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Flux-driven nucleation at interfaces during reactive diffusion

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Nucleation of intermetallic compounds and of voids at interfaces during reactive diffusion is treated with account of influence of the flux divergence in the nucleation regions of the real space as an additional term for drift in the size space (in Fokker–Planck equation for nucleation). Such approach enables the construction of effective Gibbs nucleation barrier which may (in the broad region of parameters) increase to infinity meaning the full suppression of nucleation, or, by the contrast, decrease assisting the nucleation. The introduced effective nucleation barriers depend on kinetic factors – on the ratio of diffusivities in nucleating and in neighboring phases. Thus, the competition of stable and metastable phases is reconsidered, as well as nucleation of Kirkendall/Frenkel voids at the interfaces.

Keywords: nucleation; diffusion; voids; interfaces; intermetallic compounds; kinetics

1. Introduction

Numerous modern technologies (micro- and nano-electronics, photonics, high-temperature superconductivity etc.) are based on different materials and their combinations obtained by solid state reactions (SSRs). Moreover, solid state reactions often determine the mean time to failure (MTF) of the working schemes. Therefore, investigation of all stages of SSRs in all kinds of times, temperatures and external forces is important [1–4].

Physicists prefer to treat 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 outgoing fluxes of matter. Since common first-order phase transition in initially homogeneous system includes three main stages (nucleation, independent growth of the just born nuclei, and coarsening), one might also expect three corresponding stages of SSR: flux-driven nucleation (FDN) in the concentration gradient, flux-driven individual growth and flux-driven coarsening. Theories of flux-driven coarsening – Flux-Driven Ripening (FDR) and Flux-Driven

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Grain Growth (FDGG) – had been suggested in [5–7]. Models of “flux-driven individual growth” (DIGM-like growth of IMC precipitates due to lateral diffusion along moving interphase interfaces) were proposed in [8–10] and will not be discussed here.

History of nucleation models is more complicated. Typically, the first (but wrong) reaction on the idea of considering nucleation in reactive diffusion is the postulation that nucleation has only negligible impact. Typical critical sizes for most of intermetallic compounds nuclei range from 1 Å to 1 nm. Nucleation barriers for heterogeneous nucleation at interfaces are, typically, low, so that nucleation periods are, typically, short, and formation of the first phase in reactions is typically not nucleation-controlled, with only a few exceptions [11,12]. On the other hand, reactive diffusion in thin film couples demonstrates sequential phase formation, instead of simultaneous growth [1,2,4,11,12]. It means that, contrary to bulk case, in thin film case and in nanosystems some phases are suppressed so that they may have no chance to appear at all. To predict the time-dependent observed phase spectrum of such system, we do not need absolute values of nucleation periods, but instead their ratios. This task appeared to be complicated, and so far was solved only partially. Detailed analysis of nucleation thermodynamics and simplified approach to nucleation kinetics in diffusion zone was made in [13–24] and reviewed in [4].

Main idea of FDN. We will demonstrate below that external fluxes may assist nucleation if their divergence is negative, and may suppress nucleation if divergence is positive. Qualitatively, it looks obvious. Divergence means disbalance of outgoing and incoming fluxes at the surface of elemental volume divided by the size of this volume. Then

$$(dn/dt)^{\text{external}} = -\text{div}(J^{\text{diffus}}) * (V^{\text{nucl}}). \quad (1)$$

If divergence is negative, incoming flux is larger than outgoing one. So, in this case the flux divergence should help the growth of even subcritical embryo. So, one may expect that, under otherwise constant 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.

Classical nucleation in terms of attachment and detachment frequencies. At first, we shortly remind to classical nucleation theory by considering formation of a spherical nucleus of an IMC in initially homogeneous supersaturated solution of B in A. We assume that nature “takes care” about stoichiometry (atomic fraction c_1 of B in IMC remains constant). Dependence of system’s Gibbs potential change on the number of atoms n in the embryo/nucleus is

$$\Delta G(n) = -n\Delta g + \gamma \cdot 4\pi r_0^2 n^{2/3} \quad (2)$$

($r_0 \equiv (3\Omega/(4\pi))^{1/3}$, Ω – atomic volume, γ – the interfacial energy per unit area).

