**Summary.** *T. V. Zaporozhets. Modeling of SHS-reaction steady state regime in the nanofoils (phenomenologic model). Double-stage reaction. Within the framework of the reactive phase growth kinetics in thin films at unisothermal regime the self-consistent temperature profile model of self-propagating high temperature synthesis (SHS) reaction as a result of two successive phases formation in the multilayered nanostructure is suggested. The influence of intermediate reaction on SHS-front parameters is investigated. It is shown that the order of phase formation has strong effect on the front parameters of SHS-reaction.*

**Keywords:** self-propagating high temperature synthesis (SHS), reactive diffusion, heat conductivity, phase formation, layered nanofilms.

**F.Hodaj, A.M.Gusak, B.B.Straumal**

## NUCLEATION IN OPEN NANOSYSTEMS –
## RECENT HISTORY AND PERSPECTIVES

*Solid state reactions start from nucleation of the reaction product phase in the open nano-sized region. Nucleation in the open nanosystem is influenced not only by size dependence of Gibbs free energy but as well by the divergence of external fluxes in the nucleation place. This influence can be formulated as an additional term in the effective nucleation barrier proportional to the flux divergence magnitude and the fifth or fourth power of linear size depending on the nucleation controlling stage (diffusion or interface kinetics).*

**Keywords: nucleation, diffusion, flux divergence, open nano-system**

### I. Introduction

Numerous modern technologies (micro- and nano-electronics, photonics, high-temperature superconductivity etc.) are based on the materials and their combinations obtained by solid state reactions. Moreover, solid state reactions often determine the mean time to failure (MTF) of the working schemes. Therefore, investigation of all stages of solid state reactions in all kinds of times, temperatures and external forces is extremely important [1].

Physicists prefer to treat solid state reactions (SSRs) with formation of intermetallic compounds (IMCs) as the first-order phase transitions proceeding in sharply inhomogeneous open system (contact zone) under gradients of thermodynamic driving forces and under continuing incoming and outcoming fluxes of matter. Since common first-order phase transition in initially homogeneous system includes 3 main stages (nucleation, precipitation – independent growth of the just born nuclei, and coarsening), one might also expect 3 corresponding stages of SSR: flux-driven nucleation in the concentration gradient, flux-driven individual growth and flux-driven coarsening. Theories of flux-driven coarsening (FDR(Flux-Driven Ripening) and FDGG (Flux-Driven Grain Growth)) had been suggested by one of present authors (AMG) jointly with King Ning Tu [2-4]. Models of "flux-driven individual growth" (DIGM-like growth of IMC precipitates due to lateral diffusion along moving interphase interfaces) were proposed in [5-7] and will not be discussed here.

History of nucleation models is more complicated. Here we will distinguish thermodynamics and kinetcs of nucleation in the contact zone of two reagents. Thermodynamics of nucleation in the sharp concentration gradient (under full solubility in the metastable solid solution) was first published in [8]. Main idea was: if, prior to intermediate

phase formation, narrow layer of metastable solid solution or amorphous alloy had been formed at the base of initial interface, the sharp concentration gradient inside this layer provides decrease of the total bulk driving force of nucleation, and corresponding increase of nucleation barrier. Nuclei were taken to be spheres, appearing in the strongly inhomogeneous concentration profile of the parent phase, so that local driving force of transformation could change significantly from the left to the right along the diameter of nucleus. This effect appeared to be non-negligible, since usually the intermediate phases have very strong concentration dependence of the Gibbs energy. Main result was the new size dependence of the Gibbs energy – it contained, in addition to the terms of second order (surface energy, positive) and third order (bulk driving force, negative), the new term proportional to the 5-th power of size and the squared concentration gradient:

$$\Delta G(R) = \alpha R^2 - \beta R^3 + \gamma \left( \nabla C \right)^2 R^5, \tag{1}$$

$\gamma$ being positive and proportional to the second derivative of the new phase Gibbs energy over concentration. Expression (1) means that for large enough gradient $\nabla C > \nabla C^{crit}$ (typically $\nabla C^{crit} \propto 10^8 \, m^{-1}$) the dependence $\Delta G(R)$ becomes monotonically increasing (infinitely high nucleation barrier) meaning thermodynamic suppression of nucleation by the very sharp concentration gradients. Thus, according to our model, at the very initial stage of reactive diffusion the nucleation can be suppressed even without diffusive competition, just due to too narrow space region, favorable for transformation.

