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Introduction

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While writing the introduction to our book, I had in front of me the cover of the book by Slezov “Kinetics of first-order transitions,” which was then almost ready for publication and has now been published by Wiley-VCH. This book is written by the “S” in the famous LSW (Lifshitz–Slezov–Wagner) theory of coarsening and will undoubtedly become a milestone in theoretical materials science. Our book is a logical (though, due to the complexity of the phenomena discussed, much less rigorous) continuation of Slezov’s book, because it treats the kinetics of first-order transitions in open inhomogeneous systems, characterized by sharp gradients of chemical potentials and bypassing fluxes of matter, charge, and heat.

Solid state reactions (SSRs) are obviously the most interesting topic in the world since they mean birth, competition, and growth of new “worlds” (phases) as a result of interactions between parent phases. So, those who plan, realize, and analyze SSRs, are in fact the local gods with their six days (hours, seconds) of creation/annealing. SSRs are governed by two magic powers – thermodynamics and kinetics. Thermodynamics is something like a parliament, which decides how things should evolve, what is possible and impossible. Kinetics is something like a government or a local authority. It implements (or delays the implementation of) the laws given by the parliament. Common understanding is that kinetics determines only the rate of fulfilment (implementation) of thermodynamic laws. In this book we will see that life is more complicated.

For systems far from equilibrium, the problem of evolution path choice of an appropriate path of evolution appears frequently – which way to the equilibrium (among a variety of possibilities) should a system choose, and what factors influence the decision-making procedure. Well-known examples of such systems are the diffusion couples for reactive diffusion in binary and especially, ternary systems and supersaturated highly defectuous alloys. For a rather long time, the phase spectrum of such nonequilibrium systems differs significantly from the equilibrium phase diagram. From the theoretical point of view, the best way of solving the problem of choice would be some kind of Prigogine-like principle. Yet, up to now there has been no simple algorithm that would allow one to predict, say, the sequence of phase formation by calculating, for example, the rate of free energy changes

for different evolution paths. Moreover, in Chapter 11 we will see that Prigogine's principle cannot help us in this situation. So, to make some predictions, one should take into account the initial stage of the system's evolution including nucleation of the new phase.

It has been well known for several decades that reactive diffusion in thin films usually demonstrates "one-by-one" (sequential) phase formation. Despite the existence of several stable intermediate phases in the phase equilibrium diagram, only one growing phase layer is usually observed. The next phase appears or at least becomes visible, after one of the terminal materials has been consumed, so that the first phase has no more material for growth, becoming a material for second phase formation itself, and so on. Such sequential growth has at least three possible explanations:

1) "Just Slow Growth".

The first phase to grow usually has the maximum diffusivity and, hence, grows fast (according to d'Heurle, "fast is the first" or "first is fast"). Other phases, with lower diffusivities, grow even more slowly than they could do alone. It means that if, by some reason (for example, nucleation problem), the fast growing phase would be missing, other phases would grow faster. Thus, according to this first explanation, other phases exist and grow, but too slowly, and their layers are so thin, that it is just difficult to detect them.

2) Interfacial Barriers Plus Competition (Gösele and Tu, 1982).

Interfacial barriers are believed to cause the initial linear phase growth. In the case of single-phase formation the interfacial barriers simply slow down the rate of formation, making it linear instead of parabolic. For two phases, the barriers can make the growth rate of a certain phase formally negative even for zero thickness, which means that this phase will be not be present at all.

3) Diffusive Suppression of Critical Nuclei.

In 1981, one of the authors (AMG) jointly with his teacher, the late Professor Cyrill Gurov (Institute for Metallurgy, Moscow) presented a simple (even "naive," as we see it today) model of phase competition taking into account the nucleation stage of each phase. Actually, the only concept, which had been taken in this initial work from the nucleation theory, was the existence of critical nuclei. They appear due to some miracle called *heterophase fluctuations*, which are stochastic events and cannot be described by some deterministic model. The initial idea was just that each phase cannot start from zero thickness – it should start from a critical size particle (about a nanometer). Contrary to standard nucleation theory, the critical nuclei of intermediate phases during reactive diffusion are formed in a strongly inhomogeneous region – the interface between other phases. Therefore, from the very beginning they have to allow the diffusion fluxes pass through themselves. Evidently, fluxes change abruptly when passing across each new-formed boundary of the newly formed nucleus, and thus drive the boundary movement. This picture of interface movement due to flux steps is well known for diffusion couples under the name of *Stephan problem* and refers to diffusive interactions between neighboring phases. Yet,

the initial width of each phase is taken to be the critical nucleus size (instead of zero). The peculiarity of the initial stage is just the possibility that the width of some phase nucleus (distance between left and right boundaries) can decrease as well as increase. If it decreases, the nucleus becomes subcritical and should disappear. Usually it happens if the neighboring phases have larger diffusivity and comparative thickness. Then these neighbors (“vampires” or “sharks”) will destroy and consume all of the newly forming nuclei, making the new phase to be present only virtually – in the form of constantly forming (due to heterophase fluctuations) and vanishing (due to diffusive suppression by the neighbors) embryos.

