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NUCLEATION AND COMPETITION OF COMPOUNDS IN STRONGLY INHOMOGENEOUS OPEN SYSTEMS – NEW DEVELOPMENTS[*]

Competitive nucleation of an intermediate phase in a sharp concentration gradient proceeds usually at the initial stages of the solid-state reaction between materials. Theory of nucleation at such conditions has almost 40 years of history briefly reviewed and discussed in the present paper. This theoretical treatment is based on two basic ideas: (1) kinetic suppression of the emerging embryos/nuclei by the fast-growing neighboring phases, (2) thermodynamic suppression of nucleation by sharp concentration gradients. Here some new theoretical and simulation results in this field are presented, as well as their experimental verifications.

Keywords: diffusion, nucleation, phase growth, supersaturation, concentration gradient, Monte Carlo method, solid solution.

1. Introduction

With nucleation in a sharp concentration gradient is meant, at least in this paper, nucleation of intermediate phases in the contact zone of two solid materials. So, we consider nucleation at the initial stage of solid-state reactions. In most cases, the initial contact zone is a region of nanometric sizes around a 2D-contact (initial interface) [1], but it can be as well a nanometric zone around a 1D (linear) contact or even 0D (point) contact [2- 4]. Chemical phenomenon of solid-state reaction, from the physical point of view, can be considered as a chain of competitive phase transformations in the evolving composition profiles with initially sharp concentration gradients. If the driving force of the phase transformation is large, then the nucleation barrier is low and nucleation is not the controlling stage of reaction. Yet, reactions can, generally, proceed via different, alternative evolution paths (alternative chains of reactions). As known from the Ostwald rule and its modern interpretation [5,6], nature chooses the evolution path with maximal nucleation rate (which commonly corresponds to the minimal nucleation barrier). Therefore, we should compare the nucleation barriers for all possible paths even if all these barriers are low. Moreover, very often the appearance of the first phase to nucleate and grow at the contact may drastically change the nucleation rates for subsequent transformations.

Thus, nucleation of intermediate phases during solid-state reactions have two main peculiarities:

(1) The nuclei/embryos of the intermediate phase are formed in the presence of external fluxes. It follows that nucleation can be kinetically suppressed or kinetically promoted by these external fluxes.

(2) Nucleation proceeds in the very sharp gradients of chemical potential and concentration. It follows as a consequence that, in general, these gradients affect the value of the nucleation barrier. Here we do not mean the Cahn-Hilliard gradient terms leading to a diffusive interface between nucleus and parent phase(s), but the gradient terms related to various driving forces of transformation in the "left boundary", "central" and "right boundary" regions of the nucleus. In order that such a mechanism can be effective, the contact zone should be of a size of few nanometers, but it is just the situation at the initial stage of solid-state reactions!

The first attempt to take into account the peculiarity 1 (kinetic suppression of nucleation by the divergencies of external fluxes) was made in [7] and developed further in [8-12]. This approach provides us with the prediction of possible phase formation sequences and of the kinetic suppression periods for each phase starting from the second phase to form (however, it could not predict the incubation period for the first phase to form). For example, the formation and growth of phase 2 nuclei are kinetically suppressed by the growing neighboring phase layer when its thickness satisfies the following condition:

$$\Delta X_1 < \Delta X_1^* = \frac{1-C_2}{1-C_1} \frac{D_1 \Delta C_1}{D_2 \Delta C_2} l_2^{cr} \tag{1}$$

where l_2^{cr} is a longitudinal size of the phase 2 critical nucleus at the interface 1/B. Here $D_1 \Delta C_1, D_2 \Delta C_2$ are the Wagner integrated diffusivities [13-16]. An account of peculiarity 2 (thermodynamic constraints on nucleation in a the sharp concentration gradient) was made by us first simultaneously with Pierre Desre [17-20] and later jointly with P. Desre and F. Hodaj [21-24]. In brief, the results can be summarized as follows: The influence of concentration gradient in the nucleation region on the dependence of Gibbs free energy on nuclei size or volume depends on the so-called nucleation mode (polymorphic, lateral, or total-mixing one). It differs for two possible thermodynamic conditions at which such processes may occur:

(1) The composition of the intermediate new phase can be provided by the common down-hill diffusion within the old metastable phase (Fig.1).
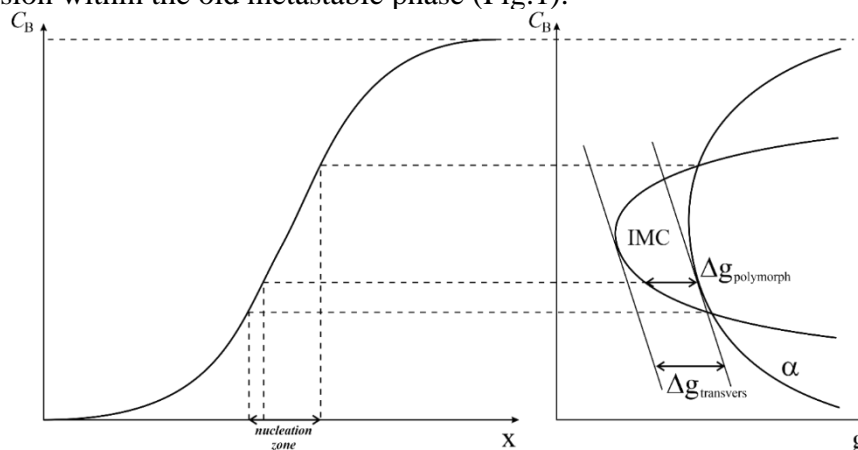

Fig. 1. Right: Composition dependence of the Gibbs free energy of the metastable parent phase with full metastable solubility and new intermediate phase, and also local driving forces of nucleation by: polymorphic – a, transversal (lateral) – b, and total mixing (longitudinal) – c modes. Left: Evolution of the concentration profile within the metastable parent phase with full solubility – a spatial region within which the nucleation is favorable, is widening with time.