The bulk driving force per atom is

$$\Delta g = kT \ln(C/C_{\text{eq}}). \quad (3)$$

C and C_{eq} are the B atomic fractions in supersaturated solution and at equilibrium with IMC. Critical size and nucleation barrier are found from extremum condition

$$n_{\text{cr}} = \frac{4\pi}{3\Omega} \left(\frac{2\gamma\Omega}{\Delta g} \right)^3, \quad G^* = \frac{4\pi\gamma}{3} \left(\frac{2\gamma\Omega}{\Delta g} \right)^2. \quad (4)$$

Overcoming the nucleation barrier is a stochastic process consisting of random attachments and detachments of atoms, ν_+ , ν_- being the frequencies of these events. Their combinations $\bar{\nu} = (\nu_+ + \nu_-)/2$, $\Delta\nu = \nu_+ - \nu_-$ are often used. The first combination is a diffusivity (rate of random walk) of clusters in the size space, the second combination is a drift velocity of clusters: for subcritical clusters $\Delta\nu < 0$, for overcritical nuclei $\Delta\nu > 0$. The flux of clusters in the size space is given by combination of the diffusion and drift terms:

$$j(n) = \Delta\nu \cdot f(n) - \bar{\nu} \frac{\partial f}{\partial n} \quad (5)$$

with $f(n)$ being the number of clusters (per unit volume) containing n atoms. In equilibrium case this flux is zero, and f is a Boltzmann distribution

$$f_{\text{eq}}(n) = \text{const} \cdot \exp(-\Delta G(n)/kT). \quad (6)$$

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

$$\Delta\nu(n) = -\frac{\bar{\nu}(n)}{kT} \frac{\partial \Delta G}{\partial n}. \quad (7)$$

It is well-known [25] that in the case of diffusion-controlled nucleation in a closed system, the drift term not far from the critical size ($|\delta n| \equiv |n - n_{\text{cr}}| \ll n_{\text{cr}}$) is

$$\Delta\nu^{\text{internal}} \cong \frac{4\pi D\alpha}{c_1\Omega} \left(\left(\frac{n}{n_{\text{cr}}} \right)^{1/3} - 1 \right) \cong \frac{4\pi D\alpha}{3c_1\Omega n_{\text{cr}}} \delta n, \quad (8)$$

and the diffusion term in size space is

$$\bar{\nu}(n) = 3 \frac{c_{\text{eq}} D}{c_1 r_0^2} n^{1/3}. \quad (9)$$

In Equation (8), $\alpha = \frac{2\gamma\Omega}{kT} C_{\text{eq}}$, D is the diffusion coefficient of B in the dilute solution. If nucleation is interface controlled, then $\bar{\nu}(n)$ is proportional to $n^{2/3}$ instead of $n^{1/3}$ [26].

Account of external flux divergence. If nucleation proceeds in the field of external fluxes with nonzero divergence, the drift term in the size space is changed:

$$\Delta\nu^{\text{total}} \cong \Delta\nu^{\text{internal}} + \left. \frac{dn}{dt} \right|_{\text{external}} = \Delta\nu^{\text{internal}} + \Delta\nu^{\text{external}}. \quad (10)$$

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 the case of a closed system, thermodynamic and kinetic approaches give the same result – zero drift corresponds to zero of Gibbs potential derivative. If the system has a global distribution of fluxes, thermodynamic and kinetic approaches give different results [18]: a thermodynamically unstable embryo may survive and grow, if the second term at the right side of Equation (10) is positive and larger than the absolute value of negative first term ($\Delta v^{\text{internal}}$) – Flux-Assisted Nucleation (FAN), nucleation barrier decreased. Vice versa, if second term in Equation (18) is negative then even “thermodynamically viable” nuclei can be suppressed – Flux-Suppressed Nucleation (FSN), nucleation barrier increased. In general, we will call this situation FDN. It seems convenient to introduce an **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 Equation (6) and corresponds to zero flux in the size space. If the flux divergence in usual space is not zero, then the condition of zero flux in size space leads to another distribution $f_0(n) \neq f_{\text{eq}}(n)$,

$$\frac{\Delta v^{\text{total}}}{\bar{v}} = \frac{\partial \ln f_0}{\partial n}, \quad \frac{\Delta v^{\text{internal}}}{\bar{v}} = \frac{\partial \ln f_{\text{eq}}}{\partial n}. \tag{11}$$

