

## Flux Driven Nucleation at Interfaces During Reactive Diffusion – New Solution of an old Problem

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**Abstract.** The problem of phase competition during reactive diffusion is revisited. Nucleation of an intermediate phase at an interface under external fluxes in the neighboring phases is considered in the frame of kinetic Fokker-Planck approach. Effective nucleation barrier depending on the divergence of external fluxes is introduced. New suppression/growth criteria are obtained.

### I. Introduction

Understanding of all stages of solid state reactions for various intervals of annealing times, temperatures and external forces is extremely important in modern technologies (micro- and nano-electronics, photonics, high-temperature superconductivity etc.) [1-4]. Real understanding of chemical reaction is possible only from the physical point of view, when formation of intermetallic compounds (IMCs) is treated as the first-order phase transition proceeding in a sharply inhomogeneous open system (contact zone) under gradients of thermodynamic driving forces and under continuing incoming and outgoing fluxes of matter. Since traditional first-order phase transformations include three main stages (nucleation, simultaneous growth of precipitates and coarsening), one might also expect three corresponding stages of solid-state reaction (SSR): flux-driven nucleation in case of concentration gradient, flux-driven individual growth and flux-driven coarsening. Theories of flux-driven coarsening (Flux-Driven Ripening and Flux-Driven Grain Growth) had been suggested by one of present authors (AMG) together with King Ning Tu [5-6]. Models of “flux-driven individual growth” (DIGM-like growth of IMC precipitates due to lateral diffusion along moving interphase interfaces) were proposed in [8-9] and are not discussed here. The history of nucleation models is more complicated [9-17]. To predict a phase spectrum in reactive diffusion and its time evolution, we need ratios of nucleation periods for different phases. This task, so far, was solved only partially [4]. Here we will distinguish thermodynamics and kinetics of nucleation in the contact zone. Modification of **nucleation thermodynamics** (under full solubility in a metastable solid solution) was discussed in [10-15]. The main idea was: if, prior to an intermediate phase formation, a narrow layer of a metastable solid solution or amorphous alloy had been formed at the base of initial interface, a sharp concentration gradient inside this layer provides decrease of the total bulk driving force of nucleation, and corresponding increase of nucleation barrier. The main result was a 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), a new term proportional to the 5-th power of size and the squared concentration gradient:

$$\Delta G(R) = \alpha R^2 - \beta R^3 + \gamma (\nabla C)^2 R^5, \quad (1)$$

$\gamma$  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 very sharp concentration gradients. Thus, according to this model, at the very initial stage of reactive diffusion the nucleation can be suppressed even without diffusive competition, just due to a too narrow space region favorable for transformation. Later this approach was modified for a case when the solubility even

in a metastable phase is limited, and an intermediate phase nucleates at an interface of two preexisting phases [14]. In this case the “gradient” term appears to be proportional to the fourth power of size instead of the fifth power. “Thermodynamic suppression” of the new phase nucleation may be effective as long as the thickness of a ‘suppressing’ phase remains less than a few tens or even hundreds of nanometers. Special experiments on first phase nucleation in Al-Co couple by 3D atomprobe demonstrated polymorphic nucleation mode as preferable one [15].

Peculiarities of **nucleation kinetics** at interfaces of reacting materials is studied much less [16-17, 13]. In the very first naïve model [16] we assumed that at the initial period successive layers of critical nuclei pertaining to all phases allowed by phase diagram, appear as a result of heterophase fluctuations. Nuclei arise in the chemical potential gradient field, so that finite differences  $\Delta\mu$  over the thickness of each layer exist from the very beginning. Chemical potential gradients inside the nuclei cause diffusion fluxes through them. Owing to the differences in diffusivities and sizes, the flux densities vary for different phases. The jumps of diffusion fluxes at interfaces make the boundaries move. Thus, nuclei layers come into diffusive interaction. The result of the interaction depends on diffusion parameters of all phases. Those phases, for which  $d\Delta X/dt > 0$ , start growing and reach the observed phase layers. The nuclei of those phases, for which  $d\Delta X/dt < 0$ , shrink, become subcritical and are consumed by their neighbors. The new ones arise at their place, and they suffer the same fate: they become exhausted by fast-growing neighbouring phases (“vampires”). The growth of such phases is suppressed, they exist in the contact zone only “virtually”, in form of nuclei that appear and dissolve and decay straight away. This explains the disagreement between the phase composition of the zone and a phase diagram. Yet, the phase suppression lasts for a finite period of time. When growing phases reach certain thickness and the fluxes through them are reduced, the value of  $(d\Delta X/dt)_{cr}$  for the previously suppressed phase gets positive, and it starts growing as well. Such approach was indeed naïve - it was built in the frame of oversimplified picture: any nucleus was excluded just after shrinking below critical size, and appeared as a miracle from nowhere at once with critical size. Now we present the more rigorous approach.

