EFFECTS OF ENERGY
FLUXES ON MATERIALS

The Competition of Intermediate Phases in the Diffusion Zone

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Abstract—The competition of intermediate phases at the initial stages of reactive diffusion is analyzed in the context of two fundamental ideas that were put forward together with K.P. Gurov in 1981−1990. The first deals with the kinetic suppression of certain phases during the nucleation stage by the adjacent phase layers. The second idea considers the thermodynamic suppression of the intermediate phase nucleation due to the dependence of the nucleation barrier on the local concentration gradient in the initial phases. The critical concentration gradient makes the nucleation impossible. The experimental data are shown to justify the theoretical suppositions.

INTRODUCTION

The combination of dissimilar materials is mostly due to the mutual diffusion with the formation, growth and competition of intermediate phases. The long-term stages of this process (reactive diffusion) were theoretically described in the 1960s−1970s by K.P. Gurov and Yu.E. Ugaste [1−4]. The known analogy between phase transitions with changing temperature T and concentration C can be expanded through the comparison of the influence of temperature over time, dT/dt, and the concentration variation rate over space, dC/dx, i.e., the concentration gradient in the contact zone of materials. It is also well known that an increase in cooling rate leads to the reduction of the observed phase transition spectrum up to the quenching of the initial high-temperature state. Similar processes may arise at high concentration gradients in the contact zone as well. Meanwhile, the first algorithms for the prediction of suppression of the phase formation appeared only in the 1980s and were associated with K.P. Gurov.

The breakthrough in microelectronics led to the comprehensive study of the reactions in thin layers at the micro- or even nanolevel, first of all between the metal film and the silicon substrate in microelectronic devices. Their analysis revealed the fundamental problems of a mismatch between the observed phase composition of the diffusion zone and the appropriate state diagram [5−7], such as the alternating, but not simultaneous, phase growth, a lack of many stable phases, and the manifestation of temporary metasta-

ble buffer layers (e.g., the amorphous layer in solid-phase amorphization reactions). A solution was proposed in joint works with K.P. Gurov [8−15] by taking into account the nonequilibrium thermodynamic and kinetic conditions of intermediate phase nucleation. In this respect, the time suppression of intermediate phase nucleation was implied to be due to the two following reasons: (i) kinetic suppression of critical nuclei of the intermediate phases because of diffusion interaction with adjacent growing phase layers and (ii) thermodynamic suppression of nucleation of some phases owing to elevated nucleation barriers in regions with a high gradient of concentrations. Unfortunately, at that time, the above theories could be verified only indirectly because of experimental difficulties of direct observation of intermediate phase nuclei in the diffusion zone. However, the development of 3D atomic tomography made it possible to verify directly the concept of competitive phase nucleation in a sharp concentration gradient field. The present work is aimed at a brief review of fundamental theoretical ideas, as well as their application for the interpretation of experimental data acquired in the last years using the appropriate systems.

THE CONVENTIONAL MODEL OF FAR STAGE OF REACTION DIFFUSION IN AN UNLIMITED DIFFUSION PAIR

The flow balance equation on moving interfaces in the approximation of constant flow along the diffusion direction in each phase layer is reduced to a system of

differential equations describing the kinetics of increase in thickness of phase buffer layers [16, 17]:

$$\frac{d\Delta X_i}{dt} = \sum_{k=1}^{M} a_{ik} \frac{D_k \Delta C_k}{\Delta X_k}. \tag{1}$$

In other words,

$$\frac{d\Delta X_i}{dt} = -\frac{1}{C_i - C_{i-1}} \frac{D_{i-1}\Delta C_{i-1}}{\Delta X_{i-1}}$$
$$+ \left(\frac{1}{C_i - C_{i-1}} + \frac{1}{C_{i+1} - C_i}\right) \frac{D_i \Delta C_i}{\Delta X_i} \tag{2}$$
$$- \frac{1}{C_{i+1} - C_i} \frac{D_{i+1}\Delta C_{i+1}}{\Delta X_{i+1}},$$