Both models (b and c) (published simultaneously) predict suppression/growth criteria and a certain critical thickness of the first growing phase under which growth of other phases is kinetically suppressed. A simple mathematical scheme was built predicting the sequence of phase formation and incubation periods, provided that one knows the integrated Wagner diffusivities and critical nucleus size for each phase. The most simple example of this scheme is presented in Chapter 3. This scheme was applied to the competition of intermediate phase with solid solutions (Chapter 3), to the phase growth under strong electric current (jointly with Semen Kornienko, Chapter 8), to reactive diffusion in ternary systems (jointly with Semen Kornienko and Yuriy Lyashenko, Chapter 9), and to phase competition in reacting powder systems. Applications to the electric field case demonstrated that the phase spectrum in the reaction zone can be influenced and even controlled by sufficiently strong current density. Large current densities become real due to miniaturization of integrated schemes and introduction of the flip-chip technology. Latter results on reactive diffusion in UBM-solder contacts (UBM-standard abbreviation for “under-bump metallization” in microelectronics) under strong current crowding confirm the mentioned idea: without current or under a weak current, the reaction between copper and a dilute solution of tin in lead at 150 °C demonstrates only Cu_3Sn_1 phase formation. A current density of $j > 10^8 \text{ A m}^{-2}$ leads to the formation and fast growth of the Cu_6Sn_5 phase.

In our naive model of phase competition, we had taken the inhomogeneity of the nucleation region into account only partially. For instance, we treated the diffusive interactions of the newly formed nuclei, but we had not considered the possible change of the nucleation barrier, size, and shape, caused by the very fact of the existence of a sharp concentration gradient. Thus, we had to reconsider the thermodynamics of nucleation in a concentration gradient. The very first version of such theory was presented at DD-89 “river Volga boat-conference” in Russia and first published in the Ukrainian Journal of Physics in May 1990. The main idea was as follows: if, prior to intermediate phase formation, a narrow layer of the metastable solid solution or amorphous alloy had been formed at the base of the initial interface, the sharp concentration gradient inside this layer provides the decrease of the total bulk driving force of nucleation, and correspondingly the increase of the nucleation barrier. The nuclei were taken to be spheres, appearing in the strongly inhomogeneous concentration profile of the parent phase, so that the

local driving force of transformation could change significantly from the left to the right along the diameter of the nucleus. This effect appeared to be nonnegligible, since the intermediate phases usually have a very strong concentration dependence on the Gibbs free energy. The main result was a principally new size dependence of the Gibbs free energy it contained, in addition to the terms of second-order (surface energy, positive) and third-order (bulk driving force, negative), and a new term proportional to the fifth power of size and the square of the concentration gradient, that is,

$$\Delta G(R) = \alpha R^2 - \beta R^3 + \gamma (\nabla c)^2 R^5 \quad (1.1)$$

Here the parameter γ has positive values and is proportional to the second-order derivative of the new phase Gibbs energy with respect to concentration. Equation 1.1 implies that for rather large gradients (typically larger than 10^{+8} m^{-1} (one hundred millions reciprocal meters) which means diffusion zone of about 10^{-8} m thickness), the dependence becomes monotonically increasing (infinitely high nucleation barrier) meaning thermodynamic suppression of nucleation by very sharp concentration gradients. Thus, according to our model, at the very initial stage of reactive diffusion, nucleation can be suppressed even without diffusive competition, due to a too narrow space region, favorable for transformation. Similar results were independently published by Pierre Desre *et al.* in 1990 and 1991. This approach had been applied then to the description of solid-state amorphizing reactions, explaining why stable intermetallics appear in the diffusion zone only after the amorphous layer exceeds some critical thickness.

