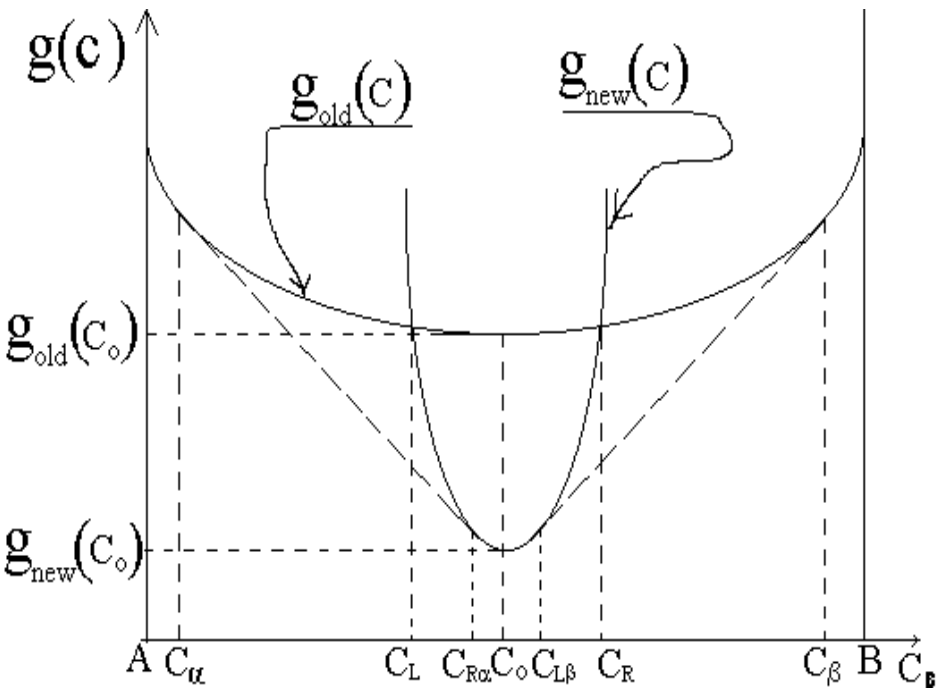

Fig. 3. Gibbs free energy density (energy per unite of volume) dependence on concentration for parent phase (old) and intermediate phase (new).

The parent solid solution is nonhomogeneous and is formed by interdiffusion in the diffusion couple A-B before new phase formation. The result of this previous diffusion stage is the error function concentration dependence

$$C_O(X) = \frac{1}{2} + \frac{1}{2}\,erf\left(\frac{X}{2\sqrt{D\cdot t}}\right),$$

where D - is an interdiffusion coefficient in parent phase (assumed to be constant), t - is annealing time before the attempt of nucleation. The concentration gradient at X=0: $\frac{dC}{dX} = \frac{1}{L_0} = \frac{1}{2\sqrt{\pi Dt}}$. As one can see from eqs. (1-3) the energy density is a function of the concentration, which is in turn a function of the coordinates. So this fact originates to Gibbs free energy dependence on nucleus geometry and spatial distribution of the concentration (concentration gradient) in it. The initial (before nucleation) concentration gradient determines the value of the nucleation barrier

ΔG_{CR}. Our aim is to find the dependence $\Delta G_{CR}\left(\frac{1}{L_0}\right)$.

The formation of the nucleus leads to the following change of free energy:

$$\Delta G\{C(X,R)\}=\int_{-\infty}^{+\infty}\pi R^2\left\{g(C(X))-g_{old}(C_0(X))+\frac{\beta}{2}\left(\frac{\partial C(X)}{\partial X}\right)^2-\right.$$
$$\left.-\frac{\beta_0}{2}\left(\frac{\partial C_0(X)}{\partial X}\right)\right\}dX+2\pi Rh\sigma \qquad (4)$$

Here $C_0(X)$ - is an initial profile (3), $C(X)$ - new profile, which is a result of redistribution in the nucleation process. Function g(C(X)) is equal to $g_{new}(C(X))$ if $C_L < C < C_R$ and is equal to $g_{old}(C(X))$ outside this interval. β and β_o- are parameters describing nonlocal interactions according to Cahn-Hilliard theory, σ - surface energy for the side surface of cylinder (constant in our case). In eq. (4) the surface energy for the cylinder face is not introduced since the surface effects for this continuous boundaries are taken into account by the gradient term β. β and β_o values depend on interatomic interaction potentials and are functions of concentration, but in our model they are assumed to be constant. One may estimate them by such formula: $\beta_o \cong \beta \cong Zna^2E_{mix}$, where a- lattice parameter, Z - coordination number, E_{mix} - two-particle energy of interaction (mixing energy), n – number of atoms per unite of volume.

Let's use the quasi one-dimensionality of our model. We will fix the radius R, then will optimize the profile and will determine the thickness $h=2X_R$ and after that we will change the radius once more. For every fixed R we will find the driving force corresponding to the optimal profile. The cross point on the ΔG(R) dependence gives the nucleation barrier. So we will find the critical radius R_{CR}, the critical thickness $h=2X_R$, optimal concentration profile $C_{CR}(X,R_{CR})$ in the critical nucleus and in the parent phase, volume $V_{CR}=2\pi R_{CR}^2\cdot 2X_R$ and nucleation barrier ΔG_{CR}.