Combining Equation (11) one gets

$$\frac{\partial \ln(f_0/f_{\text{eq}})}{\partial n} = \frac{\Delta v^{\text{total}} - \Delta v^{\text{internal}}}{\bar{v}} = \frac{\Delta v^{\text{external}}}{\bar{v}}. \tag{12}$$

If the external drift term vanishes at size n tending to zero (and we will treat only such examples), one can conclude that external influence for n tending to zero, should be negligible, so that $\lim_{n \rightarrow 0}(f_0/f_{\text{eq}}) = 1$, and, respectively, $\lim_{n \rightarrow 0} \ln(f_0/f_{\text{eq}}) = 0$. Then

$$\ln(f_0/f_{\text{eq}}) = \int_0^n \frac{\Delta v^{\text{external}}(n')}{\bar{v}(n')} dn', \quad f_0(n) = f_{\text{eq}}(n) \exp\left(\int_0^n \frac{\Delta v^{\text{external}}(n')}{\bar{v}(n')} dn'\right). \tag{13}$$

Taking into account Equation (6), we can represent zero-flux distribution as

$$f_0(n) = \text{const} \cdot \exp(-\Delta G^{\text{eff}}(n)/kT) \tag{14}$$

with newly introduced **effective Gibbs potential change**

$$\Delta G^{\text{eff}}(n) = \Delta G(n) - kT \int_0^n \frac{\Delta v^{\text{external}}(n')}{\bar{v}(n')} dn'. \tag{15}$$

Obviously, the maximum of effective Gibbs potential change corresponds to zero drift – unstable equilibrium, and should be treated as the effective nucleation barrier. In this letter, we consider two examples of FDN – suppression of IMC formation and acceleration of Kirkendall/Frenkel void formation.

2. FSN of intermediate phase in binary couples

Eventually, we consider nucleation of a second intermediate phase at the interface between a growing intermediate phase and one of pure components of a diffusion couple. For that, we will consider first the nucleation and growth of a single IMC at initial A/B interface and afterwards we will discuss the nucleation of a second phase at $1/B$ interface.

2.1. Nucleation and growth of single intermediate phase at initial A/B interface

It is well known (see, for example, [1,27–29]), that the growth rate of the compound i layer of thickness ΔX_i with almost stoichiometric composition c_i within narrow interval Δc_i growing between practically insoluble components, is equal to

$$\frac{d\Delta X_i}{dt} = \frac{1}{c_i(1-c_i)} \frac{D_i \Delta c_i}{\Delta X_i + \lambda_i}. \quad (16)$$

Characteristic length λ_i accounts for interface barriers. It is related to finite time needed by an atom to overcome barriers. Less known is the interpretation of the product $D_i \Delta c_i$ of mean interdiffusivity and equilibrium phase concentration range. Actually, one should write $D_i \Delta c_i = \int_{c_{iL}}^{c_{iR}} \tilde{D}(c) dc$ (Wagner diffusivity) with the Darken interdiffusion coefficient [4,28]

$$\tilde{D}(c) = (cD_A^* + (1-c)D_B^*) \frac{c(1-c)}{kT} \frac{\partial^2 g}{\partial c^2}, \quad (17)$$

g – Gibbs free energy per atom, varying to a little extent inside the phase but its first derivative $\partial g / \partial c$ typically, changes drastically, so that the second derivative $\partial^2 g / \partial c^2$ becomes large (correlating with the outstanding stability of IMC). Simple transformations (using common tangent rule) give

$$\begin{aligned} \int_{c_L}^{c_R} \tilde{D}(c) dc &= \overline{D}_j^* \frac{c_j(1-c_j)}{kT} \left(\left. \frac{\partial g}{\partial c} \right|_{i,B} - \left. \frac{\partial g}{\partial c} \right|_{i,A} \right) = \overline{D}_j^* \frac{c_j(1-c_j)}{kT} \left(\frac{g_B - g_j}{1-c_j} - \frac{g_j - g_A}{c_j - 0} \right) \\ &= \overline{D}_j^* \frac{\Delta g_j(A+B \rightarrow j)}{kT}. \end{aligned} \quad (18)$$