Independently similar results were published by P.Desre et al in [9,10]. This approach had been applied to description of solid state amorphizing reactions, explaining why do the stable intermetallics appear in diffusion zone only after amorphous layer exceeds some critical thickness.

In spite of similar results, the mentioned models of nucleation in the sharp concentration gradient treated quite different possible mechanisms (nucleation modes). In [8] a *polymorphous mode* has been suggested according to the following picture: Initial diffusion leads to formation and growth of metastable parent solution with sharp concentration profile. When this profile becomes smooth enough to provide sufficient space for compositions favorable for new intermediate phase, this very phase nucleates just by reconstruction of atomic order, without changing immediately the concentration profile (at "frozen" diffusion) - polymorphic transformation. P.Desre [9] suggested the *transversal nucleation mode* bearing in mind the following picture: Each thin slice of the new-formed nucleus, perpendicular to direction of concentration gradient, is considered as a result of decomposition in corresponding thin infinite slice of parent solution, leading, of course, to redistribution of atoms among new and old phases. In this transversal mode, the redistribution proceeds within each slice, independently on others.

In 1996 one more mechanism has been suggested by F.Hodaj [11] - *total mixing (longitudinal) nucleaëtion mode*, when the redistribution of atoms proceeds during nucleation, but only inside the new forming nucleus. Contrary to two previous modes, in this case the concentration gradient assists the nucleation – in expression (1) coefficient $\gamma$ is negative. Effect of shape optimization was discussed in [12]. Interference of different nucleation modes was suggested in [13]

A new possible explanation for sequential phase growth in thin films was proposed in 2004 [14] by modifying the context of the 'nucleation in concentration gradient' approach. Namely, if at least one phase with narrow homogeneity range is already growing, the sharp chemical potential gradient in it strongly influences the nucleation barrier for the next phase to appear. In the expression of Gibbs free energy change, the additional term, due to gradient concentration, appears to be proportional to the fourth power of size instead of the fifth power in previous models (developed for the case of a broad range of parent phase concentration).

As a result, thermodynamic suppression of the new phase nucleation (in addition to kinetic suppression) may be effective as long as the thickness of the 'suppressing' phase remains less than a few tens or even hundreds of nanometers. Thus, the 'gradient term effect' may well lead to the total absence of suppressed phases prior to consumption of the thin film by the 'suppressing' growing phase. Comparison with available experimental data demonstrated [14] that the approach presented was at least reasonable. Special experiments on first phase nucleation in Al-Co couple by 3D atomprobe demonstrated polymorphic nucleation mode as preferable one [15].

Recent discovery of point contact reactions between metals and silicon nanowires demonstrate that the existing theoretical scheme needs further development. First, silicide nucleation proceeds outside the contact zone. Namely, in case of one point contact between silicon nanowire and nickel nanowire or nanodot, the first nuclei of silicide appear near the tip of silicon nanowire, instead of contact place. In case of multiple point contacts of silicon nanowire with metallic nanodots, silicide tends to nucleate between two point contacts with two nanodots [16-18]. Second, the first nucleated phase differs from that in thin film case. For example, in case of point contact with nickel nanowire the first nucleated phase is nickel monosilicide instead of Ni2Si1, typical for thin film couples. Third, all abovementioned features happen if the silicon nanowire is covered by natural amorphous silicon dioxide of 1-2 nm thickness. If by special measures the direct contact is realized of metal with unoxidized silicon nanowire, the nucleation proceeds at the contact and the first nucleated phase is the same as in thin film couple. Fourth, the nucleated silicide used to exibit jerky growth, consisting of waiting period of 2D island nucleation at the epitaxial interface silicide/silicon and fast lateral growth of each new atomic layer. Rigorous theory of this phenomenon is still under construction. Yet, intuitively it seems clear that nucleation at the tip instead of contact place should be caused by interplay of the following factors:

1. The contact place is a narrow channel of nickel penetration via nanometric SiO2 diffusion barrier enveloping the silicon wire. Flux through this channel is small.

2. Nickel atoms diffuse interstitially in silicon, so that large diffusivity prevents the accumulation of nickel in the vicinity of contact place.

3. Nucleation at the spherical tip of nanowire corresponds to lower nucleation barrier than that at the cylindrical surface.