In fact the integral in the eq. (4) falls into three intervals: $\int_{-\infty}^{X_L}$, $\int_{X_L}^{X_R}$ and $\int_{X_R}^{+\infty}$, where X_L and X_R are determined by the conditions: $C(X_L)=C_L$, $C(X_R)=C_R$. For simplicity we will consider the symmetric case when the minima of both g(C) functions coincide with respect to concentration $C(X=0)=C_O$ and we will limit ourselves with symmetrical case, when the center on new-born nucleus coincides with the position of the initial interface X=0. Then $X_L=-X_R$. The expression (4) for the change of the Gibbs free energy is a functional of the arbitrary concentration dependences C(X). If the nucleation is possible the surface of ΔG in the multidimensional configuration space must determine the critical nucleus. The configuration space includes the possible concentration profile C(X,R), the possible radius R of the tablet.

Obviously, in order to find the critical parameters, one should solve the variational problem δΔG=0, taking into account the conservation of matter.According to the Lagrange method one should find extreme of the functional:

$$F\{C(X,R)\}=\Delta G\{C(X,R)\}-2\mu\int_0^{+\infty}\pi R^2(C(X,R)-C_O)dX$$

μ - Lagrange coefficient, determined from the boundary conditions. Last equation takes the symmetry into account.

The transition from variation principle to Euler-equation is not trivial here since the expression (4) for ΔG contains the variable X_R, which is determined by the form of C(X). To obtain the standard Euler-equation one needs to represent the variation in the integral form [11].

The usual variation procedure for the functional F provide the set of Euler-Lagrange equations:

$$\alpha_{NEW}\left(C_I(X,R)-C_0\right)-\mu-\beta C_I''(X,R)-\frac{2\sigma}{R}\cdot\frac{C_I''(X,R)}{\left[C_I'(X,R)\right]^2}=0 \qquad (5)$$
$$0<X<X_R$$

$$\alpha_{OLD}\left(C_{II}(X)-C_0\right)-\beta_o C''_{II}(X)-\mu=0$$
$$X>X_R \qquad (6$$

The boundary conditions are: $C_I(X=0,R)=C_0$, $C_I(X=X_R,R)=C_R=C_{II}(X=X_R,R)$, $C_{II}(X\to\infty)=1$. We demand the solution to be smooth (with continuous first derivatives) at the boundary $X=X_R$: $C_I'(X=X_R)=C_{II}'(X=X_R)$. The position of the boundary itself is found from above mentioned boundary conditions.

2.2. Solution of the boundary problem

The set of equations (5-6) have no analytical solution because of essential nonlinearity in eq. (5). To obtain semianalytical solution, assume the derivative $C'_I(X)$ inside the nucleus to be approximately constant:

$$C_I'(X=0,R)=\frac{1}{L}\approx const \quad ,$$

where the parameter L - is unknown and must be determined from the condition of self-consistency. Using eq. (7) one can easily obtain the analytical solution of the eqs. (5-6):

$$C_I(X,R)=C_0+\frac{\mu}{\alpha_{NEW}}\left[1-\exp(-\chi_1 X)\right]+\left[\frac{1}{\chi_1 L}-\frac{\mu}{\alpha_{NEW}}\right]sh(\chi_1 X) \qquad X<X_R,$$
$$C_{II}(X,R)=1+\left[C_R-1\right]\cdot\exp\left(\chi_2\left(X_R-X\right)\right) \qquad X>X_R,$$

where $\chi_1=\sqrt{\alpha_{NEW}\Big/\left(\beta+2\sigma L^2/R\right)}$, $\chi_2=\sqrt{\alpha_{old}/\beta}$, $\mu=\alpha_{OLD}(1-C_0)$.

Substituting this solution into the eq. (7) one obtains the expression for parameter L [11]. Taking into account the boundary conditions yields the expression for the thickness of the critical nucleus. The optimal concentration profile without account of Cahn-Hilliard terms in driving force (4) has discontinuities corresponding to the rule of common tangent. Calculation of the gradient terms leads to continuous curve of the optimal concentration profile.

To check the correctness of above mentioned approximation we solved the same problem by numeric finite-difference method. To do this we modified the numeric solution of the Cauchy problem for the case of unknown boundary position. Considering a set of possible X_R values we solved eq. (5) with given function $C_I(X)$ and it's derivative $C_I'(X)$ by finite difference method and found the value of $C_I(X=0)$. If this value coincided with the left boundary condition C_0 (with given accuracy ε) we took the position X_R on the right boundary and corresponding concentration dependence as a solution. The results of numerical calculations practically coincided with the semianalytical approach. In particular, a concentration profile inside the nucleus was practically linear, so that the nucleus thickness can be well approximated by the simple formula:

$$h=2X_R=\frac{2(C_R-C_0)}{\chi_2\left(1-C_R\right)}$$

Substituting the concentration profiles $C(X)$ at fixed R in the eq. (4) for the Gibbs energy change yields the dependence $\Delta G(R)$. This dependence has a familiar form with the maximum, corresponding to a nucleation barrier. The solution of the boundary problem (5-6) corresponds to extreme of the functional ΔG. To check whether this extreme is a saddle point, one must investigate the sign of the second variation [11,12]. In the case of the saddle point this sign must be different for different directions in the configuration space.