Here \overline{D}_j^* – combination of tracer diffusion coefficients averaged over the phase, $\overline{D}_j^* \equiv cD_A^* + (1-c)D_B^*$, $\Delta g_i(A+B \rightarrow i)$ – thermodynamic driving force (per one atom) of IMC formation. So, the growth rate can be written as some effective mobility times driving force:

$$\frac{d\Delta X_i}{dt} = \frac{1}{c_i(1-c_i)} \frac{\overline{D}_i^*}{\Delta X_i + \lambda_i} \frac{\Delta g_i(A+B \rightarrow i)}{kT}. \quad (19)$$

We will reorganize Equation (19) to the form suitable for nucleation theory. Let S_j be the area of interfaces i/A and i/B , so that $n = S_j \Delta X_j / \Omega$ is the number of atoms of IMC. On the other hand, for far overcritical volumes of IMC (when one can neglect surface energy),

$$\Delta g_j(A+B \rightarrow j) = -\partial G / \partial n. \quad (20)$$

Then the rate of uptake of atoms into the growing IMC phase is

$$\frac{dn}{dt} = \left(\frac{\overline{D}_i^*/\Omega}{c_i(1-c_i)\Delta X_i + \lambda_i} \frac{S_i}{\Delta X_i + \lambda_i} \right) \left(-\frac{1}{kT} \frac{\partial G}{\partial n} \right) = \bar{v}_i \cdot \left(-\frac{1}{kT} \frac{\partial G}{\partial n} \right) = \Delta v. \quad (21)$$

$$\text{The coefficient } \bar{v}_i \equiv \left(\frac{\overline{D}_i^*/\Omega}{c_i(1-c_i)\Delta X_i + \lambda_i} \frac{S_i}{\Delta X_i + \lambda_i} \right) \quad (22)$$

can be well used as an average attachment/detachment frequency in Fokker–Planck approach.

Now consider the initial stage of IMC formation – its nucleation, which appears most probably at the interface (but sometimes not [30]). If solubilities of A in B and of B in A can be neglected, only interdiffusion inside newly born nucleus determines the rate of its growth or elimination. For the sake of simplicity we take nucleus shape to be disc-like with radius R and thickness $h = h_\alpha + h_\beta$. The aspect ratio $\varphi = h/R$ should be optimized. The Gibbs free energy change due to nucleation of such disc-like particle is

$$\Delta G(n, \varphi) = -n\Delta g_i + W^{\text{surf}}(n, \varphi), \quad (23)$$

$$W^{\text{surf}}(n, \varphi) = (\gamma_{\alpha i} + \gamma_{\beta i} - \gamma_{\alpha\beta})\pi R^2 + (\gamma_{\alpha i}h_\alpha + \gamma_{\beta i}h_\beta)2\pi R, \quad (24)$$

$$h_\alpha = \frac{c_\beta - c_i}{c_\beta - c_\alpha} h, \quad h_\beta = \frac{c_i - c_\alpha}{c_\beta - c_\alpha} h \quad (\text{from conservation of matter}), \quad (25)$$

$$R = (\Omega/\pi)^{1/3} n^{1/3} \varphi^{-1/3}, \quad \Delta X_i = h = (\Omega/\pi)^{1/3} n^{1/3} \varphi^{2/3}. \quad (26)$$

Optimization of surface energy gives

$$\varphi_{\text{opt}} = \frac{\gamma_{\alpha i} + \gamma_{\beta i} - \gamma_{\alpha\beta}}{\frac{c_\beta - c_i}{c_\beta - c_\alpha} \gamma_{\alpha i} + \frac{c_i - c_\alpha}{c_\beta - c_\alpha} \gamma_{\beta i}} \equiv \frac{\Delta\gamma}{\gamma_i}, \quad \Delta\gamma \equiv \gamma_{\alpha i} + \gamma_{\beta i} - \gamma_{\alpha\beta}, \quad \gamma_i \equiv \frac{c_\beta - c_i}{c_\beta - c_\alpha} \gamma_{\alpha i} + \frac{c_i - c_\alpha}{c_\beta - c_\alpha} \gamma_{\beta i}, \quad (27)$$

$$W^{\text{surf}}(n, \varphi_{\text{opt}}) = \tilde{\gamma} s_0 n^{2/3}, \quad \tilde{\gamma} = (\Delta\gamma \gamma_i^2)^{1/3}, \quad s_0 = 3(\pi\Omega^2)^{1/3}. \quad (28)$$