Despite the similarity of the results, our models of nucleation in a sharp concentration gradient treated quite different possible mechanisms (nucleation modes). We treated a polymorphous mode keeping in mind the following picture: The initial diffusion leads to the formation and growth of a metastable parent solution with a sharp concentration profile. When this profile becomes smooth enough to provide sufficient space for compositions favorable for a new intermediate phase, this very phase nucleates just by reconstruction of atomic order, without immediately changing the concentration profile (at “frozen” diffusion) – polymorphic transformation. Desre suggested the transversal nucleation mode bearing in mind the following case: each thin slice of the newly formed nucleus, perpendicular to the direction of the concentration gradient, is considered as a result of decomposition in a corresponding thin infinite slice of the parent solution, leading, of course, to a redistribution of atoms among new and old phases. In this transversal mode, the redistribution proceeds within each slice, independent of others.

In 1996, one more mechanism had been suggested by Hodaj – the total mixing (longitudinal) nucleation mode, when the redistribution of atoms proceeds during nucleation, but only inside the newly forming nucleus. Contrary to the two previous modes, in this case the concentration gradient assists nucleation – in Equation 1.1, the coefficient γ is negative. The above-mentioned approach was generalized taking into account shape optimization, stresses, ternary systems, heterogeneous nucleation at grain boundaries and at interphase boundaries. Readers will find an almost full description in Chapter 4. The latest

developments of this approach including atomic tomography experiments by Guido Schmitz and Monte Carlo simulations of Mykola Pasichnyy are described in Chapter 5.

It is quite possible to expect that nature will commonly use the mechanism with the lowest nucleation barrier – the total mixing mode. Yet, nucleation is ruled not only by thermodynamics but by kinetics as well. Thermodynamics of nucleation with constraints indicates only some probable paths of evolution. The real path is chosen by kinetics, taking into account not only the free energy profit, but also different “mobilities” along each path. Mobilities often appear to be inverse to profit – a kind of compensation rule, analogous to the relation between activation enthalpy and frequency factor in diffusion.

To understand nucleation kinetics quantitatively, we used the Fokker–Planck approach, first applied to nucleation problems by Farkas and recognized after the classical work of Zeldovich. Our contribution to this approach was just taking into account that the driving force depends on the concentration gradient, which in turn depends on time according to diffusion laws. It has been shown that the relative contribution of each mechanism depends on the ratio of atomic mobilities in the parent to that in nucleating phases. If atomic mobility in the new phase is much lower than in the parent one, we can forget about total mixing mode. In the opposite case (high mobility inside the new phase), nucleation will proceed via total mixing, in the very fast (“fast is the first”) mode. One of the “raisins” of the total mixing (assisting) mode was that the easily formed nuclei, if not growing too fast in comparison with the decrease of the concentration gradient, after some period can find themselves to be subcritical and be destroyed. Unfortunately, so far we could not check the mentioned “kinetic nucleation” results experimentally, so, we did not risk including them in our book.

After discovering that a concentration gradient can function as a constraint on nucleation, it was natural for us to start looking for other constraints. Sharp concentration gradient means narrow layers, suitable for nucleation, for example, limited volume. So, the most natural thing was to treat the nucleation in small (nano-size) particles and multiple simultaneous nucleations during formation of bulk nanocrystalline materials. We tried it with Aram Shirinyan (Chapter 13). The main result was as follows: depending on the volume of the parent particle (or, in bulk, on the volume of “responsibility region” around the nucleation site), the same three possibilities exist as in a sharp concentration gradient – nucleation and growth (large size), metastable state (medium size), and forbidden nucleation (small size). Later we learned that similar results had been published by Rusanov 40 years earlier and later developed by Schmelzer *et al.* Yet, we hope that our application of these ideas to the “traffic jam” effect in bulk glasses might be of some interest: when many persons try to pass through a narrow door simultaneously, the process stops. A similar effect can be responsible for long-living nanocrystalline states. Moreover, we tried to generalize this approach to the case of competitive nucleation of two intermediate phases in nanovolumes. Later, Aram Shirinyan and I, jointly with Michael Wautelet, concluded that the common notions of phase transitions (like phase diagrams)

should be revised accordingly in the case of transformations in nanosystems. This approach is not commonly accepted yet, and is also discussed in Chapter 13.