2.3 Dependence of the nucleation barrier on the concentration gradient.

Further we use the nondimensional parameters and turn to new variables:

$$\Omega = \frac{\alpha_{NEW} \cdot \beta}{\sigma^2},\ K = \frac{\alpha_{OLD}}{\alpha_{NEW}},\ P = \frac{\beta_o}{\beta},\ \xi = \frac{\alpha_{NEW}}{\sigma},$$

$$XX = X \cdot \xi,\ RR = R \cdot \xi,\ LL = L \cdot \xi,\ LL_0 = L_0 \cdot \xi, \text{ where } \xi = \frac{\alpha_{NEW}}{\sigma}.$$

For equation (4) it yields:

$$\Delta G = \Delta GG \cdot 2\pi\alpha_{new} \Big/ (\xi)^3, \quad \Delta GG = \Delta GG_1 + \Delta GG_2 + \Delta GG_3. \tag{8}$$

Here:

$$\Delta GG_1 = \int_0^{XX_R} RR^2 \left\{ -\frac{\Delta g(C_0)}{\alpha_{NEW}} + \frac{[C_I(XX) - C_0]^2}{2} - \frac{K}{2}[C_0(XX) - C_0]^2 + \right.$$
$$\left. + \frac{\Omega}{2}\left[\left(\frac{\partial C_I(XX)}{\partial XX} \right)^2 - P\left(\frac{\partial C_0(XX)}{\partial XX} \right)^2 \right] \right\} dXX,$$

$$\Delta GG_2 = \int_{XX_R}^{\infty} RR^2 \left\{ \frac{K}{2}\left([C_{II}(XX) - C_0]^2 - [C_0(XX) - C_0]^2 \right) + \right.$$
$$\left. + \frac{\Omega}{2}\left[\left(\frac{\partial C_{II}(XX)}{\partial XX} \right)^2 - P\left(\frac{\partial C_0(XX)}{\partial XX} \right)^2 \right] \right\} dXX,$$

$$\Delta GG_3 = 2 \cdot RR \cdot XX_R,\ \Delta g(Co) \big/ \alpha_{NEW} = (1 - K)(C_R - C_0)^2 / 2.$$

For numeric calculations one needs certain upper limit instead of infinite the integral ΔGG_2. This upper limit was determined under condition when new optimal concentration profile coincides with the initial profile at infinity. The nucleation barrier ΔGG_{CR} is found as a maximum of the dependence $\Delta GG(RR)$ calculated for optimized concentration profiles C(XX,RR) at fixed parameters Ω, LL_0, C_R, K and P.

In this paper we investigate the dependence of nucleation barrier on the initial concentration gradient. First of all, emphasize that the finite nucleation barrier exists at any concentration gradient, so that there is no absolute prohibition of intermediate phase nucleation by the sharp concentration gradient, contrary to the results [5-10]. We believe that the main reasons are the redistribution calculation outside the nucleus in X-direction (which is not taken into account in [5-10]) and assumptions of different diffusion mechanisms in [5-11]. The dependence $\Delta GG_{CR}\left(1 \big/ LL_0 \right)$ is monotonously decreasing (figure 4).

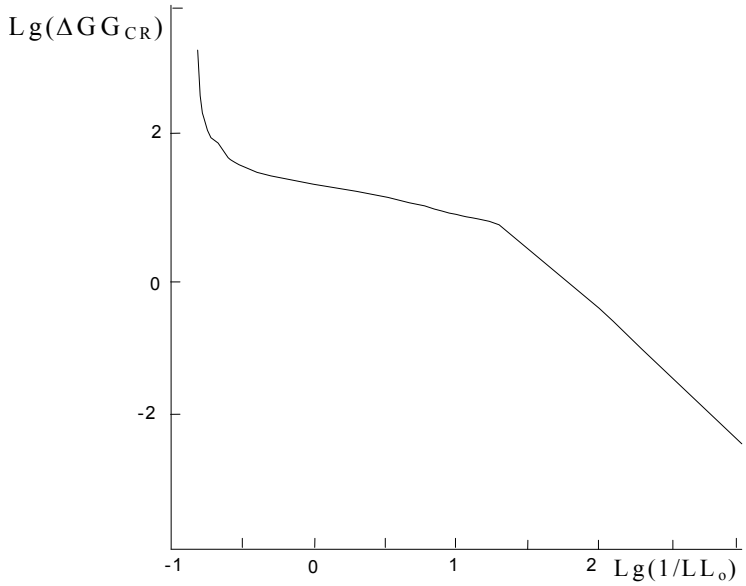

Fig. 4. Nucleation barrier ΔGG_{CR} dependence on initial concentration gradient LL_o^{-1} (in non-dimensional quantity) or on annealing time of the binary diffusion couple for thermodynamic driving force (4), which is determined by set of parameters: C_R=0.85 и K=1/4, Ω=0.1, P=1.