The solubility of the two-parent phases (i-1) and (i+1) is limited, so that the new phase "i" can be formed only as the result of two simultaneous decompositions in two metastable phases divided by an interface, i.e., phase (i-1) is supersaturated with B and phase (i+1) is supersaturated with A (Fig.2).
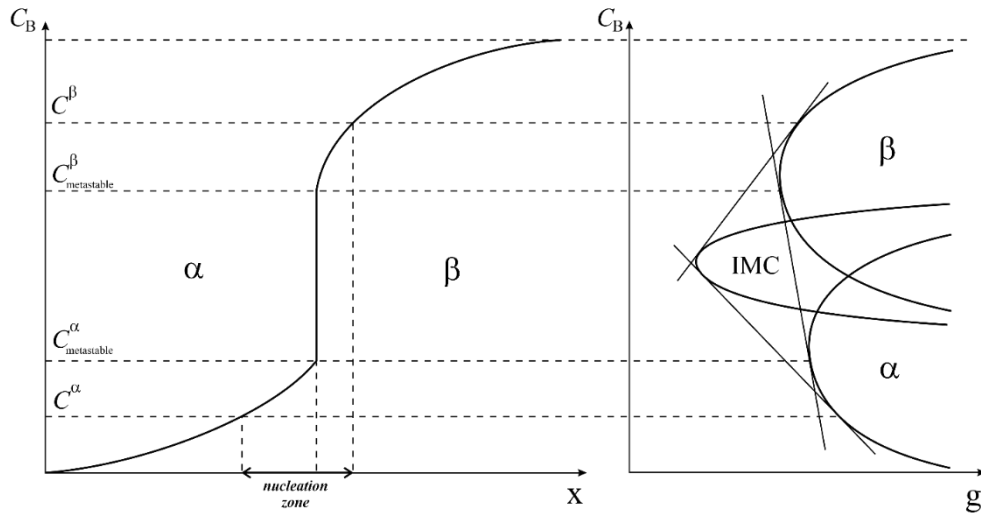

Fig.2. Stable and metastable equilibria in a binary system with limited solubility in the parent phases α and β. Compositions within intervals $\left(c_{\alpha\gamma}, c_{\alpha\beta}\right)$, $\left(c_{\beta\alpha}, c_{\beta\gamma}\right)$ correspond to metastable (supersaturated) alloys and provides the decomposition starting from nucleation of the γ-phase in the reactions $\alpha^{metast} \rightarrow \alpha + \gamma, \beta^{metast} \rightarrow \beta + \gamma$ at both sides of the initial α / β - interface. The right part of the figure shows the concentration dependencies for Gibbs free energies of all phases. The left part presents the typical concentration profile provided by interdiffusion before nucleation of the intermediate phase. The spatial interval between α^{m} and β^{m} around the concentration step shows the region within which nucleation is favorable.

For case (1) we discovered a new relation for the work of critical cluster formation adding the fifth-power size term to the well-known Gibbs dependence:

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

Here the coefficient γ is positive for polymorphic and transversal modes and negative for total-mixing mode. This relation can be further advanced. Actually, more correct is a dependence on the nucleus volume plus the nucleus shape dependence on volume – this problem was thoroughly analyzed in [1, 18, 21-24] and will not be discussed here. The main consequence of our result expressed by eq.(2) is a suppression of nucleation unless the concentration gradient becomes smaller (due to diffusion) than some critical value.

For case (2) the dependence is somewhat different – it contains a fourth-power term instead of fifth-power. In addition, it also contains a combination of concentration gradients on both sides of the initial α / β - interface:

$$\Delta G(R) = \alpha' R^2 - \beta' R^3 + \gamma' q^2 R^4, \tag{3}$$

$$q^2 = \frac{A_\alpha A_\beta}{A_\alpha + A_\beta}, A_\alpha = \left(C_{\gamma\alpha} - C_{\alpha\beta}\right) \frac{\partial^2 g}{\partial C^2}\Bigg|_{C_{\alpha\beta}} (\nabla C)\Big|_{C_{\alpha\beta}}, A_\beta = \left(C_{\beta\alpha} - C_{\gamma\beta}\right) \frac{\partial^2 g}{\partial C^2}\Bigg|_{C_{\beta\alpha}} (\nabla C)\Big|_{C_{\beta\alpha}}$$

(notations coincide with the those used in Fig.2)

In 2011 we came back to kinetic suppression ideas, but on more rigorous basis than in 1982. Namely, we introduced the concept of Flux Driven Nucleation (FDN) which can be

actually denoted also as FAN (Flux Assisted Nucleation) or FIN (Flux Inhibited Nucleation) [25].The main idea of this concept is using Fokker-Planck (FP) approach for the theoretical description of nucleation in the cluster size space (just as in classical nucleation theory (CNT)) but with two terms for the drift of nuclei/embryos in the size space:

$$\Delta v^{total} \cong \Delta v^{internal} + \Delta v^{external}$$

. (4)

The first term in the right-hand side of eq.(4) is a common drift term caused by the size dependence of the Gibbs free energy change due to nucleation:

$$\Delta v^{internal}(n) = \frac{\bar{v}(n)}{kT} \cdot \left(-\frac{\partial \Delta G}{\partial n} \right)$$

(n is the number of monomers – say, atoms or molecules inside nucleus). The second term is caused by the divergence of external fluxes. For example, as shown in [25], in the case of disc-like nuclei of phase 2 formation at the interface of the growing layer of phase 1 and material B the first and the second terms are:

$$\Delta v^{internal}(n_2) = \frac{\bar{v}(n_2)}{kT} \cdot \left(\Delta g_{1+B \to 2} - \frac{2}{3} \tilde{\gamma} s_0 n_2^{-2/3} \right),$$