4. Frequently the tip is actually a result of cutting the nanowire, providing the site of heterogeneous nucleation.

All these factors remain if the silicon nanowire has two or more point contacts with Ni, instead of one. Yet, in this case silicide forms and grows from the place somewhere inbetween two contacts.

What additional factor could cause the change of nucleation place? According to standard Gibbs nucleation theory, it could be (A) change of bulk driving force, (B) change of surface energy term due to some heterogeneous sites. Let us analyze shortly both possibilities:

(A) Change of bulk driving force in our case means the change of supersaturation in respect to silicide phase. So, preferential nucleation between contacts could happen if there is a local maximum of concentration in the middle. On the other hand, prior to the first successful nucleation event, the diffusion of nickel should obey common Fick's law, we can not find any reason for local spikes of concentration leading to preferential nucleation. The expected concentration profile at each time moment in, say, right half of the silicon wire, should have the form of non-symmetrical wings with left wing shorter and higher. So, concentration of nickel in the middle is higher than at the tip. Yet, both of them are lower than concentration near the contact place. According to this argumentation, the maximal driving force corresponds to vicinity of the contact place.

(B) Wire surface in the middle is the same as near contact place - so, surface term does not help nucleation in the middle. (Moreover, in the contact place we can expect some defects or stresses helping nucleation, in the middle there is no additional defects)

The just mentioned paradoxal situation shows necessity of looking for kinetic factors, in addition to thermodynamic.

Notice, that nucleation proceeds in nonstationary conditions, in the field of diffusion fluxes with non-zero divergence. **Aim** of this paper is develop a first version of new theory – **Theory of FAN (Flux Assisted Nucleation).** We will demonstrate below that external fluxes may assist nucleation if divergence is negative, and may suppress nucleation if divergence is positive. Qualitatively, it looks almost obvious. Divergence means disbalance of outcoming and incoming fluxes at the surface of some elemental volume divided by the value of this volume.

$$\left.\frac{dn}{dt}\right|^{external} = -div\left(J^{diffus}\right) * \left(n\Omega\right) \tag{2}$$

If divergence is negative, incoming flux is larger than outcoming one. So, in this case the flux divergence should help the growth of even subcritical embryon. So, one may expect that, under other equal conditions, nucleation should happen first in the place with maximal (by absolute value) negative flux divergence, meaning, in case of Fick's law, the maximal positive second spatial derivative of concentration.

## II. Classical nucleation in terms of attachment and detachment frequencies

Let's consider at first a nucleation of silicide spherical nucleus in initially (prior to nucleation) homogeneous supersaturated solution of nickel in silicon, in terms of classical nucleation theory (Gibbs-Folmer-Zeldovich). Dependence of system's Gibbs potential change on the number of atoms in the embryo/nucleus is

$$\Delta G(n) = -n\Delta g + \gamma \cdot 4\pi \left(\frac{3\Omega}{4\pi}\right)^{2/3} n^{2/3}, \tag{3}$$

Where bulk driving force per atom

$$\Delta g = kT \ln \frac{C}{C_{Ni}^{eq}}. \tag{4}$$

Critical size and nucleation barrier, as usual, are found from extremum condition

$$\partial \Delta G(n)/\partial n = 0 = -\Delta g + \gamma \frac{8}{3}\pi \left(\frac{3\Omega}{4\pi}\right)^{2/3} n^{-1/3},$$

$$\partial^2 \Delta G(n)/\partial n^2 = -\gamma \frac{8}{9}\pi \left(\frac{3\Omega}{4\pi}\right)^{2/3} n^{-4/3}, \tag{5}$$

$$n_{cr} = \left(\frac{3\Omega}{4\pi}\right)^2 \left(\frac{8\pi\gamma}{3\Delta g}\right)^3 = \frac{32\pi}{3}\left(\frac{\gamma\Omega}{\Delta g}\right)^3, \tag{6}$$

$$G^* = \gamma \cdot \left(4\pi/3\right)\left(\frac{3\Omega}{4\pi}\right)^{2/3} n_{cr}^{2/3} \tag{7}$$