The decrease of nucleation barrier at big gradients is caused by the big difference between initial and optimal concentration profile, which leads to the integration of bulk driving force over the larger distances outside the nucleus. In particular, the nucleation barrier appears to be finite at any concentration gradient and can depend on it (∇C) monotonously. With decreasing concentration gradient the nucleation barrier increases. And only after a certain value ∇C_{CR} nucleation should be unsuccessful. Let's imagine the concentration gradient forming as a result of previous diffusion (see eq. (3)). It means that the probability of nucleation can be big at the very beginning of interdiffusion and that the new-born nuclei may became subcritical and vanish if they had no time to grow.

In common case all three modes (longitudinal, transversal, polymorphous) of nucleation may exist simultaneously. In such case the presented longitudinal nucleation mode will be most preferable (most probable) on initial stage of reactive diffusion. In other words the initial concentration gradient may stimulate the formation of a new phase as it observed by tomographic atom-probe method for binary couple Al/Ni in [4].

Optimization procedure determines shape of the nucleus at once. For the case $1/LL_0 \to \infty$ the nucleus has needle-like shape. Decreasing the initial gradient $1/LL_0$ to the certain critical value ∇C_{CR} leads to changing the f shape of the nucleus – it became pancake-like.

The nucleation in this mode is impossible when the initial concentration gradient became smaller than certain critical value ∇C_{CR}, which is approximately equal to the gradient of the optimized profile $1/LL$. That is for big annealing time (the gradient will be small), when $0 < 1/LL_0 < \nabla C_{CR}$ the nucleation in such mode will be impossible. In this case polymorphous and transversal modes will operate.

The mode of the total mixing inside a new-born nucleus [7] is the particular case of the above shown coherent method [11,12]. It takes place when the optimized gradient is equal zero. There is a principal difference in results of presented here longitudinal nucleation mode from the total mixing mode. In longitudinal nucleation mode the nucleation became impossible after the certain critical value of gradient whereas in total mixing mode there is no such critical gradient so that the nucleation is always possible for all gradients. This difference is connected with the absence of the gradient in the nucleus.

In next chapter we will see that the choosing the diffusion mechanism will determine the nature of the dependence

of the nucleation barrier on concentration gradient.

3. Other diffusion approaches.

3.1. Modified transversal mode - allowing transversal mode.

To feel the main peculiarities of the previous model, compare it with the results of more traditional approach [6], when diffusion during the nucleation is allowed only in the region (- X_R , X_R) and proceeds independently in every slice ($X, X+dX$) perpendicular to the ∇C - direction (figure 5).

The driving force is written only in the transformation region (in the nucleus). Gibbs free energy densities (per atom) for old and new phases are parabolic:

$$g(C) = \begin{cases} g^{old}(C) = g_0^{old} + \dfrac{\alpha^{old}}{2}\left(C - C_0^{old}\right)^2 \\ g^{new}(C) = g_0^{new} + \dfrac{\alpha^{new}}{2}\left(C - C_0^{new}\right)^2 \end{cases},$$

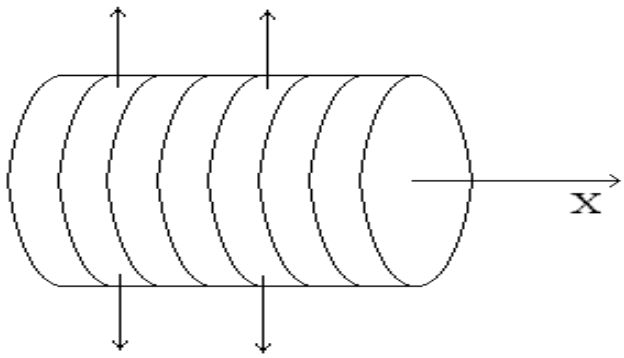

Fig. 5. Scheme of multi-layer tablet in which the components supply the nucleus perpendicular to the ∇C - direction. Scheme is done on a base of the model in [6].

This transversal diffusion is supposed to be fast enough to satisfy the rule of parallel tangents (figure 6).

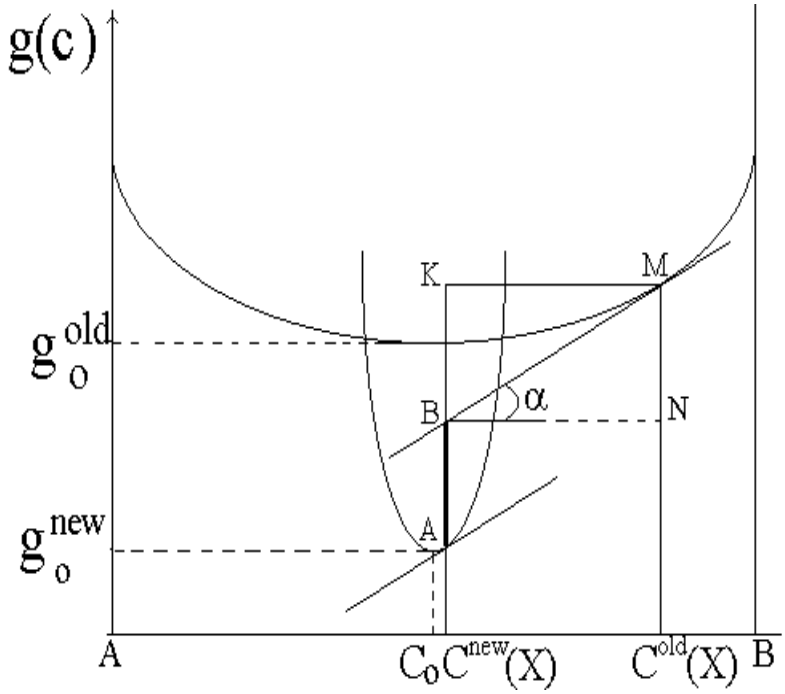

Fig. 6. Gibbs free energy density (energy per atom) dependence on concentration for parent phase (old) and intermediate phase (new). Parabolas are symmetric with respect to $C_o^{new} = C_o^{old} = C_o$.