Diffusion controlled SSRs are, in fact, phase transitions in a concentration gradient. It is very important to keep in mind that the controlling step is not just diffusion but interdiffusion. It means that in most SSRs the vacancy fluxes appear as a result of different mobilities of diffusing species. Divergence of vacancy fluxes leads to competing Frenkel (Kirkendall) voiding and Kirkendall shift, depending on the relative efficiency of voids and dislocation kinks as vacancy sinks/sources. Competition of Frenkel and Kirkendall effects recently (in 2004) found interesting applications in the new method of hollow nanoshell production by SSRs (by Paul Alivisatos group). In this method, metallic nanoparticles react with oxygen or sulfur forming a compound in which metal atoms diffuse outside faster than oxygen or sulfur diffuse inside. Thus, the vacancy flux directed inside eventually leads to a hollow nanostructure with a central symmetric void. Tu and Gösele immediately noticed that such structures should be unstable due to the Gibbs–Thomson effect: the vacancy concentration at the inner shell boundary should be higher than that at the external one. Therefore, a vacancy gradient should exist leading to vacancy outflux and corresponding void shrinkage. Together with King-Ning Tu and Tatyana Zaporozhets, we analyzed the process of formation and collapse of nanoshells taking into account not only Frenkel, Kirkendall, and Gibbs–Thomson effects, but the inverse Kirkendall effect as well (segregation in the vacancy flux and corresponding damping of shrinking rate). We also demonstrated that the Gibbs–Thomson effect is important not only at the shrinking stage but also at the stage of formation, and may suppress the formation itself. These results are discussed in Chapter 7. Very recent results of Nakamura *et al.* (2008) prove that the shrinkage process is very real. In the same Chapter 7, we present a model of nanovoid evolution under high-density electric current in copper interconnects of VLSI (Very Large Scale Integrated) circuits. This model explains the recent discovery of a new failure mechanism by electromigration, when failure happens due to drift and coalescence of nanovoids along copper/dielectric interface instead of migration of individual vacancies. The latter two mentioned problems are examples of the flux-driven morphology of evolution. This general concept was formulated jointly with Professor King-Ning Tu.

In 2001, I visited Professor Tu at the Department of Materials Science at UCLA (Los Angeles) for the first time. These two months of stay were rather dramatic (they overlapped with the 9/11 tragedy). On the other hand, the joint work with Professor Tu appeared to be really exciting – we tried to theoretically address a very complicated experimental problem – the simultaneous growth and ripening of intermetallic compounds (IMCs) with scallop-like morphology during reaction between solid copper (or nickel) substrate and a liquid bump of tin-based solder. Despite our best efforts, the general picture remained unclear. I remember the moment, when we realized a very simple idea – in the case of almost hemispherical scallops, their growth and ripening on the fixed substrate area proceeds with growing volume and almost constant solid/liquid interface area

(contrary to classic ripening – constant volume and decreasing area). Everything else was not easy, but more a technical task. The results (theory of flux-driven ripening) are presented in Chapter 6. After this, Prof. Tu reminded me of a Chinese saying, “if you see the corner of the table, please keep in mind that this table has three more corners.” We therefore tried to look for other processes with growing volume and almost constant interface area. We first (mainly during my second visit in 2002) developed the FDGG (flux-driven grain growth) theory for lateral grain growth during deposition of thin films (see also Chapter 6). The above-mentioned ideas were applied to the behavior of two-phase systems (namely, solders) under electromigration and thermomigration, as well as for grain rotation under electromigration.

There is one more very interesting problem at the junction of interdiffusion and flux-induced morphology evolution in SSRs – it is a problem of bifurcation and instability of Kirkendall planes (K-planes). The honor of discovery of multiple K-planes (Section 5 of Chapter 6) has to be assigned to the Eindhoven diffusion group (van Loo, Kodentsov, van Dal, Cherhati). I was just lucky to come to the right place (Eindhoven) at the right time (beginning of 2000) to understand that K-planes can be stable or unstable, and a situation may be possible when only a single unstable K-plane exists leading to a broadening crowd of markers instead of a plane. Later, such a situation was experimentally verified. Actually, the problem is fundamental and exciting: the initial concentration step in the standard diffusion couple contains all the future of this couple like the initial fireball of Big Bang contained the future of our universe. Moreover, similar to small scales in the modern nonhomogeneous structure of the universe, small fluctuations of inert Kirkendall markers’ distribution in the vicinity of the initial interface can lead to bifurcations and instabilities of K-planes. From a naive, purely intuitive point of view, it seems strange that markers, at first “overlapping” the whole concentration range of the diffusion couple, subsequently gather into a single plane corresponding to only one fixed (constant in time) composition, this plane usually being called a *Kirkendall plane*. It is commonly adopted that the K-plane represents the initial contact plane moving according to the parabolic law, its velocity being proportional to the difference of partial diffusivities and to the concentration gradient in the vicinity of the fixed composition. The existence of such a K-plane implies that this plane is a kind of attractor for markers. It is natural to ask why a system should have only one attractor. Is it possible for a binary diffusion couple to have two or more attractors? Is there any possibility for a system to interdiffuse without any attractors at all (without a stable K-plane), with a broadening, in time, of the distribution of markers? In the latter case, a system should “forget” the initial contact interface, which should lead to an especially tight bonding of the starting materials. Thus, the problem of bifurcations and instabilities of K-planes arises. As we will see below, this problem has a strong experimental background.