(5a)

$$\Delta v^{external} = -\frac{\pi R_2^2 / \Omega}{C_2 - C_1} \cdot \frac{D_1 \Delta C_1}{\Delta X_1} = -\frac{(\pi/\Omega)^{1/3} n_2^{2/3}}{C_2 - C_1} \left(\frac{\gamma_i}{\Delta \gamma} \right)^{2/3} \cdot \frac{D_1 \Delta C_1}{\Delta X_1}.$$

(5b)

(here R_2 is a radius of disc-like nucleus of phase 2, γ_i, $\Delta \gamma$, γ-various combinations of surface tensions between phases – for details see [25])

In [25] we demonstrated that the inclusion of external fluxes into the FP-scheme provides us with an effective nucleation barrier of the form

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

(6)

In the case of compound 2 nucleation at the interface 1/B of the already growing phase layer 1, this effective dependence can be reduced to the form similar to eq. (3):

$$\Delta G^{eff}(n_2) = a_{surf} n_2^{2/3} - a_{bulk} n_2^1 + a_{inhib} \frac{D_1 \Delta C_1}{\Delta X_1} n_2^{4/3}.$$

(7)

(exact definitions of coefficients a_{surf}, a_{bulk}, a_{inhib} are given in [25])

Simple analysis shows that this dependence is monotonically increasing (nucleation is kinetically suppressed) if the thickness of the growing layer 1 is less than some threshold value given by

$$\Delta X_1 < \Delta X_1^* = \frac{32 a_{surf}}{9 a_{bulk}^2} a_{inhib} D_1 \Delta C_1.$$

(8)

The substitution of the realistic parameters into this equation results in values of the threshold thickness in the range from tens to hundreds of nanometers [25].

A comprehensive review of the developments connected with the account of peculiarities 1 and 2 in nucleation in solid-state reactions was published in 2010 [1]. In the present paper, we will discuss some new developments in theory and simulation as well as experimental verification of the above-described concepts.

2. New developments of the kinetic suppression concept

2.1. Suppression of silicide nucleation at the point contact reaction between nanowires

About 12 years ago, a new type of nano-reactions was discovered – silicide formation due to the contact of a silicon nanowire and a metal (first of all, Ni) nanowire or nanoparticle [2-4,

12

26-27]. In this case the contact is formally point-like (actually, nanometer-sized or even Angstroem-sized) – see Fig.3.
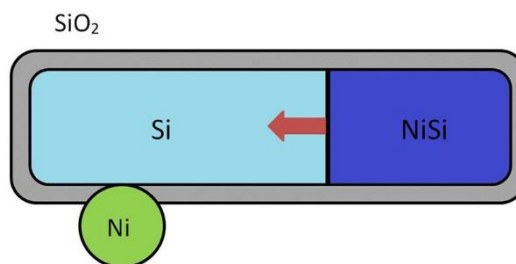

Fig.3. Growth of the intermediate phase proceeds far from the point contact, and the growing phase is not the common Ni_2Si phase.

Moreover, silicon nanowire (with typical diameter about 20 nm) is covered by the natural amorphous oxide of 1-2 nm thickness. Most probably, in the place of contact this very thin oxide layer is damaged, and metal atoms penetrate into Si nanowire via this damaged "window" of atomic size. The results and kinetics of this reaction are very interesting. For example, in case of Ni the NiSi silicide appears inside Si nanowire and grows, which is expectable. Yet, the phase which was nucleated, the place of nucleation, and the way of further growth seemed to be unexpectable. Indeed, in typical Ni-Si thin film couples the first phase to grow is Ni_2Si, second is monosilicide NiSi, and third is $NiSi_2$ (usually at sufficiently high temperatures). On the contrary, in point contact reaction the nucleated phase is monosilicide, NiSi. In the thin-film couples the new phases are nucleated at the interface Ni-Si. On the contrary, in point contact reaction, nothing is nucleated near the contact point – instead, NiSi is nucleated far from the contact - typically, at the end of Si nanowire or between the contact points in case of multiple contacts. After nucleation, the further growth of silicide proceeds in stop-and-go mode: each new atomic layer waits a few seconds before nucleation of the island and then very fast lateral growth of atomic layer takes place – see Fig.4.
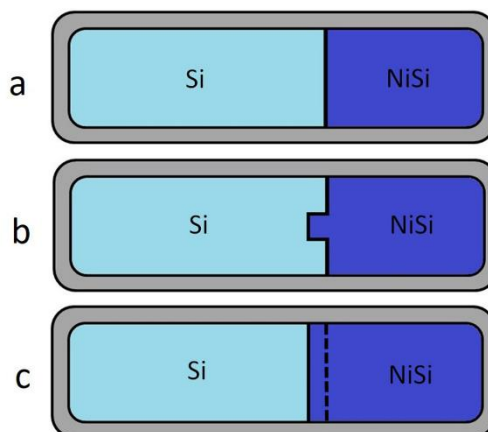