The obvious correlations AB=AK-KB=AK-MN yield: $AB = AK - BN \cdot tg(\alpha)$, $\mathrm{BN} = \left(\mathrm{C}^{\mathrm{old}}(\mathrm{X}) - \mathrm{C}^{\mathrm{new}}(\mathrm{X})\right)$, $tg(\alpha) = \dfrac{\partial g^{old}(C)}{\partial C}$ and $tg(\alpha) = \alpha^{old} \cdot \left(C^{old}(X) - C_O\right)$. New $C^{new}(X)$ and old $C^{old}(X)$ concentrations are linked by condition:

$$\alpha^{old} \cdot \left(C^{old}(X) - C_O\right) = \alpha^{new} \cdot \left(C^{new}(X) - C_O\right).$$

Then the change of Gibbs free energy due to nucleation of a cylindrical tablet has the following form:

$$\Delta G\left\{C(X,R)\right\} = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 ,$$

Here

$$\Delta G_1 = \int_0^{X_R} 2\pi R^2 n \cdot \left\{ g(C^{new}(X)) - g(C^{old}(X)) + \frac{\partial g(C^{old}(X))}{\partial C} \cdot \left(C^{old}(X) - C^{new}(X)\right) \right\} dX ,$$

$$\Delta G_2 = \int_0^{X_R} 2\pi R^2 \left\{ \frac{\beta}{2} \left(\frac{\partial C^{new}(X)}{\partial X} \right)^2 - \frac{\beta_o}{2} \left(\frac{\partial C^{old}(X)}{\partial X} \right)^2 \right\} dX ,$$

$$\Delta G_3 = \sigma \cdot 2\pi R \cdot 2X_R , \quad \Delta G_4 = \sigma' \cdot 2\pi R^2 .$$

σ' is the surface energy (per unite of area) of the nucleus interfaces, perpendicular to the ∇C - direction. Approximating concentration profile in the parent phase as linear dependence: $C(x) \cong C_O + x \cdot \nabla C$, one obtains the

resulting expression for the changes ΔG_1 и ΔG_2 :

$$\Delta G_1 = -\Delta g(C_0)\cdot \pi R^2 \cdot 2X_R + \alpha^{old}\left(1-\frac{\alpha^{old}}{\alpha^{new}}\right)\cdot(\nabla C)^2 \cdot \pi R^2 \cdot \frac{X_R^3}{3},$$

$$\Delta G_2 = \frac{\beta}{2}\cdot(\nabla C)^2 \cdot \left[\left(\frac{\alpha^{old}}{\alpha^{new}}\right)^2 - P\right]\cdot X_R \cdot 2\pi R^2 .$$

According to the eq. (9) if $C_o^{new} = C_o^{old}$ then it yields $\Delta g(C_0) = n\left(g_o^{old} - g_o^{new}\right)$.

Expressions ΔG_1 and ΔG_2 represent the bulk contributions into the energy of transformation. And ΔG_3, ΔG_4 corresponds to the surface energies on each side and along the face of cylinder with surface tension values σ и σ' respectively.

The expression for gradient energy ΔG_2 is: i) negative ($\beta_o \cong \beta > 0$, $P = \beta_o/\beta \cong 1$ and $\left(\frac{\alpha^{old}}{\alpha^{new}}\right)^2 < P$) because of the concentration gradient in the nucleus necessarily less than initial in the parent phase ($\alpha^{old} << \alpha^{new}$), ii) proportional to the volume of the nucleus. The gradient energy ΔG_2 is determined here only in the volume of the new phase. In our previous problem the gradient energy is determined on the all X axis and consist of as bulk energy contribution as effective surface energy.

The energy of transformation ΔG is function of the volume $V = \pi R^2 \cdot 2X_R$ and shape parameter $\varphi = \frac{R}{X_R}$ (further P=1). Eq. (10) yields:

$$\Delta G = -A\cdot V + \frac{B}{(2\pi)^{\frac{2}{3}}}\cdot V^{\frac{5}{3}}\cdot \varphi^{-\frac{4}{3}} + (2\pi)^{\frac{1}{3}}\cdot V^{\frac{2}{3}}\cdot \sigma'\left(\varphi^{\frac{2}{3}} + 2\cdot S\cdot \varphi^{-\frac{1}{3}}\right), \qquad (11)$$

where $S = \frac{\sigma}{\sigma'}$ - Wulf parameter,

$$A = \Delta g(C_0) + \beta\left(1-\left(\frac{\alpha^{old}}{\alpha^{new}}\right)^2\right)\cdot(\nabla C)^2,\ B = \frac{\alpha^{old}}{6}\left(1-\frac{\alpha^{old}}{\alpha^{new}}\right)\cdot(\nabla C)^2 .$$

There is the principal difference of dependence (11) from obtained one in [6]. In our case the sharp concentration gradient makes influence on driving force in two ways: on one side, it makes increasing the effective driving force of transformation (due to second term in the coefficient A), on the other side, big gradient makes decreasing the stimulus (because of the coefficient B, B>0). So for small volumes the big gradient helps the nucleation process ($\Delta G \sim -AV$) in such modified transversial mode, and it suppresses the growth of the nucleus for big volumes ($\Delta G \sim BV^{\frac{5}{2}}$).