where C_k is the average atomic (molar) fraction of component B in the kth phase, ΔC_k is the width of the homogeneity range of the kth phase, and ΔX_k is the thickness of the corresponding phase layer. Then $\Delta C_k/\Delta X_k$ is the concentration gradient averaged over the phase layer thickness, $D_k = \frac{1}{\Delta C_k} \int_{\Delta C_k} \tilde{D}(C)dC$ is the phase-averaged mutual diffusion coefficient, and its product by the width of the homogeneity range $D_k \Delta C_k$ is sometimes called the integral Wagner coefficient or the "diffusion permittivity." It is worth mentioning that measuring separately the concentration width of a quasi-point phase and the mutual diffusion coefficient at a very low concentration gradient inside the phase layer is a challenge, but their product can be simply expressed through the measurable values, i.e., the diffusion coefficients of labeled atoms in the phase and the thermodynamic stimulus of the formation of this phase from two adjacent states [7]:

$$D_k \Delta C_k \approx \frac{C_k(1 - C_k)(C_{k+1} - C_{k-1})}{(C_{k+1} - C_k)(C_k - C_{k-1})}$$
$$\times (D_k^{*A} C_k^B + D_k^{*B} C_k^A) \frac{\Delta g(k-1, k+1 \rightarrow k)}{k_B T}. \tag{3}$$

THE CRITERION OF SUPPRESSION AND GROWTH OF CRITICAL NUCLEI

For a system with two stable intermediate phases ($M = 2$), the matrix in the right-hand part of Eq. (1) is expressed as follows:

$$a_{ik} = \frac{1}{C_2 - C_1} \begin{pmatrix} C_2/C_1 & -1 \\ -1 & (1 - C_1)/(1 - C_2) \end{pmatrix}.$$

In accordance with the initial concept of the theory of diffusion competition between phases, the diffusion interaction of layers of critical nuclei of all intermediate phases is a priority. Within the framework of the theory, a diffusion interaction should be considered starting from a critical size of each nucleus defined by the classical theory of nucleation (but not from a zero thickness, which is impossible) [18]:

$$\left.\frac{d\Delta X_i}{dt}\right|_{\Delta X_i = l_i^{cr}} = \sum_{k=1}^{M} a_{ik} \frac{D_k \Delta C_k}{l_i^{cr}} >< 0. \tag{4}$$

The arising nuclei are predetermined by the value of the ratio $r \equiv \dfrac{D_1 \Delta C_1}{D_2 \Delta C_2} \dfrac{l_2^{cr}}{l_1^{cr}}$, yielding the following cases:

(i) If $r \equiv \dfrac{D_1 \Delta C_1}{D_2 \Delta C_2} \dfrac{l_2^{cr}}{l_1^{cr}} > \dfrac{1 - C_1}{1 - C_2}$, then $\left.\dfrac{d\Delta X_1}{dt}\right|_{\Delta X_1 = l_1^{cr}} > 0$, and $\left.\dfrac{d\Delta X_2}{dt}\right|_{\Delta X_2 = l_2^{cr}} < 0$. At the initial stage, phase layer 1 increases, and phase 2 is inhibited by the diffusion, because its nuclei at the interface 1/B, induced by heterophase fluctuations, are dissolved by the growing phase 1.

(ii) If $\dfrac{C_1}{C_2} < r \equiv \dfrac{D_1 \Delta C_1}{D_2 \Delta C_2} < \dfrac{1 - C_2}{1 - C_1}$, then $\left.\dfrac{d\Delta X_1}{dt}\right|_{\Delta X_1 = l_1^{cr}} > 0$ and $\left.\dfrac{d\Delta X_2}{dt}\right|_{\Delta X_2 = l_2^{cr}} > 0$, and both phases grow from the outset.

(iii) Finally, if $\dfrac{C_1}{C_2} < r \equiv \dfrac{D_1 \Delta C_1}{D_2 \Delta C_2} \dfrac{l_2^{cr}}{l_1^{cr}}$, then $\left.\dfrac{d\Delta X_1}{dt}\right|_{\Delta X_1 = l_1^{cr}} < 0$ and $\left.\dfrac{d\Delta X_2}{dt}\right|_{\Delta X_2 = l_2^{cr}} > 0$. In that case, phase layer 2 grows during the initial stage, and phase 1 is diffusionally suppressed; i.e., nuclei of phase 2 at the interface A/2 are due to heterophase fluctuations, but dissolve in the growing phase 2.