Fig.4. Stop-and-go growth of silicide along the nanowire

Such growth mode with repeating nucleation of 2D-islands was explained and described in [3], but the absence of nucleation at the contact was not discussed. We will do this here and now.
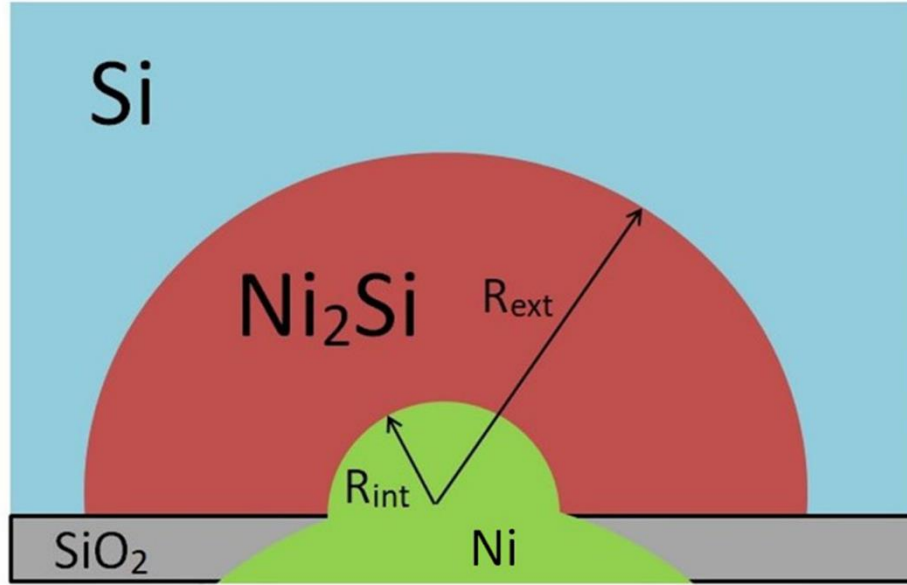
Fig. 5. Nucleus of silicide around point contact with Ni as a traffic-jam configuration for Ni-flux, leading to decomposition of nucleus due to interstitial diffusion of Ni into Si.

Let us suppose that just around the contact place inside silicon the critical nucleus of Ni2Si is formed (Fig. 5). For simplicity, the nucleus is considered to be a hemispherical shell with an inner radius $R_{int} = R_{contact} = 0.2nm$ and an external radius $R_{ext} = R_{crit}$. It's critical size can be evaluated from simple thermodynamic considerations:

$$\Delta G = -\Delta g \cdot \frac{2\pi}{3\Omega}\left(R_{ext}^3 - R_{int}^3\right) + \gamma_{i/Si} \cdot 2\pi R_{ext}^2 + \gamma_{i/Ni} \cdot 2\pi R_{int}^2 + \left(\gamma_{i/SiO2} - \gamma_{Si/SiO2}\right) \cdot \pi\left(R_{ext}^2 - R_{int}^2\right),$$

$$\frac{\partial \Delta G}{\partial R_{ext}} = 0 \Rightarrow R_{ext} = \frac{2\gamma_{i/Si} + \left(\gamma_{i/SiO2} - \gamma_{Si/SiO2}\right)}{\Delta g}\Omega.$$

Since this phase, in our virtual model, appears like "traffic jam" hindering the supply of Ni into silicon, very important is, what is the flux passing through this spherical shell. Taking steady-state approximation in spherical symmetrical case [28], one gets for the total flux

$$J^{total} = -2\pi r^2 \tilde{D}\frac{\partial C}{\partial r} \approx const\ over\ r = \frac{\int_{R_{int}}^{R_{ext}} \frac{J^{total}}{r^2}dr}{\int_{R_{int}}^{R_{ext}} \frac{1}{r^2}dr} = -2\pi\frac{\int_{\Delta C}\tilde{D}dC}{\frac{1}{R_{int}} - \frac{1}{R_{ext}}} = -2\pi R_{ext}R_{int}\frac{\tilde{D}\Delta C}{R_{ext} - R_{int}}.$$

As we can see, the total flux is controlled by the window radius R_{int}.

Thus, the flux densities at the internal and external boundaries are easily determined:

$$j_{int} = \frac{J^{total}}{2\pi R_{int}^2} = -\frac{R_{ext}}{R_{int}}\frac{\tilde{D}\Delta C}{R_{ext} - R_{int}}\ ,\ j_{ext} = \frac{J^{total}}{2\pi R_{ext}^2} = -\frac{R_{int}}{R_{ext}}\frac{\tilde{D}\Delta C}{R_{ext} - R_{int}}.$$

The velocity of motion of the external boundary is determined by the flux balance equations with difference of nickel flux densities at both sides of i/Si, divided by the difference of molar fractions of nickel at the same sides of the interface.

$$\left(\frac{2}{3} - C_{Ni}(Si)\right)\frac{dR_{ext}}{dt} = \frac{R_{int}}{R_{ext}}\frac{\tilde{D}\Delta C}{R_{ext} - R_{int}} - D_{Ni}^{interst}(Si)\frac{C_{Ni}^{Si/i} - \bar{C}_{Ni}}{R_{ext}}. \tag{9}$$

Here $C_{Ni}^{Si/i}$ is the equilibrium concentration of Ni at the silicon side of the interface silicon/silicide, $\bar{C}_{Ni}$ is a concentration of Ni in silicon. Nucleation of Ni2Si at the point contact is suppressed if $\dfrac{dR_{ext}}{dt} < 0$ (each newborn nucleus at the point contact is immediately dissolved by diffusion of nickel into the silicon matrix), which means

$$\bar{C}_{Ni} < \bar{C}_{Ni}{}^{crit}, \quad \bar{C}_{Ni}{}^{crit} = C_{Ni}^{Si/i} - \frac{R_{int}}{R_{ext} - R_{int}} \frac{\tilde{D}\Delta C}{D_{Ni}^{interst}(Si)}. \tag{10}$$

In other words, $\bar{C}_{Ni}{}^{crit}$ is the concentration of Ni in silicon which should be reached to make possible the successful nucleation of the silicide at the "window" (place of point contact between silicon nanowire and metal nanowire or nanoparticle). Three peculiarities of the point contact assist to fulfill this condition:

A. Traffic-jam effect due to small ratio, $\dfrac{R_{int}}{R_{ext}} \ll 1$. In the planar case, this parameter would be UNITY.