The dependence of the function $\Delta G(V)$ may be monotonic as well as nonmonotonic in principle. It depends on the value of the concentration gradient and other thermodynamic parameters. It is interesting that if nucleation is impossible for the case of gradient absence ($\Delta G(V)$ - is a monotonic increasing function) in the presence of the big initial concentration gradient certainly leads to that the dependence $\Delta G(V)$ will be nonmonotonic for presented mode. The

necessary condition is $\nabla C > \nabla C_1^{кр} = \sqrt{\dfrac{|\Delta g_o(C_o)|}{\beta\left(1-\left(\alpha^{old}/\alpha^{new}\right)^2\right)}}$ because of the $\beta\left(1-\left(\alpha^{old}/\alpha^{new}\right)^2\right)(\nabla C)^2 > |\Delta g_o(C_o)|$. The sufficient condition is such when the dependence $\Delta G(V)$ will be nonmonotonic with the maximum and minimum in which $\Delta G(V)=0$, $\dfrac{\partial \Delta G}{\partial V}=0$ for V≠0. The condition $\dfrac{\partial \Delta G}{\partial V}=0$ gives ∇C_{tr}^{crit}:

$$\nabla C_{tr}^{crit} = \sqrt{\frac{\Delta g(C_o) - (2\pi)^{\frac{1}{3}} V^{-\frac{1}{3}} \sigma' \left(\varphi^{\frac{2}{3}} + 2S\varphi^{-\frac{1}{3}}\right)}{\frac{5}{18}\varphi^{-\frac{4}{3}}\left(\frac{V}{2\pi}\right)^{\frac{2}{3}} \alpha^{old}\left(1-\frac{\alpha^{old}}{\alpha^{new}}\right) - \beta\left(1-\left(\alpha^{old}/\alpha^{new}\right)^2\right)}}.$$

Gradients $\nabla C > \nabla C_{tr}^{кр}$ under the additional stipulation that $\Delta G(\nabla C_{tr}^{кр}, V)=0$ for V>0, determine the sufficient condition, when big gradient stimulates new phase formation.

Thus in old prohibiting transversal mode [7] big gradient only suppresses the nucleation and growth and in presented here modified mode it stimulates the new phase appearance and suppresses the growth. So such modified mode we will call the allowing transversal mode with respect to old prohibiting mode.

Notice that if coefficients of nonlocal interaction β_o, β will be small (that is for all real gradients it meets the case $\Delta g_o(C_o) >> \beta\left(1-\left(\alpha^{old}/\alpha^{new}\right)^2\right)(\nabla C)^2$) then the prohibited mode will be obtained.

Variational procedure $\partial \Delta G/\partial \varphi = 0$ for shape factor yields:

$$\varphi_{opt} = \left(\frac{R}{X_R}\right)_{opt} = \frac{S}{2} + \sqrt{\frac{S^2}{4} + \frac{VB}{\pi\sigma'}}.$$

In the limit for small volumes and finite gradients or for finite volumes and infinitesimal gradient quantity Wulf rules yields: $\varphi_{opt}(V \to 0) = S = \dfrac{\sigma}{\sigma'}$.

For big volumes and/or for big gradients the shape factor approaches infinity as a function of $(\nabla C)V^{\frac{1}{2}}$: $\varphi_{opt}(\nabla C^2 V \to \infty) \approx \left[\dfrac{\alpha^{old}}{6\pi\sigma'}\left(1-\dfrac{\alpha^{old}}{\alpha^{new}}\right)\right]^{\frac{1}{2}} \cdot \left((\nabla C)^2 V\right)^{\frac{1}{2}}$. In this case the thickness X_R: $X_R \underset{V\to\infty}{\sim} V^{\frac{1}{3}}\varphi^{-\frac{2}{3}} \sim V^{\frac{1}{3}}\left((\nabla C)V^{\frac{1}{2}}\right)^{-\frac{2}{3}} \sim (\nabla C)^{-\frac{2}{3}}$, and the radius R: $R \underset{V\to\infty}{\sim} V^{\frac{1}{3}}\varphi^{\frac{1}{3}} \sim V^{\frac{1}{3}}\left((\nabla C)V^{\frac{1}{2}}\right)^{\frac{1}{3}} \sim (\nabla C)^{\frac{1}{3}} V^{\frac{1}{2}} \to \infty$. Hereby the nucleus form will be pancake-like.

3.2. Modified polymorphous mode - allowing polymorphous mode.

Let's reconsider this mode [5,9] by account the gradient contribution into the energy of the system. The influence of this term may be a determining factor on initial stage when the gradient of concentration is a maximum.

For eq. (9) new concentration $C^{new}(X)$ and old $C^{old}(X)$ are linked: $C^{new}(X) = C^{old}(X) = C_O + \nabla C \cdot X$.