It is natural that the phase suppression is not ultimate if one does not consider a film with limited amount of one of the reactants. So, in the first case, the suppression criterion of nuclei of phase 2 varies during the growth of phase layer 1, because it depends on the flow through phase 1 and, consequently, on the thickness of the latter:

$$\left.\frac{d\Delta X_2}{dt}\right|_{\Delta X_2 = l_2^{cr}} = -\frac{D_1 \Delta C_1}{\Delta X_1} + \frac{1 - C_1}{1 - C_2} \frac{D_2 \Delta C_2}{l_2^{cr}} < 0. \tag{5}$$

This condition is implemented until the thickness of the inhibiting phase 1 is below some critical value (meaning the suppression of neighbors, but not the characteristic nucleation):

$$\Delta X_1 < \Delta X_1^* = \frac{1 - C_2}{1 - C_1} \frac{D_1 \Delta C_1}{D_2 \Delta C_2} l_2^{cr}. \tag{6}$$

THREE NUCLEATION MODES IN THE CONCENTRATION GRADIENT FIELD

The nucleation barrier during the formation of the intermediate phase in the diffusion zone must be calculated by considering the redistribution of components beyond the forming nucleus. In connection with this, the problem of nucleation in a nonuniform system must be solved with some restrictions that are
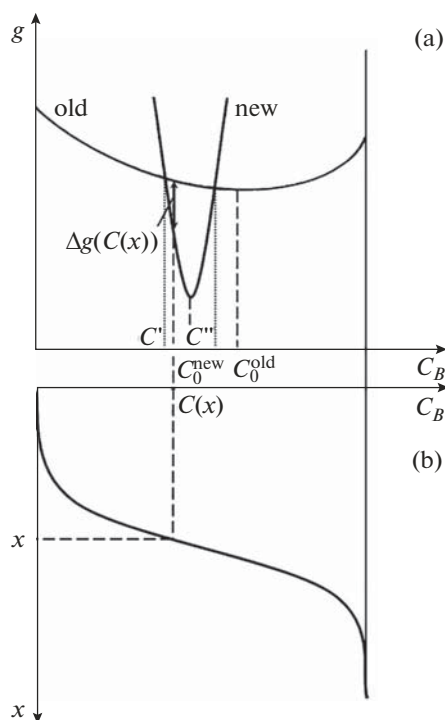
Fig. 1. Nucleation at polymorphic mode and frozen concentration profile: (a) free energy per atom versus composition of old and new phases; (b) frozen profile is approximately linear within the diffusion zone.
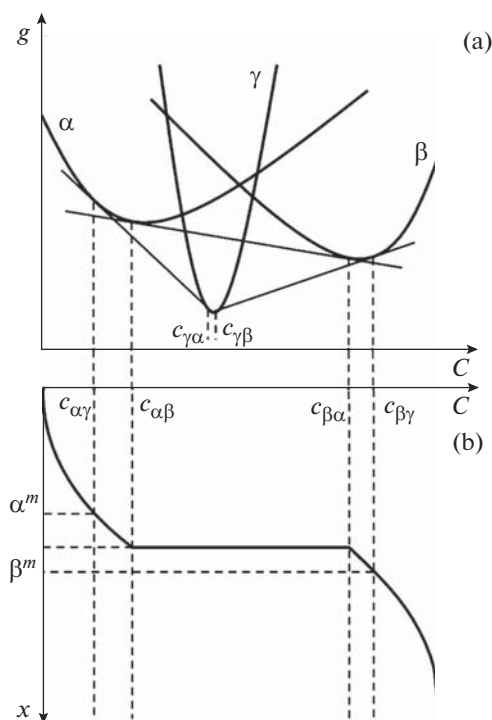

Fig. 2. (a) Stable and (b) metastable equilibrium in a binary system with limited solubility. Compositions within the intervals of $(c_{\alpha\gamma}, c_{\alpha\beta})$ and $(c_{\beta\alpha}, c_{\beta\gamma})$ make possible nucleation of the γ phase.

determined by the kinetics of diffusion. Depending on the type of limitations applied, one can distinguish three nucleation modes:

(i) Polymorphic mode [12, 13]. This mode takes place when the maternal metastable (such as amorphous) phase can exist over a broad enough concentration range for the new phase formation. The mutual diffusion in the maternal phase during the first stage yields the concentration profile with a concentration range where the new intermediate phase has the lowest Gibbs potential (Fig. 1). Subsequently, the polymorphic transformation favors the nucleation of the new phase at a constant concentration gradient, which is then followed by diffusion. The emerging nuclei interact with the maternal phase because of abruptly changing diffusion flows at the interfaces. The parental phase can be a metastable solid solution or an earlier formed amorphous layer.