B. Wagner integrated diffusivity, $\tilde{D}\Delta C$, for nickel silicide (which can be expressed in terms of bulk tracer diffusivity of Ni in silicide and interstitial diffusivity of Ni in Si) is much less than the interstitial diffusivity of nickel via silicon lattice, so that

$$\frac{\tilde{D}\Delta C}{D_{Ni}^{interst}(Si)} \sim \frac{D_{Ni}^{*}}{D_{Ni}^{interst}(Si)} \frac{\Delta g}{kT} \ll 1$$

C. There is no back diffusion of silicon into Ni.

Before reaching the level of concentration corresponding to critical conditions given by eq.(10), this concentration inside silicon nanowire will satisfy the condition of NiSi nucleation outside the contact area. Thus, suppression of silicide nucleation will continue till reaching saturation. In a saturated solution nucleation is more probable for heterogeneous nucleation of NiSi at the defect places of silicon nanowire [29].

2.2. Cu₃Sn suppression criterion for solid copper – molten tin reaction

The formation of the Cu₃Sn phase in soldering reactions increases the probability of failure at the solder contacts. It happens due to Kirkendall voiding caused by different diffusion rates of copper and tin through the IMC layer plus non-ideal vacancy sinks at Cu/Cu₃Sn interface. A criterion of suppression of this phase nucleation by the fast-growing scallop-like Cu₆Sn₅ compound is presented below.

In soldering of copper by the liquid Sn-based solder the thickness of the Cu₃Sn phase is much lower than that of the Cu₆Sn₅ phase. The reason of this phenomenon is the different nature of diffusion within Cu₃Sn and Cu₆Sn₅ layers during the reaction between molten solder and copper. Diffusion across Cu₃Sn is a solid-state diffusion. Contrary to this, Cu₆Sn₅ layer has a different morphology and different diffusion mechanism: the growth of Cu₆Sn₅ scallops takes place at the solder/metal interface by rapid liquid state diffusion through nanometric liquid channels between Cu₆Sn₅ scallops, leading thus to a rapid growth rate of this phase [30,31]. The first phase that forms and grows at the liquid solder/Cu interface is η-Cu₆Sn₅ phase and it is only afterward that the growth of the ε-Cu₃Sn phase occurs at Cu/Cu₆Sn₅ interface.

Let us assume that ε-phase layer of some minimal constant thickness l_{cr} (say l_{cr} = 2 nm) has just formed by nucleation and lateral growth and now is trying to grow normally between η-phase and Cu (Fig.6).
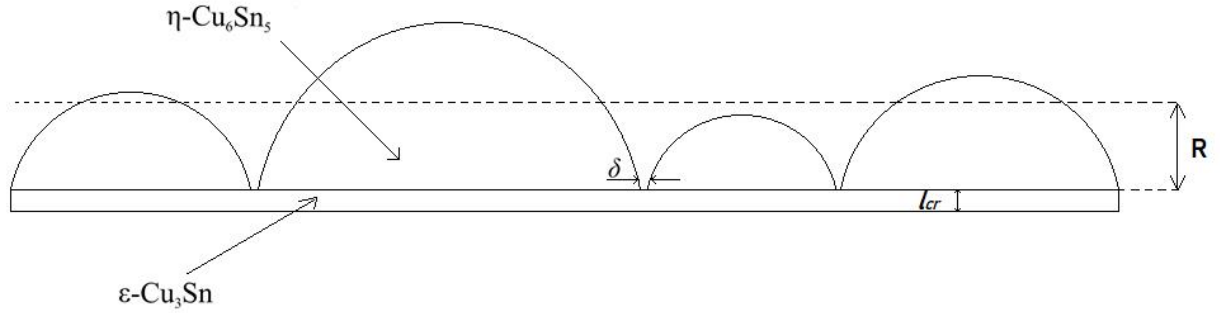
Fig. 6. Schematic morphology of the reaction zone during solder reaction. δ is a width of the liquid channels between the scallops of Cu_6Sn_5.

A simple analysis of the flux balance at the interfaces Cu/Cu₃Sn and Cu₃Sn/Cu₆Sn5 of Cu₃Sn phase leads to the following growth rate equation [32]:

$$\frac{d\Delta x^{\varepsilon}}{dt}\Big|_{l_{cr}} = \left(\frac{1}{C^{\varepsilon}-C^{\eta}}+\frac{1}{1-C^{\varepsilon}}\right)\frac{\tilde{D}^{(\varepsilon)}\Delta C_{\varepsilon}^{eq}}{l_{cr}^{\varepsilon}} - \frac{1}{C^{\varepsilon}-C^{\eta}}\frac{\delta D_{Cu}^{melt}}{R^2}\left(C^{l/\varepsilon}-C^{l/\eta}\right).\qquad(11)$$

Thus, the nucleation of the ε-phase layer stops only under the following condition:

$$\frac{1}{R^2}\frac{1}{C^{\varepsilon}-C^{\eta}}\delta D_{Cu}^{melt}\left(C^{l/\varepsilon}-C^{l/\eta}\right) < \frac{1-C^{\eta}}{\left(C^{\varepsilon}-C^{\eta}\right)\left(1-C^{\varepsilon}\right)}\frac{\tilde{D}^{(\varepsilon)}\Delta C_{\varepsilon}^{eq}}{l_{cr}^{\varepsilon}},\qquad(12)$$

it means, for a sufficiently large mean scallop size:

$$R > R^* = \sqrt{\frac{\left(C^{l/\varepsilon}-C^{l/\eta}\right)\left(1-C^{\varepsilon}\right)}{1-C^{\eta}}\frac{D_{Cu}^{melt}}{\tilde{D}^{(\varepsilon)}\Delta C_{\varepsilon}^{eq}}\delta\cdot l_{cr}^{\varepsilon}}.\qquad(13)$$

Experimental verification of this prediction is discussed in Section 4.