And expression (10) for this mode:

$$\Delta G\{C(X,R)\} = \Delta G_1' + \Delta G_2 + \Delta G_3 + \Delta G_4,$$

Here:

$$\Delta G_1' = \int_0^{X_R} 2\pi R^2 n \cdot \{g^{new}(C^{new}(X)) - g^{old}(C^{old}(X))\} dX$$

Meaning of the $\Delta G_1'$, ΔG_2, ΔG_3, ΔG_4 is evident from previous analysis for transversal mode. After the same algebra for ΔG as the function of the volume and form factor (where made assumption $C_0^{new} = C_o^{old} = C_o$):

$$\Delta G = -A' \cdot V + \frac{B'}{(2\pi)^{\frac{2}{3}}} \cdot V^{\frac{5}{3}} \cdot \varphi^{-\frac{4}{3}} + (2\pi)^{\frac{1}{3}} \cdot V^{\frac{2}{3}} \cdot \sigma' \left(\varphi^{\frac{2}{3}} + 2 \cdot S \cdot \varphi^{-\frac{1}{3}} \right), \quad (13)$$

$A' = \Delta g(C_0) + \frac{\beta_o - \beta}{2} \cdot (\nabla C)^2$, $B' = \frac{\alpha^{new} - \alpha^{old}}{6} \cdot (\nabla C)^2$, B'>0, because of $\alpha^{new} > \alpha^{old}$, $\Delta g(C_0) = n(g_o^{old} - g_o^{new})$.

In dependence of values of interatomic interaction potentials in the new phase and in the parent phase the sharp initial gradient may not only suppress the nucleation (in the case $\beta_o \le \beta$) but stimulate one (in the case $\beta_o > \beta$ under the necessary condition $\nabla C > \nabla C_2^{crit} = \sqrt{\frac{2\Delta g_o(C_o)}{\beta - \beta_o}}$).

The sufficient condition is formulated similarly: $\Delta G(V)$ will be nonmonotonic with the maximum and minimum in which $\Delta G(V)=0$, $\frac{\partial \Delta G}{\partial V} = 0$, V≠0. The condition $\frac{\partial \Delta G}{\partial V} = 0$ gives ∇C_{pol}^{crit}:

$$\nabla C_{pol}^{crit} = \sqrt{\frac{\Delta g(C_o) - (2\pi)^{\frac{1}{3}} V^{-\frac{1}{3}} \sigma' \left(\varphi^{\frac{2}{3}} + 2S\varphi^{-\frac{1}{3}} \right)}{\frac{5}{18} \varphi^{-\frac{4}{3}} \left(\frac{V}{2\pi} \right)^{\frac{2}{3}} (\alpha^{new} - \alpha^{old}) - \frac{(\beta - \beta_O)}{2}}}.$$

Such gradients $\nabla C > \nabla C_{pol}^{кр}$ for which $\Delta G(\nabla C_{pol}^{кр}, V) = 0$, V>0, determine the sufficient condition when new phase formation will be advantageous.

The influence of the gradient on shape factor in this mode is the same with comparison of the previous method. Thus we have found that gradient term account makes essential changes in thermodynamic results for all three modes.

3.3. Estimation and discussing of modes.

Let's show that influence of sharp concentration gradient in last two modes may be main on initial stage. This is obvious from the estimation of the nonlocal interaction parameter:

$\beta \approx na^2 E_{mix} Z \approx 10^{29}\left(10^{-10}\right)^2 \cdot 10^{-19} \cdot 10 = 10^{-9}\dfrac{J}{m}$, so product $\beta\left(\nabla C\right)^2 \approx 10^{-9}\left(\dfrac{1}{10^{-9}}\right)^2 = 10^{9}\dfrac{J}{m^3}$, consequently, this value is compatible with the bulk contribution in the energy of transformation : $\Delta g\left(C_0\right) = n\left(g_o^{old} - g_o^{new}\right) \approx 10^{29} \cdot 10^{-20} = 10^{9}\dfrac{J}{m^3}$. These estimations confirm our criticism directed to imperfection of the problem description in inhibiting polymorphous and transversal modes.

Notice that for the case of $\beta_o \leq \beta$ the polymorphous mode will be prohibiting whereas the transversal mode will be allowing anyway (due to $\alpha^{old} << \alpha^{new}$).

In principle, for these two modified modes in dependence of the parameters of a system there exist four different ways of evolution of the Gibbs free energy, evolution of the ΔG at the beginning of annealing (t=0), when gradient is maximum to moment of total smoothing of concentration profile (t→∞), when gradient is equal to zero. We demonstrate it on figure 7.

When dependence in some mode will be monotonously increasing function then nucleation will take place by another mechanism, other mode. For example, in the case (c) on fig. 7 nucleation in polymorphous and transversal modes will be forbidden but it may be allowed in longitudinal nucleation mode.