Overcoming of nucleation barrier is a stochastic process consisting of random attachments and detachments of atoms, $\nu_+, \nu_-$ being the frequencies of these events. In nucleation theory one uses the following combinations of the attachment and detachment frequencies:

$$\overline{\nu} = (\nu_+ + \nu_-)/2, \quad \Delta\nu = \nu_+ - \nu_-.$$

The first combination is actually a diffusivity of clusters in the size space (rate of random walk), the second combination gives a drift of clusters: for subcritical clusters $\Delta v < 0$, for overcritical nucleis $\Delta v > 0$. The flux of clusters in the size space is given by combination of the mentioned diffusion and drift terms:

$$j(n) = \Delta v \cdot f - \overline{v}\frac{\partial f}{\partial n} \tag{8}$$

with f being a number of clusters with size n per unit volume of the system. In equilibrium case this flux is zero, and distribution f is an equilibrium Boltzmann distribution

$$f_{eq}(n) = const \cdot \exp(-\Delta G(n)/kT). \tag{9}$$

Substituting equilibrium distribution into zero flux condition, one gets interrelation between the drift and diffusion terms in size space which is identicakl with Nernst-Einstein relation between mobility and diffusivity in usual space:

$$\Delta v(n) = -\frac{\overline{v}(n)}{kT}\frac{\partial \Delta G}{\partial n}. \tag{10}$$

For overcritical nuclei (far beyond critical size) the diffusive term is no more important, and precipitate evolution is governed by deterministic equation

$$\frac{dn}{dt} = \Delta v(n) \tag{11}$$

On the other hand, from phenomenology we know that

$$\frac{dn}{dt} = \frac{4\pi r^2}{\Omega}\frac{dr}{dt} = \frac{4\pi r^2}{\Omega}\frac{D}{c_1 - c_s}\frac{\Delta c - \alpha/r}{r} \tag{12}$$

With $\alpha = c_{eq}\frac{2\gamma\Omega}{kT}$, $\Delta c = c - c_{eq} = \alpha/r_{cr}, c_s \ll 1$.

Thus, $\dfrac{dn}{dt} \cong \dfrac{4\pi D}{c_1\Omega}(r\Delta c - \alpha) = \dfrac{4\pi D\alpha}{c_1\Omega}\left(\left(\dfrac{n}{n_{cr}}\right)^{1/3} - 1\right)$ (13)

Comparing eqs (12) and (13), and limiting ourselves to the vicinity of critical sizes, $n = n_{cr} + \delta n$, we obtain linearized relation for drift in the vicinity of critical sizes for the case when globally system is uniform (local fluxes appear only after nucleation):

$$\Delta v^{\mathrm{int\,ernal}} \cong \frac{4\pi D\alpha}{3c_1\Omega n_{cr}}\delta n \tag{14}$$

Substituting eq. (11) and eq. (5) into eq. (10), one can find expression for diffusivity in the size space as a function of size:

$$\overline{v}(n) = -\frac{\Delta v(n)}{\frac{\partial \Delta G}{\partial n}}kT = \frac{\frac{4\pi D\alpha}{3c_1\Omega n}\delta n}{(-\Delta G'')\delta n} = \frac{\frac{4\pi D}{3c_1\Omega n}\frac{2\gamma\Omega}{kT}c_{eq}}{\gamma\frac{8}{9}\pi r_0^2 n^{-4/3}} = 3\frac{c_{eq}D}{c_1 r_0^2}n^{1/3} \tag{15}$$

(Here $r_0 \equiv \left(\dfrac{3\Omega}{4\pi}\right)^{1/3}$)

### III. Account of external flux divergence

If the arising nucleus is situated in the field of external fluxes with nonzero divergence, it changes the drift term in the size space:

$$\Delta v^{total} \cong \Delta v^{\mathrm{int\,ernal}} + \left.\frac{dn}{dt}\right|^{external} \tag{16}$$

Here the second term is a result of disbalance of global diffusion fluxes (additional to local fluxes arising with nucleation):

$$\frac{dn}{dt}\bigg|^{external} = -div\left(J^{diffus}\right)*\left(n\Omega\right) \tag{17}$$

Actually, the superposition law (16) is an assumption since the presence of just appeared nucleus may distort the flux distribution. The same assumption has been made in the elementary Huntigton-Fiks theory of electron wind, when one neglects the distortion of electric current density due to scattering of electrons at the defect. Like in electromigration story, one may expect that the distortion is weak if nucleus is close to critical one.