3. Monte Carlo simulation
3.1. *Nucleation in homogeneous solid solution*

At first, we verify the predictions of our model by simulations of nucleation considering the standard case of homogeneous nucleation in a metastable (supersaturated) solid solution with positive mixing energy. To have realistic estimates of the supersaturation, we cannot use the approximation of the regular solution, since Monte Carlo simulation automatically takes the correlation effects into account. Therefore, one should, first of all, simulate the equilibria in solid solutions and construct the Monte Carlo (MC) phase diagram. It was done in [53].

Monte Carlo simulations employ an exchange mechanism of diffusion, first coordination shell interactions for the decomposition of the solid solution and two shells for nucleation of the ordered phases, Metropolis algorithm, periodic boundary conditions for a model sample containing 15x15x15*4 sites of the FCC lattice.

A model system in a computer experiment was characterized by two parameters - temperature and concentration of parent phase. Incubation time was obtained as average in the ensemble of 1000 tests with the system at same parameters. The results of the computer experiment are represented at Fig. 7.

The obtained dependencies correlate with the classical nucleation theory. According to CNT, the incubation time should be inversely proportional to the flux of nuclei in the size space and, accordingly, proportional to the exponent of the height of the nucleation barrier divided by kT. The nucleation barrier in CNT is proportional to the cube of surface tension and inversely proportional to the squared bulk driving force. This driving force is determined by the rule of

parallel tangents and at small supersaturation it is proportional to it. Thus, CNT predicts that the logarithm of the incubation time is a linear function of the inverse squared supersaturation $\dfrac{1}{\left(\ln\left(C/C_{eq}\right)\right)^2}$ (supersaturation appears to be better represented by $\ln\left(C/C_{eq}\right)$ than by $\left(C-C_{eq}\right)$.

The dependencies presented at Fig.8 can be approximated as

$$\ln\tau = \alpha\,\frac{1}{\left(\ln\left(C/C_{eq}\right)\right)^2} + \beta\,, \qquad (14)$$

where α is the proportionality coefficient between $\ln(\tau)$ and $\dfrac{1}{\left(\ln\left(C/C_{eq}\right)\right)^2}$; β is a constant.

The value of β, in theory, should be common for all dependencies for the systems of the fixed size, but in this case, we have some deviation from the constant. However, these deviations are small.

Computer experiments using the Monte Carlo method indeed provide us with the linear dependence of the logarithm of incubation time on inverse squared supersaturation at the decomposition of solid solution (eq. (14)). Our results of computer modeling are consistent with the predictions of CNT, in which the nucleus is born at once with almost optimal composition, and then just grows. These results are also consistent with MC simulations in [33]. The interpretation of the temperature dependence of the slope α (Fig.8) in eq.(14) will be discussed elsewhere.
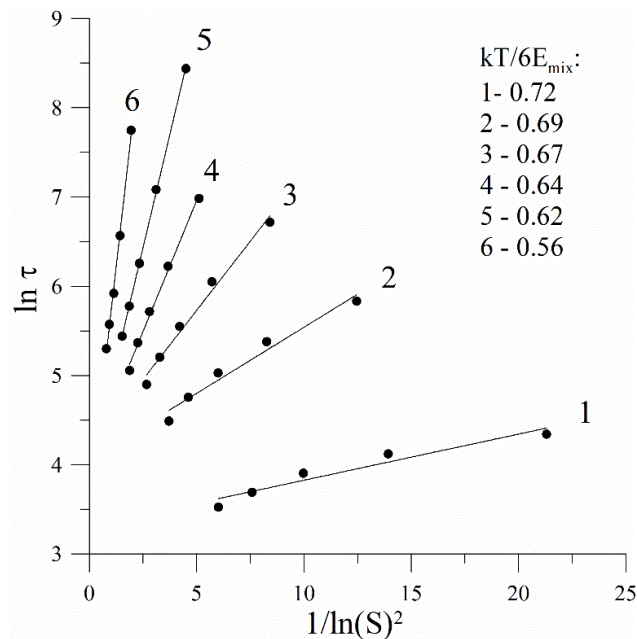
Fig. 7. Series of dependencies of the logarithm of incubation time on the inverse squared logarithm of supersaturation $S = C/C_{eq}$ at various reduced temperatures.
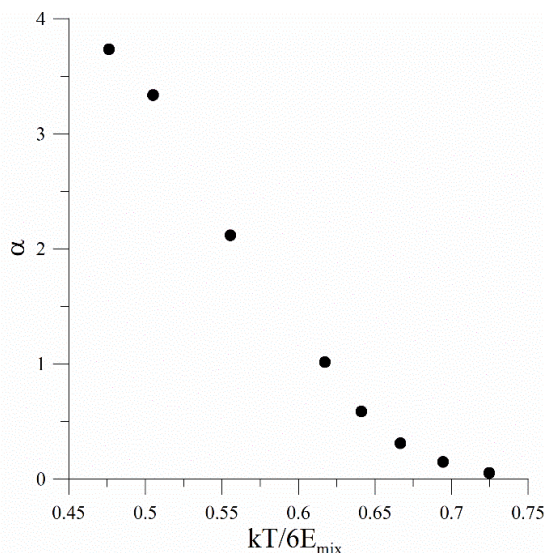
Fig. 8. Dependence of proportionality coefficient α in eq. (16) on the reduced temperature.

3.2. Nucleation in a concentration gradient: MC-simulation

Now we simulate nucleation in a sharp concentration gradient. We realize it for two cases – nucleation of the ordered phase AB of FCC-lattice (structure $L1_0$) and nucleation of the ordered AB (alpha-brass) phase B2 of BCC lattice in the nanometrically narrow diffusion couple with fixed boundary compositions. To make the intermediate phases more distinct, we introduced interactions within two coordination shells, with negative mixing energy for the nearest neighbors ($E_{mix}^{I}/kT = -0.280$) and positive mixing energy for the next-nearest neighbors ($E_{mix}^{II}/kT = 0.653$).