(ii) Transversal mode [19, 20]. This type of nucleation mode is possible in both situations illustrated in Figs. 1 and 2. In the case of Fig. 2, the mutual diffusion prior to the nucleation of the ith phase leads to $\alpha-\beta$ "meta-quasi-equilibrium" with metastable concentration ranges $(c_{\alpha\gamma}, c_{\alpha\beta})$ and $(c_{\beta\alpha}, c_{\beta\gamma})$ that are unsteady relative to the decay into $\alpha + \gamma$ and $\gamma + \beta$. According to [19, 20], the nucleation in a concentration gradient in the x direction is represented by a situation where each thin layer $(x, x + dx)$ of this nucleus is formed by the unlimited redistribution of components within this layer independently of other layers. The concentration $C^{new}(x)$ in this nucleus layer is determined by the concentration $C^{old}(x)$ in the environment (for the same layer) in accordance with the rule of parallel tangents (not a common tangent), i.e., $\partial g^{new}/\partial C^{new} = \partial g^{old}/\partial C^{old}$. It is obvious that the transversal mode is implementable if the diffusion coefficient in the maternal phase is much larger than that in the new phase ($D_m \gg D_i$).

(iii) Total mixing/longitudinal mode [21−23]. This mode assumes the nucleation on account of the transformation of maternal phase sites only in the bulk of the future nucleus at the same concentration beyond it. It is clear that the mode takes place when the diffusion coefficient of the intermetallic is significantly above that of the parental phase ($D_i \gg D_m$).

In accordance with theoretical predictions, the dependence of the Gibbs potential on the nucleus size for the total metastable solubility (Fig. 1) is as follows:

$$\Delta G = \alpha R^2 - \beta R^3 + \gamma (\nabla C)^2 R^5, \qquad (7)$$

where coefficient g is positive for the polymorphic and transversal modes, negative for the longitudinal mode, and proportional to the second derivative of the Gibbs potential with respect to concentration.

In the case of limited metastable solubility (Fig. 2) [24], this dependence takes the following form:

$$\Delta G = \alpha R^2 - \beta R^3 + \lambda (\nabla C)^2 R^4. \qquad (8)$$

In both situations, the presence of the concentration gradient in the polymorphic or transversal mode increases the nucleation barrier, and this dependence at the gradient above some critical value (in case 1, $\nabla C > (\nabla C)^{\mathrm{crit}} \approx \frac{\beta}{\alpha} \sqrt{\frac{\beta}{5\gamma}}$) is found to be monotonically increasing; i.e., the intermediate phase nucleation in too narrow a concentration gradient seems to be impossible. This shows that no intermediate phase can be expected in a very narrow diffusion zone of the maternal phase. The experimentally evaluated critical thickness of the diffusion zone ranges from several to tens of nanometers.

EXPERIMENTAL CONFIRMATION OF THE CONCEPT OF DIFFUSION PHASE COMPETITION AND CRITICAL GRADIENT

Amorphization in Ni–Zr System

One pioneering verification of the concept of critical gradient and phase competition was the explanation of diffusion amorphization upon the low temperature reaction of nickel with zirconium [25–27]. Instead of crystalline intermetallics, a fine crystalline nickel–polycrystalline zirconium diffusion pair exhibits an amorphous buffer at a temperature of 300°C, which begins to transform into intermetallics only after achieving a thickness of ~200 nm. This effect is explained by the fact that the amorphous phase has no obstacles to be born at triple junctions of grain boundaries and therefore begins to grow first, and its comparatively quick growth kinetically inhibits the emergence of intermetallic nuclei at the boundary of the amorphous buffer. In this case, the nucleation of intermetallics inside a buffer layer is thermodynamically suppressed because of the abrupt concentration gradient in a ~200-nm-thick amorphous layer.