## II. Idea of Flux Driven Nucleation (FDN)

External fluxes may assist nucleation if their divergence is negative, and may suppress nucleation if the divergence is positive. 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 combinations of the attachment and detachment frequencies:  $\bar{\nu} = (\nu_+ + \nu_-)/2$ ,  $\Delta\nu = \nu_+ - \nu_-$ . The first combination is actually a diffusivity of clusters in the size space (rate of random walk), and the second combination gives a drift: for subcritical clusters  $\Delta\nu < 0$ , and for overcritical  $\Delta\nu > 0$ . The flux of clusters in the size space is given by combination of the diffusion and drift terms:

$$j(n) = \Delta\nu \cdot f - \bar{\nu} \cdot \partial f / \partial n \quad (a), \quad f_{eq}(n) = const \cdot \exp(-\Delta G(n)/kT), \quad (b) \quad (2a, b)$$

with  $f$  being a number of clusters the size of  $n$  per a unit volume of a system. In equilibrium case this flux is zero, and distribution  $f$  is an equilibrium Boltzmann distribution. Putting flux in eq.(2a) to zero, one gets an interrelation, identical to Nernst-Einstein relation between mobility and diffusivity in usual space:  $\Delta\nu(n) = -\bar{\nu}(n)/kT \cdot (\partial\Delta G/\partial n)$ . For overcritical nuclei (far beyond critical size) the diffusive term is no more important, and precipitate evolution is governed by deterministic equation  $dn/dt = \Delta\nu(n)$ . If nucleation proceeds in the field of external fluxes with nonzero divergence, the drift term in the size space is changed:

$$\Delta\nu^{total} \cong \Delta\nu^{internal} + (dn/dt)^{external}. \quad (3)$$

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. (6) 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  $f_0(n) \neq f_{eq}(n)$ ,

$$\frac{\Delta v^{total}}{\bar{v}} = \frac{\partial \ln f_0}{\partial n}, \quad \frac{\Delta v^{internal}}{\bar{v}} = \frac{\partial \ln f_{eq}}{\partial n}, \quad \frac{\partial \ln(f_0 / f_{eq})}{\partial n} = \frac{\Delta v^{external}}{\bar{v}} = \frac{(dn/dt)^{external}}{\bar{v}} \quad (4)$$

Boundary conditions:  $\lim_{n \rightarrow 0} (f_0 / f_{eq}) = 1, \lim_{n \rightarrow 0} \ln(f_0 / f_{eq}) = 0$ . Integration gives:

$$\ln(f_0 / f_{eq}) = \int_0^n \frac{\Delta v^{external}(n')}{\bar{v}(n')} dn', \quad f_0(n) = f_{eq}(n) \exp\left(\int_0^n \frac{\Delta v^{external}(n')}{\bar{v}(n')} dn'\right) \quad (5)$$

Thus, we can represent zero-flux distribution via effective Gibbs potential change:

$$f_0(n) = const \cdot \exp(-\Delta G^{eff}(n)/kT), \quad \Delta G^{eff}(n) = \Delta G(n) - kT \int_0^n \frac{\Delta v^{external}(n')}{\bar{v}(n')} dn' \quad (6)$$

The maximum of effective Gibbs potential change corresponds to a zero – unstable equilibrium, and should be treated as the effective nucleation barrier.

We can modify Zeldovich theory for the case of external flux divergence. Modification gives the following expression for a steady state flux of viable nuclei in the size space:

$$j = \sqrt{\frac{1}{2\pi} \frac{\partial(\Delta v^{total} / \bar{v})}{\partial n}} \bar{v} f_0(n_{cr}), \quad \text{where } n_{cr} \text{ is found from extremum of dependence (6).}$$

### III. Growth of single intermediate phase at initial A/B interface - diffusion controlled and interface controlled regimes