3.2.1. Formation of $L1_0$ ordered phase in the sharp concentration gradient

We generated diffusion couples of nanometric width and kept the compositions at the left and right boundaries constant. Our couples were 0-1, 0.05-0.95, 0.1-0.9, 0.15-0.85, 0.2-0.8, 0.25-0.75. We calculated the sum of absolute values of the local order parameters over the central plane. We fixed the formation of the intermediate phase when this sum exceeded the threshold value.

At Fig. 9, we show the logarithm of the waiting (incubation) time versus the squared concentration difference between left and right boundaries. It is proportional to the squared mean concentration gradient. Results are shown for three choices of the threshold order values (0.75, 0.775, and 0.8). These dependencies are well-approximated by linear functions which correlate well with the squared gradient term in eq. (2) for the nucleation barrier.
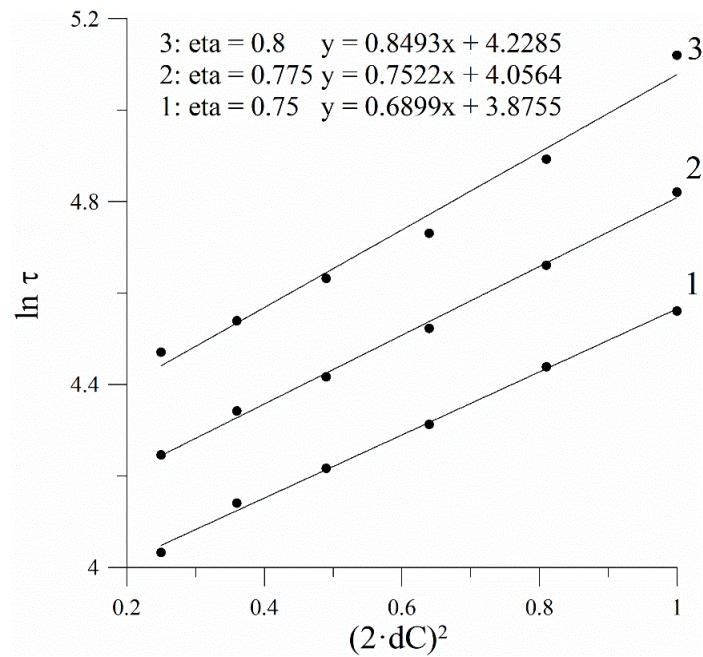
Fig.9. The logarithm of $L1_0$ intermediate phase formation time linearly depends on the squared fixed concentration step in nanometric diffusion couple. A linear fit is made for three cases with threshold order in the contact plane equal to 0.75, 0.775, and 0.8.

3.2.2. Formation of B2 ordered phase in a sharp concentration gradient

We repeated the same simulations for the nanometric couple with BCC lattice forming the intermediate phase with B2 (alpha-brass) structure. The results are similar and shown at Fig.10.
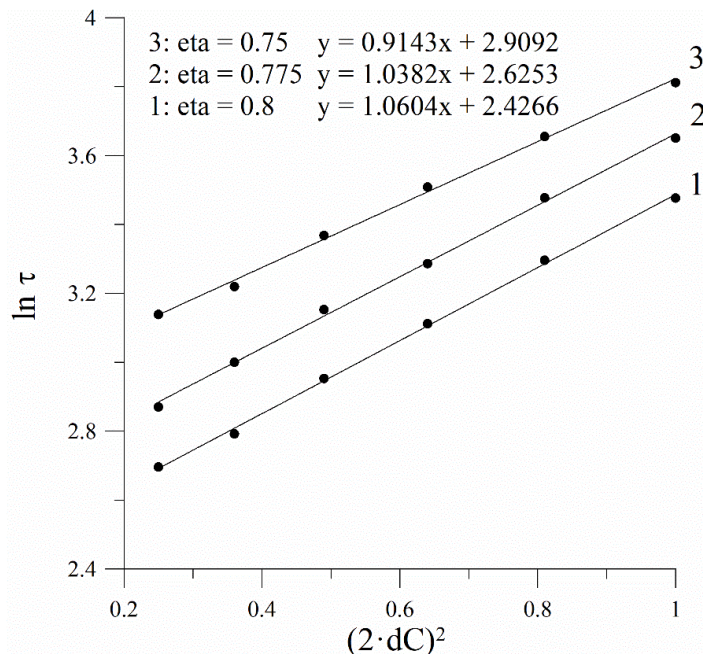

Fig.10. The logarithm of B2 intermediate phase formation time linearly depends on the squared fixed concentration step in nanometric diffusion couple.

Thus, direct computer experiments of phase formation in the contact zone correlate with our theoretical prediction of nucleation inhibition by sharp concentration gradients. Now, let us see, what real experiment tells us (Section 4).

4. Experimental verification of the concepts of kinetic and/or thermodynamic suppression of nucleation in concentration gradients

4.1. SSAR

One of the first arguments in favor of the concept of critical gradient and phase competition was the diffusion-driven amorphization at low temperature (SSAR- Solid State Amorphization Reactions). A typical example of SSAR is a reaction of nickel with zirconium [9,37,38]. At temperature 300 ^{o}C, the first phase to grow in a Ni-Zr reaction is a metastable amorphous layer with a composition of about 50 percent, instead of the "legal" (stable) crystalline intermetallics. This picture is observed when both Ni and Zr are polycrystalline providing triple grain-boundary junctions as the natural formation site for amorphous phase.