Phase Formation in Co–Al System [28]

This system exhibits a delay in the development of the first Co_2Al_9 phase in Al/Co thin films, which can be interpreted within the concept of critical concentration gradient as a result of thermodynamic suppression of phase nucleation due to the sharp composition gradient in the diffusion zone. Experimental data on delayed formation of the Co_2Al_9 phase cannot be explained by the action of the transversal mode of nucleation [19, 20], whereas involvement of the polymorphic mode of nucleation with completely optimized shape of nuclei causes a release of overly small Co_2Al_9 particles in the concentration gradient direction. Only a polymorphic mode with limited shape

optimization or without it describes the experimental results well.

Phase Formation in Cu–Si System [29, 30]

The nucleation of the Cu_3Si phase was studied on three-layer Cu/Si/Cu samples in both the curvilinear and plane geometries. Atomic probe tomography confirms that the boundary of Cu on Si is much broader than that of Si on Cu (5.3 and 2.4 nm, respectively). It is shown that improved stirring on the upper interface leads to a decrease in the nucleation barrier for the silicide phase. The presence of the barrier for a narrow interface, as well as its lack for a broad interface, is adequately described in the case of polymorphic nucleation, whereas the attempts to explain this effect via the classical theory of nucleation and the model of transversal nucleation model failed.

Phase Formation in Ni–Si System [31]

The beginning of the process starts with the emergence of a disordered (amorphous) buffer layer with a nickel-to-silicon ratio of 2 : 1, which is afterwards the basis for the well-known Ni_2Si phase. Previously, the latter was thought to form first.

Phase Formation in Ni–Al System [32, 33]

The first independent confirmations of the validity of the concept of critical gradient were obtained on Ni–Al multilayers in [32]. Study of the interaction between nickel and aluminum in the SHS processes, which may favor the formation of liquid nickel solutions in aluminum, is of particular interest. The molecular dynamics simulation of homogeneous nucleation of the NiAl intermetallic phase from the liquid solution upon cooling means the inhibition of this phase transition in the presence of concentration gradients. The gradient was simulated on account of the constant composition at the interface between two materials. An increase in the composition gradient enlarged the energy barrier of nucleation and the critical size of the nucleus, while the nucleus itself became more asymmetric. These results were shown to be well described by the polymorphic nucleation mode for a disklike nucleus.

Phase Formation in Point Reactions between Ni (Co) and Si Nanowires [34–36]