The growth rate of the compound layer of thickness  $\Delta X_i$  with almost stoichiometric composition  $c_i$  within a narrow interval of  $\Delta c_i$  ( $c_i$  - atomic fraction of component B) growing between practically insoluble components A and B [18, 1] is equal to  $\frac{d\Delta X_i}{dt} = \frac{1}{c_i(1-c_i)} \frac{D_i \Delta c_i}{\Delta X_i + \lambda_i}$ . Here characteris-

tic length  $\lambda_i$  accounts for possible interface barriers. The product  $D_i \Delta c_i = \int_{c_{iL}}^{c_{iR}} \tilde{D} dc$  (Wagner diffusivi-

ty) has “chemical interpretation”. Here  $\tilde{D} = (cD_A^* + (1-c)D_B^*) \frac{c(1-c)}{kT} \frac{\partial^2 g}{\partial c^2}$  is Darken interdiffusivity,  $g$  – Gibbs free energy per atom. Tracer diffusivities and  $g$  vary to a little extent inside the phase but the first derivative  $\partial g / \partial c$  as a rule, changes drastically, so that the  $\partial^2 g / \partial c^2$  is typically large.

$$\int_{c_L}^{c_R} \tilde{D}(c) dc = \overline{D_i^*} \frac{c_i(1-c_i)}{kT} \left( \frac{\partial g}{\partial c} \Big|_{i,B} - \frac{\partial g}{\partial c} \Big|_{i,A} \right) \cong \overline{D_i^*} \frac{c_i(1-c_i)}{kT} \left( \frac{g_B - g_i}{1-c_i} - \frac{g_i - g_A}{c_i - 0} \right) = \overline{D_i^*} \frac{\Delta g_i}{kT} \quad (7)$$

Here  $\overline{D_i^*}$  is tracer diffusion coefficient averaged over the phase:  $\overline{D_i^*} \cong c_i \overline{D_A^*} + (1-c_i) \overline{D_B^*}$ , and  $\Delta g_i = \Delta g_i(A+B \rightarrow i)$  is a driving force of i-phase formation (from A and B). Thus, the growth rate for thickness can be written in form of some effective mobility times driving force:

$$\frac{d\Delta X_i}{dt} = \frac{1}{c_i(1-c_i)} \frac{\overline{D}_i^*}{\Delta X_i + \lambda_i} \frac{\Delta g_i(A+B \rightarrow i)}{kT}. \quad (8)$$

We will represent the last equation in the form suitable for nucleation theory. Let  $S_i$  be an area of interfaces i/A and i/B,  $\Omega$  – atomic volume in the IMC-phase, so that  $n = (S_i/\Omega)\Delta X_i$  is a number of atoms of IMC. On the other hand, for far overcritical volumes of IMC (when one can neglect surface energy input),  $\Delta g_i(A+B \rightarrow i) = -\partial G/\partial n$ . Then the rate of IMC phase growth is

$$\frac{dn}{dt} = \left( \frac{\overline{D}_i^*/\Omega}{c_i(1-c_i)} \frac{S_i}{\Delta X_i + \lambda_i} \right) \left( -\frac{1}{kT} \frac{\partial G}{\partial n} \right) = \bar{v}_i \cdot \left( -\frac{1}{kT} \frac{\partial G}{\partial n} \right) \quad (9)$$

The coefficient  $\bar{v}_i \equiv \left( \frac{\overline{D}_i^*/\Omega}{c_i(1-c_i)} \frac{S_i}{\Delta X_i + \lambda_i} \right)$  has dimension of frequency, and it can be well used as an average attachment/detachment frequency in Fokker-Planck approach.

#### IV. Nucleation of single IMC at an interface of immiscible components

Now consider the initial stage of diffusion controlled IMC formation – its nucleation at the interface A/B (sometimes it is not true, [19]). In the case when solubilities of A in B and of B in A can be neglected, only interdiffusion inside a new born nucleus determines the rate of its growth or elimination. We take a nucleus to be disc-like. After optimization of the shape [20], one gets

$$-\frac{\partial \Delta G}{\partial n} = \Delta g_i - \frac{\partial W^{surf}(n, \varphi^{opt})}{\partial n} = \Delta g_i - 2(\pi \Delta \gamma \gamma_i^2 \Omega^2)^{1/3} n^{-1/3}, \quad (10)$$

where  $\varphi_{opt} = \frac{\Delta \gamma}{\gamma_i}$ ,  $\Delta \gamma \equiv \gamma_{\alpha i} + \gamma_{\beta i} - \gamma_{\alpha \beta}$ ,  $\gamma_i \equiv \frac{c_\beta - c_i}{c_\beta - c_\alpha} \gamma_{\alpha i} + \frac{c_i - c_\alpha}{c_\beta - c_\alpha} \gamma_{\beta i}$ .