The amorphous layer starts to transform into intermetallics only after reaching a thickness of ~200 nm. The explanation seems natural: the amorphous phase has a lower driving force than the stable intermetallics but, nevertheless, it can be easily formed at the triple junctions of grain boundaries (which have very irregular structure close to amorphous) and therefore starts to grow first. Diffusion across the amorphous phase is much faster than across intermetallic, which immediately leads to the fast growth of the amorphous phase layer. This quick growth kinetically suppresses the formation of the intermetallic nuclei at the boundary of the amorphous layer according to eq. (1), as shown in [9,29].

This scenario explains the suppression of nucleation at the interface but not of nucleation inside the layer. In this case, the nucleation of intermetallics inside a preexisting amorphous inhomogeneous layer is thermodynamically suppressed by the sharp concentration gradient in a ~200-nm-thick amorphous layer, as demonstrated in [19,20] as well as in [9,39].

4.2. Phase formation and competition in multilayers

In the works of J. Perepezko's team the phase formation sequence was studied in multilayers with various wavelengths (see, for example [40,41]). In Ni-Al multilayers with large and intermediate wavelengths, the first phase formed was Al_9Ni_2. For short wavelengths, the first phase formed has a composition close to the average composition. The formation of metastable phases proves that the nucleation reaction can be controlling (metastable phase appears first if it has minimal nucleation barrier, in comparison with stable phases). For alloy systems with extensive solubility, intermediate phase nucleation proceeds by interdiffusion, which provides the supersaturation required for new phase formation. This is equivalent to the existence of the threshold concentration gradient, necessary for the phase nucleation.

4.3. Nucleation of the first phase in Co-Al reaction

Initial stages of Co-Al reaction were studied in detail in [42]. In this reaction, the first intermediate compound to form is Al_9Co_2 the intermetallic phase. Yet, by 3D atom-probe tomography it was shown that, initially, only metastable solid solution of few nanometers thickness was formed. The intermetallic compound was formed only after the thickness of solid solution exceeded some critical thickness. It is direct proof of the concept of thermodynamic suppression of nucleation by the sharp concentration gradient.

Moreover, experimental data on the formation of the Al_9Co_2 phase cannot be prescribed to the transversal nucleation mode introduced by P. Desre [19, 20]. On the contrary, polymorphic nucleation mode, introduced in [17] and modified to shape optimization in [18,21], describes the experimental results well.

4.4.   Phase formation in Cu-Si system [43]

The nucleation of the Cu3Si phase was studied by 3D atom-probe tomography in the sandwich Cu/Si/Cu "at the top of the tip" samples. The interface formed by deposition of Cu on Si is substantially broader than the interface formed by deposition of Si on Cu (5.3nm> 2.4 nm). According to our concept of nucleation in a concentration gradient, a broader interface leads to a decrease in the nucleation barrier for the Cu3Si phase. This situation is well described by the polymorphic nucleation mode, contrary to the predictions of CNT, as well as the transversal nucleation mode.

4.5.   Phase formation in Ni-Si system [44]

The reaction starts with the formation of a disordered layer with an atomic fraction of copper about 2/3. Only after this the nucleation and growth of Ni$_2$Si compound is detected. So, this also confirms the concept of critical concentration gradient.

4.6.   Phase Formation in Ni-Al system

The first verifications of the concept of critical gradients in Ni-Al reactions were obtained by Perepezko's team [41]. Possibility of metastable liquid phase formation (metastable contact melting) at temperatures below the melting point of Al was found by molecular dynamics (MD) simulations in [45]. The study of the interaction between nickel and aluminum in the SHS processes, with the formation of liquid nickel solutions in aluminum, was performed in [46]. Namely, the MD simulation of homogeneous nucleation of the NiAl intermetallic phase from the liquid solution due to cooling demonstrates the suppression of NiAl formation in the field of sharp enough concentration gradients. The gradient was simulated with keeping constant composition at the interface. It was shown that the sharper is the composition gradient, the higher is the nucleation barrier and the larger is the critical size of the nucleus. At that, the shape of the nucleus becomes more asymmetric. These results are well described by the polymorphic nucleation mode for a disc-like nucleus.

4.7.   Phase formation in copper–liquid tin systems

As we predicted in [32], the threshold scallop size, eq.(13), necessary for formation of the Cu$_3$Sn phase, should be about 500 nm. This prediction was checked recently in [47]. Copper samples were placed for very short times in a molten tin at 250°C and the studied at SEM and TEM. Exposing a foil in the liquid tin for0.04s resulted in a single η-Cu$_6$Sn$_5$ layer of 500 nm thickness at the copper/liquid tin interface. Exposing a foil in the liquid tin for 1 s has led to the formation of two intermediate phases: ~500-nm-thick $\eta - Cu_6 Sn_5$ and 100-nm-thick $\varepsilon - Cu_3 Sn$ phases. Thus, our prediction of kinetic suppression of $Cu_3 Sn$ by the fast-growing $Cu_6 Sn_5$ phase is now proven experimentally.

5.   Conclusions

Solid-state chemical reactions in the contact zone of two materials can be analyzed from the physical point of view as the alternative chains of sequential or simultaneous phase transformations in a very inhomogeneous diffusion zone. The actual chain of transformations is chosen by the condition of the fastest nucleation at each new step. Nucleation of the intermediate phases in the contact zone is controlled by two main peculiarities: (1) kinetic suppression by the diffusion fluxes across the competing growing phases, and (2) thermodynamic constraints due to sharp concentration gradients in the parent phase(s).

Kinetic suppression explains the phase formation sequence (starting from the second phase to form) in solid-solid interactions, solid-liquid interaction (soldering), point contact reactions.

Thermodynamic constraints (suppression of nucleation) explain mainly the selection of the first phase to form and grow and work mainly via the polymorphic nucleation mode in the initially formed disordered contact layer until it grows to some threshold thickness.

Acknowledgments

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