Substituting internal shift velocity in the size space from eq. (14) and divergence of diffusion fluxes in usual space from Fick's law, one obtains the resulting drift velocity in the size space not far from critical size:

$$\Delta v^{total} \cong \frac{4\pi D\alpha}{3c_1\Omega n_{cr}}\delta n + \frac{D}{\Omega}\nabla^2 c \cdot n\Omega \cong \frac{4\pi D\alpha}{3c_1\Omega n_{cr}}\delta n + D\frac{\partial^2 c}{\partial z^2} \cdot n \tag{18}$$

From kinetic point of view ability of precipitate to grow or to shrink (to be overcritical or subcritical) is determined by the sign of drift velocity. In case of uniform system thermodynamic and kinetic approaches give the same result, as follows from eq. (10) – zero of drift corresponds to zero of Gibbs potential derivative. In our case, when the system has a global distribution of fluxes, thermodynamic and kinetic approaches give different results: thermodynamically unstable embryon may survive and grow if the second term in eq (16) is positive and larger than the absolute value of negative first term.

If the second term is positive and small (so that $n_{cr}^{kinetic}$ is not so far from $n_{cr}^{ther\,mod}$), it means that the true (kinetic) critical size (for which $\Delta \tilde{v} = 0$) should shift "to the left":

$$\delta n = -\frac{3c_1\Omega n_{cr}^2}{4\pi\alpha}\frac{\partial^2 c}{\partial z^2} \tag{19}$$

Corresponding nucleation barrier should decrease respectively. Before calculating a new nucleation barrier, it seems reasonable to introduce the **effective Gibbs potential** change taking into account the additional "external" shift term.

Indeed, in the absence of external flux divergence in usual space the equilibrium distribution of clusters in size space is given by eq. (9) and it corresponds to zero flux in the size space. If the flux divergence in usual space is not zero, then a condition of zero flux in size space leads to another size distribution $f_0(n) \neq f_{eq}(n)$, so that

$$\frac{\Delta v^{total}}{v} = \frac{\partial \ln f_0}{\partial n}, \tag{20a}$$

$$\frac{\Delta v^{int\,ernal}}{v} = \frac{\partial \ln f_{eq}}{\partial n} \tag{20b}$$

Combining eqs(20a,b) one gets

$$\frac{\partial \ln\left(f_0 / f_{eq}\right)}{\partial n} = \frac{\Delta v^{total} - \Delta v^{int\,ernal}}{v} = \frac{\Delta v^{external}}{v} = \frac{D\nabla^2 c \cdot n}{v(n)}. \tag{21}$$

Taking into account that the external drift term is proportional to the size n of cluster, one can conclude that external influence for n tending to zero, should be negligible, so that $\lim_{n\to 0}\left(f_0 / f_{eq}\right) = 1, \lim_{n\to 0}\ln\left(f_0 / f_{eq}\right) = 0$.

Therefore we can integrate eq. (21) from zero to n with zero boundary condition:

$$\ln\left(f_0 / f_{eq}\right) = D\nabla^2 c \cdot \int_0^n \frac{n'}{v(n')}dn'. \tag{22}$$

Now we'll use an explicit size dependence (15) of diffusivity in the size space for taking integral in eq. (22):

$$f_0(n) = f_{eq}(n)\exp\left( DV^2c \cdot \int_0^n \frac{n'}{3\frac{c_{eq}D}{c_1r_0^2}n'^{1/3}}dn' \right) = f_{eq}(n)\exp\left( \frac{c_1r_0^2}{5}V^2\left(\frac{c}{c_{eq}}\right)n^{5/3} \right) \qquad (23)$$

Taking into account eq. (10), we can represent zero-flux distribution as

$$f_0(n) = const \cdot \exp\left( -\Delta G^{eff}(n)/kT \right) \qquad (24)$$

with effective Gibbs potential change

$$\Delta G^{eff}(n) = \Delta G(n) - kT\frac{c_1r_0^2}{5}V^2\left(\frac{c}{c_{eq}}\right)n^{5/3} =$$

$$= -n\Delta g + \gamma \cdot 4\pi r_0^2 n^{2/3} - kT\frac{c_1r_0^2}{5}V^2\left(\frac{c}{c_{eq}}\right)n^{5/3} \qquad (25)$$

It is interesting to note that expression (25) is rather similar to modified Gibbs energy for thermodynamics of nucleation in the sharp concentration gradient [8-13]. It also contains linear size in the powers of 3, 2 and 5. Yet, instead of squared gradient in thermodynamics, now we obtained laplacian (second derivatives) of the ratio $\frac{c}{c_{eq}}$.