$$\Delta v = \left( \frac{\overline{D}_i^*/\Omega}{c_i(1-c_i)} \frac{S_i}{\Delta X_i + \lambda_i} \right) \left( -\frac{1}{kT} \frac{\partial G}{\partial n} \right) = \bar{v}_i \cdot \left( -\frac{1}{kT} \frac{\partial G}{\partial n} \right) = \bar{v}_i \cdot \left( \frac{\Delta g_i}{kT} - \frac{2(\pi \Delta \gamma \gamma_i^2 \Omega^2)^{1/3}}{kT n^{1/3}} \right). \quad (11)$$

Critical size is found from zero condition for drift or for a derivative of Gibbs free energy:

$$n_{cr}^{1/3} = \frac{2(\pi \Delta \gamma \gamma_i^2 \Omega^2)^{1/3}}{\Delta g_i}. \text{ In diffusion-controlled nucleation } \lambda_i = 0.$$

#### V. Nucleation of single IMC at an interface in competition with diffusion in neighboring solid solutions.

Formation of marginal solid solutions competes with an intermediate phase [4] and decreases the phase growth rate. With account of eq. (10) and flux balance at the moving interfaces one has:

$$\frac{d\Delta X_i}{dt} = \left( \frac{\overline{D}_i^*}{c_i(1-c_i)} \frac{1}{\Delta X_i} \right) \cdot \left( \frac{\Delta g_i}{kT} - \frac{2(\pi \Delta \gamma \gamma_i^2 \Omega^2)^{1/3}}{kT n^{1/3}} \right) - \frac{1}{1-c_i} \sqrt{\frac{D_\beta}{\pi t}} c_{A\beta}^{eq} - \frac{1}{c_i} \sqrt{\frac{D_\alpha}{\pi t}} c_{B\alpha}^{eq}. \quad (12)$$

Thus, in our case an additional drift in size space due to flux divergence at interfaces is

$$\Delta v^{ext} = \frac{\pi R_{opt}^2}{\Omega} \left( -\frac{1}{1-c_i} \sqrt{\frac{D_\beta}{\pi t}} c_{A\beta}^{eq} - \frac{1}{c_i} \sqrt{\frac{D_\alpha}{\pi t}} c_{B\alpha}^{eq} \right). \quad (13)$$

Thus, the effective Gibbs free energy barrier is (with an account of eqs. (6, 11, 13)):

$$\begin{aligned} \Delta G^{eff}(n) &= -n\Delta g + \tilde{\gamma} \cdot s_0 n^{2/3} + \frac{3kT}{4\pi^{5/6}} \left( \frac{\Delta\gamma}{\gamma_i} \right)^{2/3} \frac{\Omega^{1/3} \left( \sqrt{D_\beta/t} c_{A\beta}^{eq} + \sqrt{D_\alpha/t} (1-c_i) c_{B\alpha}^{eq} \right)}{\bar{D}_i^*} n^{4/3} = \\ &= -a_3 x^3 + a_2 x^2 + a_4 x^4, \quad x \equiv n^{1/3} \end{aligned} \quad (14)$$

By equalizing to zero simultaneously the first and the second derivative, we find a condition of full nucleation suppression – when the effective Gibbs free energy is a monotonous function of size:  $x^* = 4a_2 / (3a_3)$ ,  $a_4^* = 9a_3^2 / (32a_2)$ . The suppression is full at  $a_4 > a_4^*$ . In our case it means:

$$t \gg \left( \tilde{\gamma} \Omega kT \left( \sqrt{D_\beta} c_{A\beta}^{eq} + \sqrt{D_\alpha} (1-c_i) c_{B\alpha}^{eq} \right) / \left( \bar{D}_i^* (\Delta g_i)^2 \right) \right)^2 \quad (15)$$

Thus, the first phase for which the suppression by diffusion in solution vanishes has the maximal product of self-diffusivities combination and squared driving force.