Thus, the drift in the size space can be written by analogy to Equation (21) with additional account of the surface term in Gibbs energy,

$$-\frac{\partial \Delta G}{\partial n} = \Delta g_i - \frac{\partial W^{\text{surf}}(n, \varphi^{\text{opt}})}{\partial n} = \Delta g_i - 2(\pi\Delta\gamma \gamma_i^2 \Omega^2)^{1/3} n^{-1/3}. \quad (29)$$

$$\Delta v = \bar{v}_i \cdot \left(\frac{\Delta g_i}{kT} - \frac{2(\pi\Delta\gamma \gamma_i^2 \Omega^2)^{1/3}}{kT n^{1/3}} \right). \quad (30)$$

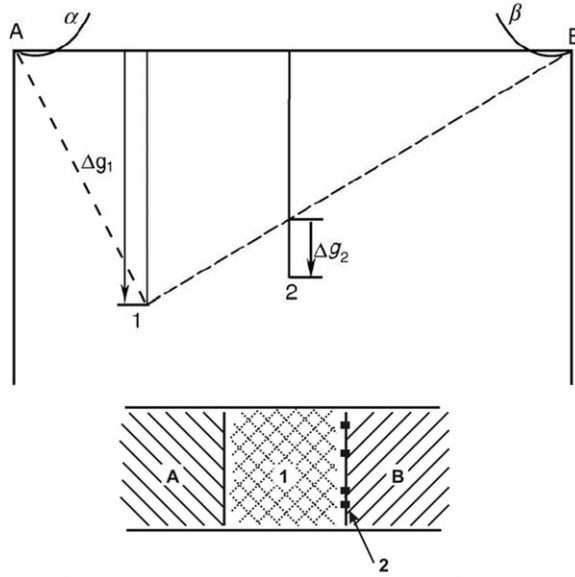


Figure 1. Nucleation of IMC 2 at the interface between IMC 1 and B.

The critical size is found from zero conditions for drift or for derivative of Gibbs free energy

$$n_{cr} = (2\tilde{\gamma}s_0/(3\Delta g))^3. \quad (31)$$

At diffusion-controlled nucleation ($\lambda_i = 0$)

$$\bar{v}_i \equiv \frac{\bar{D}_i^* S_i}{c_i(1-c_i)\Omega \Delta X_i + 0} = \left(\frac{\bar{D}_i^*}{c_i(1-c_i)} \left(\frac{\pi}{\Omega} \right)^{2/3} \left(\frac{\gamma_i}{\Delta \gamma} \right)^{4/3} \right) n^{1/3}. \quad (32)$$

2.2. FDN

Before formulating the main kinetic equation, note that the driving force to form the second IMC by reaction of the first and *B* is less than that of the direct formation from almost pure *A* and *B* (Figure 1). Therefore, formula for Wagner diffusivity differs from Equation (18):

$$\int_{c_L}^{c_R} \tilde{D}(c)dc = \bar{D}_2^* \frac{c_2(1-c_2)}{kT} \left(\frac{g_B - g_2}{1-c_2} - \frac{g_2 - g_1}{c_2 - c_1} \right) = \bar{D}_2^* \frac{c_2(1-c_1)\Delta g_2(1+B \rightarrow 2)}{c_2 - c_1 kT}. \quad (33)$$