Other interesting examples of the flux-driven morphology evolution (cellular precipitation, diffusion induced grain boundary migration) can be found in Chapter 12, written by Yuriy Lyashenko. Here, he uses some general

thermodynamic considerations introduced in Chapter 11, adding the entropy balance for steady state regimes. Of course, we could not leave aside interdiffusion and SSRs in ternary systems (Chapters 9 and 10). As early as 1989, together with my first official PhD student, Yuriy Lyashenko, we modeled interdiffusion in two-phase zones of ternary systems. Then we found (by numerical means) a so-called “stochastization” of the diffusion path in a two-phase region, and, in 1990, I published (in the Soviet Journal of Physical Chemistry) an explanation of this phenomenon, related to the degeneracy of the interdiffusivity matrix in a two-phase region. Similar results were later obtained John Morral’s group, who went much further than we did and made an experimental verification.

Yet, we start from Chapter 2. We had two reasons for this. The first reason is the magic word “nano” in its title. The second reason is that this chapter gives a good example of how academic issues discussed by “pure theoreticians” can become very fresh and practically important, due to progress in technology and experimental possibilities. From a theoretical viewpoint, this chapter supplies one with a “trace” of the long activity (published mainly in Russian), related to the role of nonequilibrium vacancies in interdiffusion processes.

Thirty years ago, in the series of papers by Andrei Nazarov and Cyrill Gurov, the theory of interdiffusion with nonequilibrium vacancies was proposed. They predicted a much less (than in Darken’s scheme) Kirkendall shift in the middle of the diffusion zone, and an interdiffusion coefficient

$$D_{NG} = \frac{D_A D_B}{C_A D_A + C_B D_B} \quad (1.2)$$

controlled by the slowest species (like in ionic crystals) instead of Darken’s expression

$$\tilde{D} = C_B D_A + C_A D_B \quad (1.3)$$

controlled by the more mobile species.

I liked the NG (Nazarov-Gurov) approach but realized that its predictions of the Kirkendall shift were far from experimental. So, my aim was to somehow combine Darken’s scheme and the NG theory. My main idea was to introduce the hierarchy of time-space scales. In “nanoscale” (when the size of a “physically small volume” is less than the free-walk distance of a vacancy to the sink) and in the corresponding time scale, the NG theory holds. In macroscale we come back to Darken. Evidently, in nanosystems the characteristic size is often less than the typical mean free path length for vacancies. Thus, nonequilibrium vacancies generated by interdiffusion obtain a second life in application to nanoshell formation and collapse, initial stages of SSR, electromigration, coarsening of nanoalloys, spinodal decomposition and so on.

The present book was written jointly with some of my former PhD students – Lyashenko (PhD, 1992), Kornienko (PhD, 1999), Zaporozhets (PhD, 1999), Shirinyan (PhD, 2001), Pasichnyy (PhD, 2006). I was happy to work with them. Many results covered by this book, were obtained jointly with such brilliant scientists as Cyrill Gurov (my teacher), King-Ning Tu, Frans van Loo and

Alexandr Kodentsov, Pierre Desre and Fiqiri Hodaj, Andrei Nazarov, and Guido Schmitz. I was very glad to discuss in detail various issues of SSRs with Dezso Beke, Boris Bokstein, Marek Danielewski, Sergiy Divinski, Patrick Gas, Christian Herzig, Francois d'Heurle, Leonid Klinger, Leonid Larikov, George Martin, Helmut Mehrer, Subodh Mhaisalkar, Anatoliy Mokrov, Ludmila Paritskaya, Jean Philibert, Jörn W. P. Schmelzer, Vitaly V. Slezov, Ulo Ugaste, and Chen Zhong. My special thanks are to King-Ning Tu, who helped us to find ourselves as a group of applied theoreticians in the diffusion and reactions community.

This book would have never appeared without Anne Vasylevska, who translated our Ukrainian Ukrainian, Russian Ukrainian, and Ukrainian English into (I hope) American English. This process was – as it turned out – so exciting that it led to another phase transformation of Anne from Vasylevska to Koval'chuk. And, finally, the authors acknowledge support of their research by collective and individual grants of the Ministry of Education and Science of Ukraine, Fundamental Research State Fund of Ukraine, INTAS, CRDF, DAAD (Germany), ISF (Soros), and BMBF (Germany).