Obviously, maximum of effective Gibbs potential change corresponds to zero drift (with account of external flux divergence) – unstable equilibrium, and should be treated as the effective nucleation barrier.

Predicting the place of most probable nucleation, in rough approximation, may be reduced to finding the place of lowest effective barrier. For this, first of all, one should solve the boundary diffusion problem with flux balance boundary conditions at the point contacts. It gives us dependence c(t,z) along the nanowire. We know the concentration dependence of the bulk driving force in supersaturated (in respect to silicide) solution of Ni in silicon. At each t (after reaching the equilibrium, with silicide, concentration) for each z one should find the effective nucleation barrier from eq. (20). The place z with minimal effective barrier is a place of most probable nucleation. Yet, the barriers change in the process of diffusion. So, first, we should modify standard Zeldovich theory for the case of external flux divergence, Second, we should modify Zeldovich theory taking into account nonstationarity of the process.

### IV. Modification of Zeldovich theory for the case of external flux divergence

Modification is almost trivial and gives the following expression for steady state flux of viable nuclei in the size space:

$$j = \sqrt{\frac{\partial \Delta v^{total}/\partial n}{2\pi\overline{v}}}\overline{v}f_0(n_{cr}) \qquad (26)$$

where $n_{cr}$ is found from extremum condition of dependence (25).

Explicitly,

$$j = \sqrt{\frac{1}{2\pi}\left(\frac{4\pi D\alpha}{3c_1\Omega n_{cr}} + DV^2c\right)\left(3\frac{c_{eq}D}{c_1r_0^2}n_{cr}^{1/3}\right)}f_0(n_{cr}) \qquad (27)$$

## V. Case of interface-controlled nucleation

Evidently, in this case, instead of being proportional to the linear size of nucleus in eq. (15), the mean attachment/detachment frequency should be proportional to the interface area, that is, to the squared linear size, or $n^{2/3}$. Then the integral $\int_0^n \frac{n'}{V(n')} dn' \propto \int_0^n \frac{n'}{n'^{2/3}} dn' \propto n^{4/3}$.

Thus the additional term in the effective nucleation barrier will be proportional to the fourth power of size.

This case is formally similar to nucleation in concentration gradient under limited mutual solubility, investigated by us in [14]. Here we do not discuss the problems of nucleus shape optimization which can modify the results.

## VI. Conclusions

1. Discovery of point contact reactions between silicon nanowire and metallic nanowire or nanodots proves that the nucleation theory for open nanosystems should be substantially developed. Development suggested in this paper may well be not enough for explanation of point contact reactions but it seems to have a general interest for nucleation theory.

2. Drift of the nucleus in size space is determined by superposition of two factors – (1) by common thermodynamic size dependence of the Gibbs free energy, (2) by the divergence of external flux of atoms necessary for nucleus growth.

3. The mentioned superposition can be formally taken into account by introducing the "effective Gibbs free energy barrier"

$$\Delta G^{eff}(n) = \Delta G(n) - kTD\nabla^2 c \cdot \int_0^n \frac{n'}{V(n')} dn' = \Delta G(n) + kTdiv(\Omega J) \cdot \int_0^n \frac{n'}{V(n')} dn'.$$

4. In case of diffusion-controlled nucleation the explicit form of effective nucleation barrier includes a third term with 5-th power of size:

$$\Delta G^{eff}(n) = -n\Delta g + \gamma \cdot 4\pi r_0^2 n^{2/3} - kT \frac{c_1 r_0^2}{5} \nabla^2 \left(\frac{c}{c_{eq}}\right) n^{5/3}$$

5. In case of interface-controlled nucleation the explicit form of effective nucleation barrier includes a third term with 4-th power of size:

$$\Delta G^{eff}(n) - \Delta G(n) \propto n^{4/3}$$

6. In principle, the nucleation itself changes the local flux divergence. This fact should modify the just suggested theory and will be discussed elsewhere. Naïve account of this fact was made by Gurov and Gusak in 1982 in the frame of phase competition theory [1(chapter 3), 19].