For the nucleation of IMC 2 between already growing layer of IMC 1 and pure *B*, one may use known growth Equations (21)–(24) with modified driving force like in Equation (29):

$$\frac{d\Delta X_2}{dt} = \frac{(1-c_1)^2 c_2}{(c_2 - c_1)^2 (1-c_2)} \frac{D_2^*}{\Delta X_2} \left(\frac{\Delta g_{1+B \rightarrow 2}}{kT} - \frac{2}{3} \tilde{\gamma} s_0 n_2^{-1/3} \right) - \frac{1}{c_2 - c_1} \frac{D_1 \Delta c_1}{\Delta X_1}. \quad (34)$$

In terms of number of atoms in the disc-like nucleus the kinetic equations are

$$\Delta v_2 = \frac{dn_2}{dt} = \frac{S_2 d\Delta X_2}{\Omega dt} = \bar{v}_2 \left(\frac{\Delta g_{1+B \rightarrow 2}}{kT} - \frac{2\tilde{\gamma}s_0 n_2^{-1/3}}{3kT} \right) - \frac{D_1 \Delta c_1 (\pi/\Omega)^{1/3}}{\Delta X_1} \frac{(\gamma_i)^{2/3}}{c_2 - c_1} n_2^{2/3}, \quad (35)$$

where

$$\bar{v}_2 = \frac{(1 - c_1)^2 c_2}{(c_2 - c_1)^2 (1 - c_2)} \left(\frac{\pi}{\Omega} \right)^{2/3} \left(\frac{\gamma_i}{\Delta \gamma} \right)^{4/3} D_2^* n_2^{1/3}. \quad (36)$$

Thus,

$$-kT \frac{\Delta v_2}{\bar{v}_2} = -\Delta g_{1+B \rightarrow 2} + \frac{2\tilde{\gamma}s_0}{3n_2^{1/3}} + kT \frac{(\frac{\Omega}{\pi})^{1/3} D_1 \Delta c_1 (1 - c_2)(c_2 - c_1) \left(\frac{\Delta \gamma}{\gamma_i}\right)^{2/3}}{D_2^* \Delta X_1 (1 - c_1)^2 c_2} n_2^{1/3}. \quad (37)$$

So, we can now construct an effective Gibbs nucleation barrier

$$\begin{aligned} \Delta G^{\text{eff}}(n_2) &= \Delta G(n_2) - kT \int_0^n \frac{\Delta v_2^{\text{external}}(n')}{\bar{v}_2(n')} dn' \\ &= -\Delta g_{1+B \rightarrow 2} x^3 + \tilde{\gamma}s_0 x^2 + kT \frac{(\Omega/\pi)^{1/3} D_1 \Delta c_1}{D_2^* \Delta x_1} \frac{3(1 - c_2)(c_2 - c_1) \left(\frac{\Delta \gamma}{\gamma_i}\right)^{2/3}}{4(1 - c_1)^2 c_2} x^4 \\ &= -a_3 x^3 + a_2 x^2 + a_4 x^4, \quad x \equiv n^{1/3}. \end{aligned} \quad (38)$$

Note that, formally, Equation (38) is formally similar to dependence obtained in [19] in the frame of nucleation thermodynamics at interface in the sharp concentration gradient – it also contains the fourth power of linear size, in addition to standard third and second powers, but now it depends on diffusivities ratio. Here the last term is positive meaning additional height of nucleation barrier (FSN). If $a_4 > a_4^* = 9a_3^2/(32a_2)$ this barrier tends to infinity so that nucleation is impossible. Nucleation becomes possible when $a_4 < a_4^*$, or

$$\Delta X_1 > \Delta X_1^{\text{crossover}} = \frac{\bar{D}_1^* \Delta g_{A+B \rightarrow 1}}{\bar{D}_2^* (\Delta g_{1+B \rightarrow 2})^2} \left(\frac{\Omega}{\pi} \right)^{1/3} \frac{(1 - c_2)(c_2 - c_1) 8\tilde{\gamma}s_0 (\Delta \gamma/\gamma_i)^{2/3}}{3(1 - c_1)^2 c_2}. \quad (39)$$

Equation (39) evidently can give cross-over thickness of the suppressing phase like tens or hundreds of nanometers. Indeed, at reasonable parameters $D_1^*/D_2^* = 10$, $c_1 = 1/3$, $c_2 = 1/2$, $\Omega = 10^{-29} \text{ m}^3$, $\Delta g|_{A+B \rightarrow 1} = 10^{-19} \text{ J/atom}$, $\Delta g|_{1+B \rightarrow 2} = 2 \cdot 10^{-20} \text{ J/atom}$, $\gamma_i = 1 \text{ J/m}^2$, $\Delta \gamma = 0.5 \text{ J/m}^2$ one gets $\Delta X_1^{\text{crossover}} = 148 \text{ nm}$.