## VI. Flux driven nucleation of IMC 2 at the interface 1/B

The driving force of phase 2 formation from 1 and B is lower than directly from A and B (Fig. 1).

$$\int_{c_L}^{c_R} \tilde{D}(c) dc = \frac{\bar{D}_2^* c_2 (1-c_2)}{kT} \left( \frac{\partial g}{\partial c} \Big|_{2,B} - \frac{\partial g}{\partial c} \Big|_{1,2} \right) = \frac{\bar{D}_2^* c_2 (1-c_1)}{(c_2 - c_1)} \frac{\Delta g_i (1+B \rightarrow 2)}{kT}. \quad (16)$$

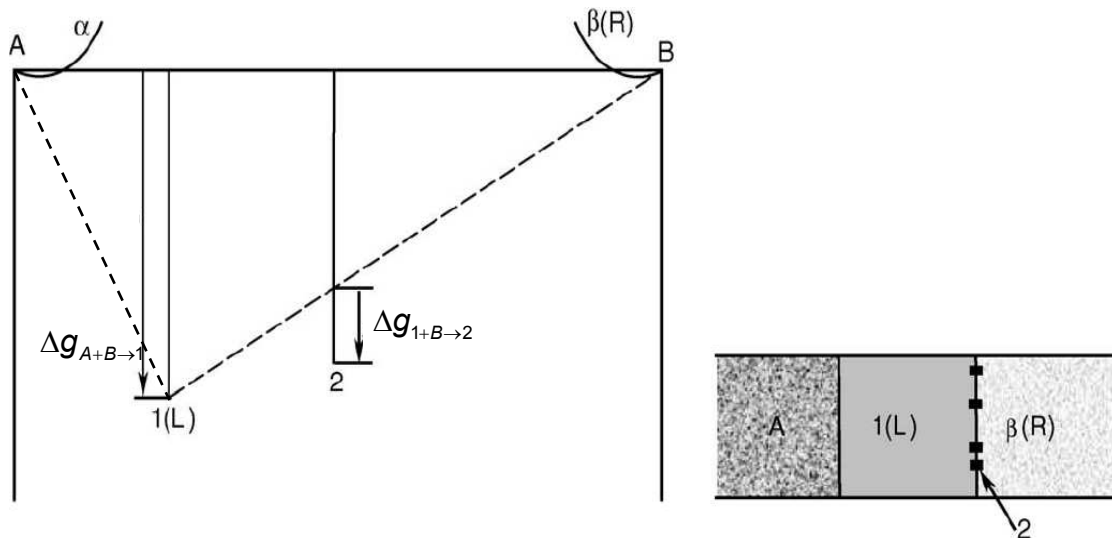


Fig. 1. Nucleation of IMC 2 at the interface 1/B.

For the nucleation of IMC 2 between already growing layer 1 and phase B one gets:

$$\frac{d\Delta x_2}{dt} = \frac{(1-c_1)^2 c_2}{(c_2 - c_1)^2 (1-c_2)} \frac{\bar{D}_2^*}{\Delta x_2} \left( \frac{\Delta g_{1+B \rightarrow 2}}{kT} - \frac{2}{3} \tilde{\gamma} s_0 n_2^{-1/3} \right) - \frac{1}{c_2 - c_1} \frac{D_1 \Delta c_1}{\Delta x_1} \quad (17)$$

As shown in [20], in this case we can construct the following effective Gibbs nucleation barrier:

$$\Delta G^{eff}(n_2) = -\Delta g_{1+B \rightarrow 2} n + \tilde{\gamma} s_0 n^{2/3} + kT \left( \frac{\Omega}{\pi} \right)^{1/3} \frac{D_1 \Delta c_1}{D_2^* \Delta x_1} \frac{3(1-c_2)(c_2-c_1)}{4(1-c_1)^2 c_2} 8\tilde{\gamma} s_0 \left( \frac{\Delta \gamma}{\gamma_i} \right)^{2/3} n^{4/3}. \quad (18)$$

Nucleation is possible if  $\Delta x_1 > \frac{\bar{D}_1^* \Delta g_{A+B \rightarrow 1}}{\bar{D}_2^* (\Delta g_{1+B \rightarrow 2})^2} \left( \frac{\Omega}{\pi} \right)^{1/3} \frac{(1-c_2)(c_2-c_1) 8\tilde{\gamma} s_0 (\Delta \gamma / \gamma_i)^{2/3}}{3(1-c_1)^2 c_2}$ . Eq. (18) gives cross-over thickness about hundreds of nanometers at typical diffusion parameters.

## VII. Summary and acknowledgement

The divergence of external fluxes in the nucleation region leads to an additional positive or negative drift term for nucleus migration in the size space and the corresponding effective nucleation barrier, which is usually time-dependent and may depend on the ratio of diffusion characteristics. In particular, fast growing phases make the effective nucleation barrier for their neighbors higher. We call this Flux Driven Nucleation (FDN) including flux assisted (FAN) as well as flux suppressed nucleation (FSN). The FAN in case of void nucleation is described in [20]. The work was supported by Ukrainian State Fund for Fundamental Research, grant Ф40.7/040.

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