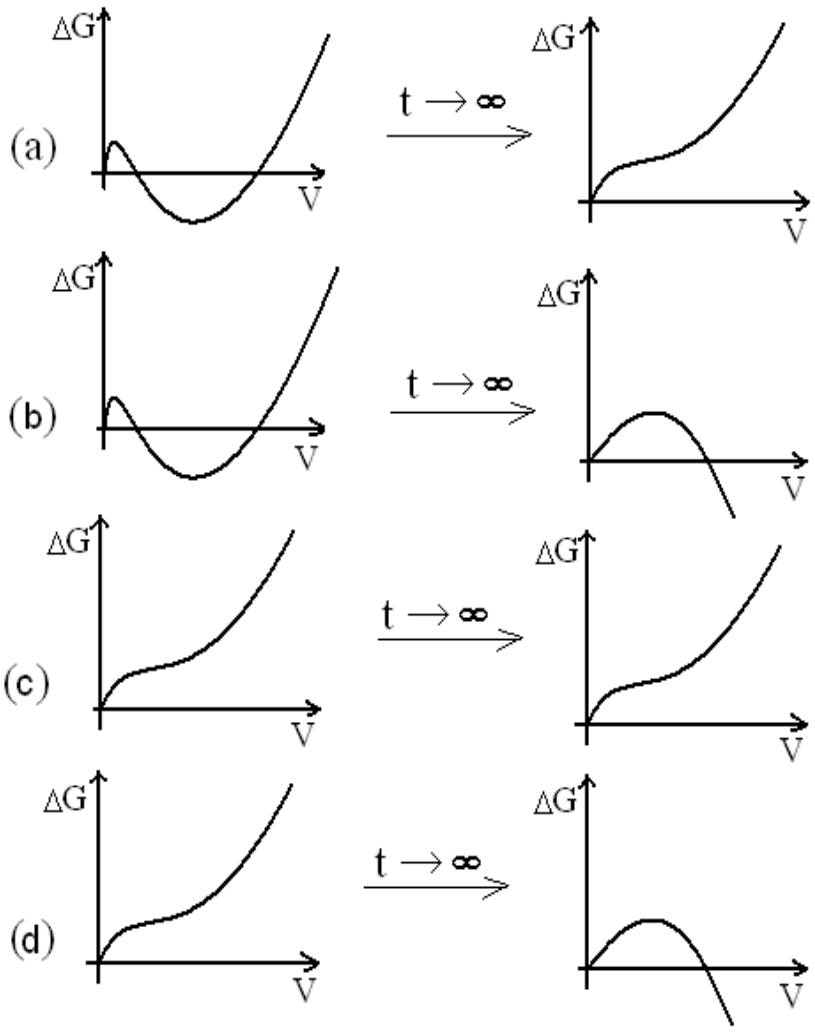

Fig.7 Evolution ways of $\Delta G(V)$ in polymorphous and transversal modes of nucleation – dependence on time:

(a) – initial gradient stimulates the new phase appearing and suppresses its growth. In final state nucleation is impossible.
(b) – initial gradient stimulates the new phase appearing and suppresses its growth. In final state nucleation is possible even without gradient.
(c) - initial gradient suppresses the nucleation. In final state nucleation is impossible even without gradient.
(d) – initial gradient suppresses the nucleation. Without gradient in final state nucleation is possible.

4. Resume

Nucleation barrier depends on concentration gradient so it depends on annealing time.

The different diffusion mechanisms make the different dependencies of the nucleation barrier on concentration gradient.

Comparing the inhibiting polymorphous and the inhibiting transversal modes with the longitudinal nucleation mode it is possible to say that the longitudinal nucleation mode is the most probable on initial stage of reactive diffusion.

The main result of reconsidering and modifying of the inhibiting modes in the concentration gradient - big concentration gradients lead to nonmonotonic dependence of Gibbs free energy on a volume of a new phase.

Depending on the parameters and choosing the nucleation modes the dependence of Gibbs free energy on new phase volume may be monotonic, nonmonotonic with the maximum and nonmonotonic with the maximum and minimum

There is a possibility of conversion of different modes – changing the modes from one to another.

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References

[1] K. Barmak, C. Michaelsen, G. Lucadamo, J. Mater. Res, 12 (1997). p. 133.
[2] A. L. Greer, Applied Surface Science, 86 (1995), p. 329.
[3] J. H. Perepezko, M. N. Bassani da Silva, J. S. Park, A. S. Edelstein, R. R. Everett, Mat. Sci. and Eng., A 195 (1995) p. 1.
[4] G. Schmitz, F. Hartung, T. Jeske, C. Lang, J. Schleiwies, Advances in Solid State Physics, 40 (2000), p. 453.
[5] A .M. Gusak, Ukr. Fiz. Jour., 35 (1990), p. 725.
[6] P. J. Desre, A. P. Yavari, Physical Review Letters, 64 (1990), p. 1533.
[7] F. Hodaj and P. J. Desre, Acta Materialia, 44 (1996), p. 4485.
[8] F. M. Heurle, Solid State Phenomena, 3 (1998), p.237.
[9] A. O. Bogatyryov, A. M. Gusak, Metal. Physics and Adv. Technologies, 18 (2000), p 897.
[10] F. Hodaj, A. M. Gusak, P. J. Desre, Philosophical Magazine, A. 77 (1998),p. 22.
[11] A. S. Shirinyan, A. M. Gusak, Ukr. Fiz. Jour., 42 (1997), p. 1276.
[12] A. G. Khachaturyan. Theory of Structural Transformation in Solids. - New York: John Wiley & Sons, 1983. – 574 p.