Change of effective nucleation barrier with changing (from 10–300 nm) width of neighboring growing phase layer 1 is illustrated at Figure 2 for just indicated parameters.

3. Flux-assisted void nucleation at the interface of growing intermetallic compound

Let us finally consider the Kirkendall (actually Frenkel) voiding in the process of growth of an IMC 1 between two mutually almost insoluble components [4,27].

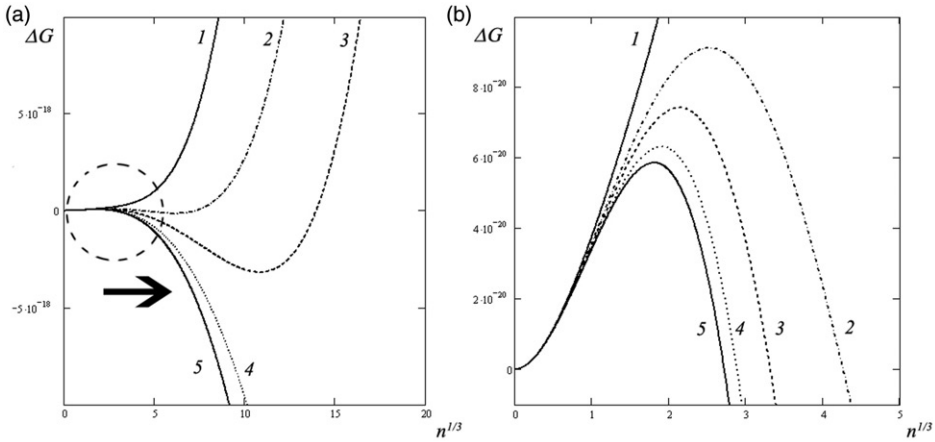


Figure 2. (a) Effective nucleation barriers (in J) as the functions of cubic root of atoms number in phase 2 embryo/nucleus, at various widths of already growing phase layer 1 (curve 1–10 nm, 2–20 nm, 3–30 nm, 4–70 nm, 5–300 nm). (b) shows the details of curves behavior near the top of ordinary nucleation barrier. Parameters are indicated in the text after Equation (39).

Sample geometry is: A – 1L (left interface) – 1R (right interface) – B. Let B is much faster, $D_A^*/D_B^* \ll 1$. Then the vacancy flux will be directed from 1L to 1R. In the case of poorly working vacancy sinks, one will observe void nucleation and growth at the moving right boundary. Let us take for simplicity that the nuclei of voids have hemispherical shape with their basis at the interface. Then, the change of Gibbs free energy due to nucleation is

$$\Delta G = -\left(\frac{2\pi R^3}{3\Omega}\right) \cdot kT \ln\left(\frac{C_V}{C_V^{\text{eq}}}\right) + \gamma_{1V} 2\pi R^2 + (\gamma_{BV} - \gamma_{1B})\pi R^2 = -n \cdot \Delta g_V + \gamma^{\text{ef}} 2\pi r_1^2 n^{2/3}. \quad (40)$$

Here $n = 2\pi R^3/(3\Omega)$ – number of vacancies collected in hemispherical void (neglecting relaxation), $r_1 \equiv (3\Omega/2\pi)^{1/3}$ characteristic atomic size ($R = r_1 \cdot n^{1/3}$), $\Delta g_V = kT \ln(C_V/C_V^{\text{eq}})$, $\gamma^{\text{ef}} = \gamma_{1V} + (\gamma_{BV} - \gamma_{1B})/2$ – “effective surface tension”, $\gamma_{1V}, \gamma_{BV}, \gamma_{1B}$ – surface energies per unit area for interfaces IMC/void, B-phase/void, B-phase/IMC, respectively. In full analogy with Equations (8) and (9), we have for the hemisphere

$$\bar{v}^{\text{hemisphere}}(n) = \frac{1}{2} \bar{v}^{\text{sphere}}(2n) = 3 \frac{c_V^{\text{eq}} D_V}{r_1^2} n^{1/3}, \quad (41)$$

$$\Delta v^{\text{internal}} = -\frac{\bar{v}^{\text{hemisphere}}}{kT} \frac{\partial \Delta G}{\partial n} \cong \frac{\bar{v}^{\text{hemisphere}}}{kT} \left(\Delta g_V - \frac{4\pi r_1^2 \gamma^{\text{ef}}}{3n^{1/3}} \right). \quad (42)$$