A curious manifestation of phase competition and nucleation is observed in reactions through a point contact between Si and Ni (or Co) nanowires. For nickel, the first phase that germinates and develops is not Ni_2Si, but NiSi. Moreover, this phase arises far from the contact, growing in accordance with a "stop-and-go" mechanism [35]. Nucleation on the contact
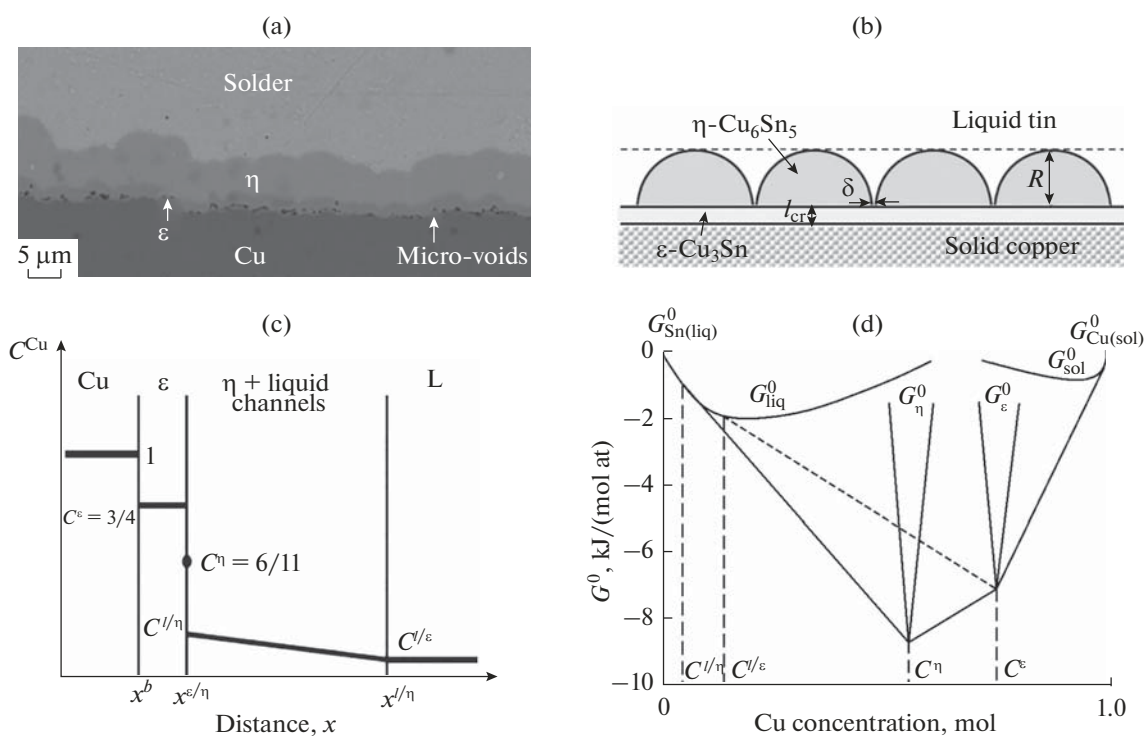
Fig. 3. Phase formation in the copper/liquid tin system: (a) SEM picture of the Cu/Sn contact zone after 7 days of aging at 180°C; voids are formed through the ε-Cu$_3$Sn phase; (b) schematic image of morphology of the η-Cu$_6$Sn$_5$ and ε-Cu$_3$Sn phases; (c) diagram of change in Cu concentration; (d) Gibbs free energies of the main phases versus composition in the Cu/liquid tin system [37].

is likely to be suppressed because of the large current density through a point contact.

Phase Formation in Copper—Liquid Tin System

Copper is frequently used in solder joints as a base layer that provides good mechanical contact owing to the chemical reaction with liquid tin or alloys on its basis. The ε-Cu$_3$Sn and η-Cu$_6$Sn$_5$ intermetallic compounds corresponding to a Cu—Sn phase diagram are formed at the interface between pure metals at conventional soldering temperatures (<350°C). Because of continuous miniaturization of solder joints in the modern microelectronics (the diameter of a solder ball can be less than 20 μm), the competition and growth of phases at the interface may play a significant role owing to the fact that the volume of intermetallics formed between the copper and the tin solder may dominate over the solder ball volume. In this respect, the properties of the entire compound will depend on the physical and chemical characteristics of intermetallics. So, the mechanical properties of a solder joint may be improved via a specific scallop-like shape of the η-Cu$_6$Sn$_5$ phase. At the same time, spherical secretions of the ε-Cu$_3$Sn phase, whose dimensions were several times less than the thickness of secretion of the η-Cu$_6$Sn$_5$ phase, exhibit pores induced through

the Kirkendall effect, which may be germination sites cracks (Fig. 3a).

The nucleation and competitive growth of these phases were the objects of extensive research in the last decades. The phase formation sequence and the criteria of inhibition of the ε-Cu$_3$Sn phase by the rapidly growing η-Cu$_6$Sn$_5$ phase were studied theoretically [37, 38] and then experimentally [39].

The inhibition of the normal growth of the ε-Cu$_3$Sn layer [37] with already some critical thickness l_{cr} (Fig. 3b), as well as the suppression of the lateral growth of nanoislets of this phase by the rapidly growing η-Cu$_6$Sn$_5$ phase [38], was simulated.