### References

1. Gusak A.M., Zaporozhets T.V., Lyashenko Yu. O., Kornienko S.V., M.O. Pasichnyy, A.S. Shirinyan. Diffusion-controlled Solid State Reactions: in Alloys, Thin-Films, and Nanosystems. – Berlin: Wiley-VCH, 2010 – 476 p.

2. Tu K.N., Gusak A.M., Li M. Physics and materials challenges for lead-free solders // Journal of Applied Physics. – 2003. – Vol. 93. – № 3. – P. 1335-1353.

3. Gusak A.M., Tu K.N. Kinetic theory of flux-driven ripening // Physical Review B. – 2002. – Vol.66. – P. 115403-16.

4. Tu K.N., Gusak A.M., Sobchenko I. Linear rate of grain growth in thin films during deposition // Physical Review B. – 2003. – Vol. 67. – P. 245408-1-5.

5. Lucenko Grig., Gusak A. A model of the growth of intermediate phase islands in multilayers // Microelectronic Engineering. – 2003. – Vol.70. – № 2-4ю – P.529-532.

6. Pasichny M.O., Gusak A.M. Modeling of Phase Competition and Diffusion Zone Morphology at Initial Stage of Reaction Diffusion. // Defect and Diffusion Forum. – 2005. – Vol. 237-240. – P. 1193-1198.

7. Pasichnyy M.O., Gusak A.M. Kinetics of Lateral Growth of Intermediate Phase Islands at the Initial Stage of Reactive Diffusion // Metallofizika i Noveishie Tekhnologii. –2005. – Vol. 27. – P. 1001-1016.

8. Gusak A.M. Peculiarities of nucleation in the concentration gradient of binary system // Ukrainian Physical Journal. – 1990. – Vol. 35. – № 5. –P. 725-729.

9. Desre P.J., Yavari A.P. Suppression of crystal nucleation in amorphous layers with sharp concentration gradients // Phys.Rev.Lett. – 1990. – Vol. 64. – P. 1553-1536.

10. Desre P.J. Effect of sharp concentration gradients on the stability of a two-component amorphous layer obtained by solid state reaction // Acta Metallurgica. – 1991. – Vol. 39. – № 10. – P.2309-2315.

11. Hodaj F., Desre P. Effect of a sharp gradient of concentration on nucleation of intermetallics at interfaces between polycrystalline layers // Acta Materialia. – 1996. – Vol. 44. – № 11. – P. 4485-4490.

12. Hodaj F., Gusak A.M. and Desre P.J., Effect of sharp concentration gradients on the nucleation of intermetallics in disordered solids: Influence of the embryo shape // Phil.Mag. – 1998. – Vol. A 77. – № 6. –P.1471-1479.

13. Gusak A. M. ,Hodaj F., Bogatyrev A. O. Kinetics of nucleation in the concentration gradient // Journal of Physics. Condensed Matter. – 2001. –Vol. 13. – № 12. – P. 2767.

14. Hodaj F., Gusak A.M. Suppression of intermediate phase nucleation in binary couples with metastable solubility // Acta Materialia. – 2004. – Vol. 52. –P. 4305-4315.

15. Pasichnyy M.O., Schmitz G., Gusak A.M., Vovk V. Application of the critical concentration gradient to the nucleation of the first product phase in Co/Al thin films // Physical Review B. – 2005. – Vol. 72. – P. 014118.

16. Lu K.-C., Tu K. N., Wu W. W., Chen L. J. ,Yoo B.-Y., Myung N. V. // Appl. Phys. Lett. – 2007. – Vol. 90. – P. 253111.

17. Lin Y.-C., Lu K.-C., Wu W.-W., Bai J., Chen L. J. , Tu K. N., Huang Yu // Nanoletters. – 2008. – Vol. 8. – № 3. – P. 913.

18. Chou Y.-C., Wu W.-W., Chen L. J., Tu K.-N. // Nanoletters. – 2008. – Vol. 9. – № 6. – P. 2337.

19. Гусак А. М., Гуров К. П. Кинетика фазообразования в диффузионной зоне при взаимной диффузии // Физика металлов и металловедение. – 1982. – Т.53. – № 5. – С. 842 – 847.