Now, we add the additional drift term due to external flux of vacancies. We consider here the most simple case that all vacancy flux goes into the void and does

not go further. Then

$$\left. \frac{dn}{dt} \right|_{\text{external}} = J_V \pi R^2 - 0 = \frac{D_B^* - D_A^*}{\Omega} \frac{c_1(1 - c_1)}{kT} \frac{\partial^2 g}{\partial c_B^2} \frac{\Delta c_B}{\Delta X_1} \pi r_1^2 n^{2/3} \approx \frac{D_B^* (\Delta g_1/kT)}{\Omega \Delta X_1} \pi r_1^2 n^{2/3}. \quad (43)$$

Here Δg_1 is a driving force of IMC formation per one atom and ΔX_1 – thickness. Thus,

$$\Delta v^{\text{total}} = \frac{\bar{v}^{\text{hemisphere}}}{kT} \left(\Delta g_V - \frac{4\pi r_1^2 \gamma^{\text{ef}}}{3n^{1/3}} \right) + \frac{D_B^* (\Delta g_1/kT)}{\Omega \Delta X_1} \pi r_0^2 n^{2/3}. \quad (44)$$

The “kinetically critical” size corresponds to $\Delta v^{\text{total}} = 0$. Let supersaturation of vacancies tends to zero, so that $\Delta g_V \rightarrow 0$. Then the condition $\Delta v^{\text{total}} = 0$ gives (with $c_V^{\text{eq}} D_V \approx D_B^*$):

$$R_{\text{cr}}^{\text{kinetic}} = \sqrt{4\gamma^{\text{ef}} \Omega \Delta X_1 / \Delta g_1}. \quad (45)$$

For reasonable parameters ($\tilde{\gamma} = 1 \text{ J/m}^2$, $\Omega = 10^{-29} \text{ m}^3$, $\Delta g = 10^{-19} \text{ J/atom}$, $\Delta x_1 = 10^{-8} \text{ m}$) one obtains $R_{\text{cr}}^{\text{kinetic}} = 2 \cdot 10^{-9} \text{ m}$, which means that even at zero supersaturation the void nucleation is still possible due to external flux. We also can introduce the effective nucleation barrier,

$$\Delta G^{\text{eff}}(n) = \Delta G(n) + kT \cdot \int_0^n \frac{\Delta v^{\text{ext}}(n')}{\bar{v}(n')} dn' = \Delta G(n) - \frac{\pi r_0^4}{c_1 \Omega} \left(\frac{\Delta g_1}{\Delta X_1} \right) n^{4/3}. \quad (46)$$

Thus, the change (decrease) of effective nucleation barrier in units of kT is

$$\frac{\Delta G^{\text{eff}}(n) - \Delta G(n)}{kT} = - \frac{\pi r_0^4}{c_1 \Omega} \left(\frac{\Delta g/kT}{\Delta x} \right) n^{4/3} \approx 6 \cdot n^{4/3},$$

which amounts to only 12 even at $n = 8$ vacancies in the void. Once more, we can see that in this situation the FAN can play a decisive role.

To summarize, divergence of external fluxes in the nucleation region (often influenced by the nucleation itself) leads to additional positive or negative drift terms for nucleus migration in the size space and in consequence to an effective nucleation barrier, which is usually time-dependent and may furthermore depend on the ratio of diffusion characteristics. We suggest calling this phenomenon FDN including FAN as well as FSN. Detailed applications of suggested approach to old problem of phase competition in thin film reactions and to recently discovered point contact reactions [31,32] will be presented elsewhere.

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