The shape of the growing η phase for simulating the inhibition of the growth of the ε-phase layer was set by hemispheres with the same radii R, separated by nanoscale channels with width δ and contacting the ε-Cu$_3$Sn layer (Fig. 3b). During the soldering, these nanochannels were filled with liquid tin in order to accelerate the transfer of copper atoms to the Sn/η-Cu$_6$Sn$_5$ interface and the rapid growth of the η phase. In the context of the law of conservation of matter for two moving plane boundaries I (copper/ε) and II (ε/η) and one averaged boundary III (η/liquid tin), one has the following expressions:
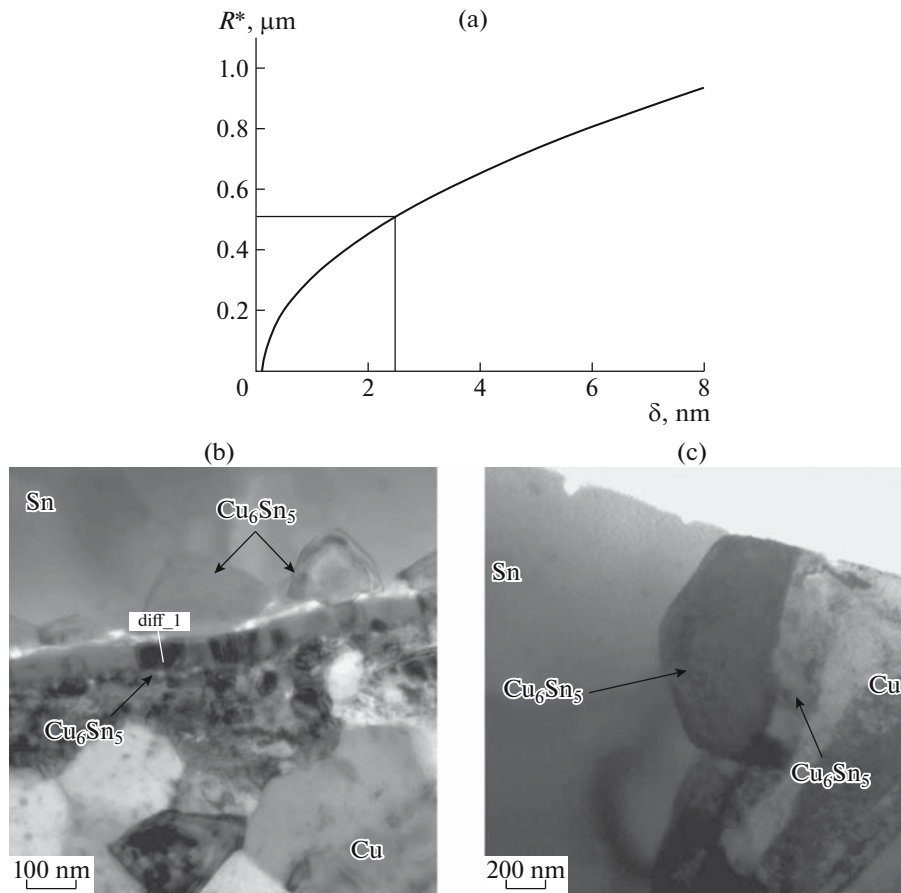
Fig. 4. Suppression of the ε-Cu$_3$Sn phase growth by the formation of the scallop-like η-Cu$_6$Sn$_5$ phase: (a) critical thickness of η-Cu$_6$Sn$_5$ versus liquid channel diameter; (b) TEM image of the Cu/Sn interface after reaction for ~50 ms, the η-Cu$_6$Sn$_5$ layer thickness is ~100 nm, no Cu$_3$Sn phase observed; (c) TEM image of the Cu/Sn interface after reaction for 1 s, the η-Cu$_6$Sn$_5$ layer thickness is ~500 nm, the thickness of Cu$_3$Sn phase is ~100 nm [39].

$$\text{I: } (1-c^\varepsilon)\frac{dx^{Cu/\varepsilon}}{dt} = 0 - \frac{\tilde{D}^{(\varepsilon)}\Delta c_\varepsilon^{eq}}{l_{cr}},$$

$$\text{II: } (c^\varepsilon - c^\eta)\frac{dx^{\varepsilon/\eta}}{dt} = \frac{\tilde{D}^{(\varepsilon)}\Delta c_\varepsilon^{eq}}{l_{cr}}$$

$$- \frac{\delta D_{Cu}^{melt}}{R^2}(c^{l/\varepsilon} - c^{l/\eta}), \qquad (9)$$

$$\text{III: } (c^\eta - 0)\frac{dx^{\eta/Sn}}{dt} = \frac{\delta D_{Cu}^{melt}}{R^2}(c^{l/\varepsilon} - c^{l/\eta}),$$