**Анотація.** *F.Hodaj (Ф. Одаж), А.М. Гусак (A.M.Gusak), В.В. Straumal (Б.Б.Страумал). Нуклеації у відкритих наносистемах – новітня історія та перспективи. Твердофазні реакції починаються з зародкоутворення фаз-продуктів реакції в нанорозмірній області. На зародкоутворення в відкритих наносистемах впливає не лише залежність від розміру зародка потенціалу Гіббса системи, але також дивергенція зовнішніх потоків у місці зародкоутворення. Цей вплив може бути виражений як додатковий член у ефективному нуклеаційному бар'єрі, пропорційний п'ятій або четвертій степені лінійного розміру, в залежності від того, чим контролюється зародкоутворення (дифузією чи граничною кінетикою).*

**Ключові слова:** зародкоутворення, дифузія, дивергенція потоку, відкрита наносистема.

**Аннотация.***F.Hodaj (Ф. Одаж), А.М. Гусак (A.M.Gusak), В.В. Straumal (Б.Б.Страумал). Нуклеации в открытых наносистемах – новейшая история и перспективы. Твердофазные реакции начинаются с зародышеобразования фаз-продуктов реакции в наноразмерной области. На зародышеобразование в открытых наносистемах влияет не только зависимость от размера зародка потенциала Гиббса системы, но также дивергенция внешних потоков в месте зародышеобразования. Это влияние может быть выражено как дополнительный член в эффективном нуклеационном барьере, пропорциональный пятой или четвертой степени линейного размера, в зависимости от того, чем контролируется зародышеобразование (диффузией или предельной кинетикой).*

**Ключевые слова:** зародышеобразование, диффузия, дивергенция потока, открытая наносистема.

УДК 539.219.3                                                    PACS 66.30.-h

**С.В. Корнієнко**

# ВПЛИВ ДЖЕРЕЛ ТА СТОКІВ ВАКАНСІЙ У МАТЕРИНСЬКІЙ ФАЗІ НА КІНЕТИКУ РЕАКЦІЙНОЇ ДИФУЗІЇ У БІНАРНІЙ СИСТЕМІ

*Розглянуто та проаналізовано вплив джерел і стоків вакансій в об'ємі материнської фази на кінетику реакційної дифузії у бінарній системі за наявності нерівноважних вакансій. Показано, що у дифузійній системі ріст товщини фази відбувається з більшою швидкістю, коли джерела та стоки вакансій діють не лише на міжфазних границях, але і в об'ємі однієї з материнських фаз.*

**Ключові слова:** реакційна дифузія, нерівноважні вакансії, джерела/стоки вакансій, бінарна система.

## 1. Вступ

Ріст проміжної фази при реакційній дифузії, як свідчать численні експерименти, у більшості випадків відбувається за параболічним законом ($\Delta x \sim \sqrt{t}$) [1-3]. Але нерідко початкова стадія цього процесу проходить за лінійним законом ($\Delta x \sim t$)[4-8]. Наявність лінійної стадії зазвичай пояснюють реакцією на міжфазній границі [9-11]. З іншого боку, у роботах А.М. Гусака було показано, що лінійна стадія росту може бути обумовлена скінченною швидкістю релаксації нерівноважних вакансій біля цих границь [12, 13]. Така ситуація може виникнути внаслідок значного вакансійного потоку, обумовленого суттєвою різницею парціальних коефіцієнтів дифузії компонентів. Експериментальним підтвердженням цієї моделі може слугувати виникнення і ріст пор на міжфазній границі у фазі, що росте. Проте, при реакційній дифузії пороутворення спостерігають також і за межами фази, що росте, а це вже може свідчити про те, що стоки/джерела вакансій діють також і в об'ємі материнських фаз дифузійної пари [14, 15]. Отже, **метою** даної роботи є дослідження впливу дії джерел та стоків вакансій в об'ємі материнської фази на кінетику реакційної дифузії.

## 2. Опис моделі

В якості модельної системи розглянемо бінарну дифузійну пару, що складається з чистих, слабо розчинних (або взаємно нерозчинних) компонентів А і В, які згідно з діаграмою станів (для температури, при якій здійснюється дифузійний процес) утворюють одну проміжну фазу – α. При ізотермічному відпалюванні у такій дифузійній парі на границі А-В росте проміжна фаза α. Нехай компонент А рухливіший за компонент В ($D_A > D_B$), тоді результуючий потік речовини буде спрямований по осі ОХ, а результуючий потік вакансій – у протилежну сторону. Розглянемо цей процес за наявності у системі нерівноважних вакансій як у фазі α, так і у фазі А (рис.1).