where $c^\varepsilon = 3/4$ and $c^\eta = 6/11$ are the copper concentrations in the ε and η phases, respectively; $c^{l/\eta}$ and $c^{l/\varepsilon}$ are the equilibrium copper concentrations at the η-Cu$_6$Sn$_5$/liquid and ε-Cu$_3$Sn/liquid tin interfaces (Figs. 3c and 3d); $\tilde{D}^{(\varepsilon)}\Delta c_\varepsilon^{eq}$ is the integral diffusion coefficient in the ε-Cu$_3$Sn phase; and $\tilde{D}^{(\varepsilon)}\Delta c_\varepsilon^{melt}$ is the diffusion coefficient of copper in liquid tin. Thus, the expression for the growing ε-Cu$_3$Sn phase is

$$\left.\frac{d\Delta x^\varepsilon}{dt}\right|_{l_{cr}} = \left(\frac{1}{c^\varepsilon| - c^\eta} + \frac{1}{1-c^\varepsilon}\right)\frac{\tilde{D}^{(\varepsilon)}\Delta c_\varepsilon^{eq}}{l_{cr}}$$

$$- \frac{1}{c^\varepsilon - c^\eta}\frac{\delta D_{Cu}^{melt}}{R^2}(c^{l/\varepsilon} - c^{l/\eta}). \qquad (10)$$

Taking into account the growth condition of the ε-Cu$_3$Sn phase ($d\Delta x^\varepsilon/dt > 0$), the growth criterion of the ε-Cu$_3$Sn phase depending on the thickness of the η-Cu$_6$Sn$_5$ phase takes the form

$$R > R^* = \sqrt{\frac{(c^{l/\varepsilon} - c^{l/\eta}(1-c^\varepsilon)}{(1-c^\eta)}\frac{D_{Cu}^{melt}}{\tilde{D}^{(\varepsilon)}\Delta c_\varepsilon^{eq}}\delta l_{cr}}. \qquad (11)$$

Substituting the numerical parameters (concentrations $c^{l/\eta} = 0.023$ and $c^{l/\varepsilon} = 0.032$, being equilibrium at a temperature of 523 K and calculated via the CALPHAD method, and the diffusion coefficients $\tilde{D}^{(\varepsilon)}\Delta c_\varepsilon^{eq} = 0.87 \times 10^{-16}$ m^2/s and $D_{Cu}^{melt} = 10^{-9}$ m^2/s) into Eq. (11), as well as taking a critical thickness of 1 nm of the ε-Cu$_3$Sn phase, we obtain a trivial mathe-

matical criterion of its existence as a function of the liquid channel diameter between scallops of the η-Cu_6Sn_5 phase. Thus, the critical η-Cu_6Sn_5 scallop radius below which the formation of ε-Cu_3Sn is suppressed can be evaluated as

$$R^* = 333\sqrt{\delta} \qquad (12)$$

(if both magnitudes are given in nanometers). Substituting a realistic channel diameter $\delta = 2.5$ nm gives a value $R^* = 500$ nm (Fig. 4a) [37].

This theoretical evaluation was justified by experimental works on the initial stages of reactions in a solid copper/liquid tin pair. In those measurements, copper foils were immersed in a liquid tin melt at a temperature of 250°C by means of a specially designed pneumatic system. After that, the reactive layers were probed via scanning and transmission electron microscopy [39]. It was found that exposing a foil for 40 ms yields a single η-Cu_6Sn_5 layer 500 nm thick at the copper/liquid tin interface (Fig. 4b), whereas immersing a foil in the melt for 1 s leads to the formation of both thermodynamically equilibrium phases at the interface, which are ~500-nm-thick η-Cu_6Sn_5 and 100-nm-thick ε-Cu_3Sn phases (Fig. 4c).

CONCLUSIONS

A study of the structural phase state in various systems via advanced experimental methods was shown to confirm the validity of K.P. Gurov's concept of competition between inhibition and growth of phases at the nucleation stage. In particular, the concept of thermodynamic suppression of intermediate phase germination at a sharp concentration gradient in metastable strongly nonuniform crystalline or amorphous solutions was experimentally justified. The results revealing the implementation of the theoretically predicted polymorphic nucleation mode in the contact zone were discussed as well.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

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