INTRODUCTORY NOTE

The improvement of existing materials as well as the development of new materials is often based on the use of a chemical reaction in which a solid reacts with another solid, a liquid or a gas to form a solid product (an intermetallic, a silicide, an oxide, a salt, *etc.*) at the interface between initial substances. Therefore, kinetics of solid-state formation of chemical compound layers are of interest not only to chemists (researchers and technologists) but also to metal and solid-state physicists, materials scientists, metallurgists, specialists in the field of corrosion, protective coating, welding, soldering and microelectronics.

A number of theoretical and experimental works were devoted to the investigation of solid-state growth kinetics of compound layers and reaction diffusion in binary heterogeneous systems. The results obtained were treated, from one viewpoint or another, in the books of V.I. Arkharov [1], G.V. Akimov [2], V.Z. Bugakov [3], O. Kubaschewski and B.E. Hopkins [4], W. Seith [5], K. Hauffe [6], U.R. Evans [7], W. Jost [8], B.Ya. Pines [9], P.P. Budnikov and A.M. Ginstling [10], I.N. Frantsevich *et al.*[11], J.A. Hedvall [12], P. Kofstad[13, 14], H. Schmalzried [15, 16], N.A. Kolobov and M.M. Samokhvalov [17], A.T. Fromhold [18, 19], Yu.D. Tret’yakov [20], Ya.E. Geguzin [21], K.P. Gurov *et al.*[22], V.N. Chebotin [23], N. Birks and G.H. Meier [24] and others.

Various aspects of compound-layer formation (growth mechanism, sequence of occurrence, phase nucleation, main diffusing species, kinetic laws, *etc.*) were considered in detail in papers by U. Gősele and K.N. Tu [25], R.A. Rapp [26], F.M. d'Heurle and P. Gas [27], G. Ottaviani [28], W.C. Johnson and G. Martin [29], U. Gősele[30], F.M. d'Heurle [31, 32], J. Philibert [33, 34], F.J.J. van Loo [35], E.G. Colgan [36], K. Barmak *et al.* [37], A.M. Gusak and K.P. Gurov [38], L.N. Larikov [39], P. Gas [40], W. Lengauer [41], V.I. Zmiy [42], R. Pretorius [43], V.I. Franchuk *et al.* [44], L.N. Paritskaya *et al.* [45] and many other researchers.

From an analysis of the available literature data, it can readily be noticed that the views of researchers of different specialization (physical chemists, metal physicists, materials scientists, metallurgists, *etc.*) in regards to the mechanism of reaction diffusion resulting in the occurrence of compound layers at phase interfaces differ, sometimes very considerably. Meanwhile, the main features of the process of growth of the layers are the same, whether these compounds are oxides arising on the surface of metals during their oxidation, or intermetallics forming in the weld between dissimilar metals, or silicides occurring when making the very-large-scale-integrated circuits for microelectronics.

In spite of their seeming variety, theoretical approaches of different authors to the consideration of solid-state heterogeneous kinetics can readily be divided into two distinct groups. The first group takes account of both the step of diffusional transport of reacting particles (atoms, ions or, in exceptional cases if at all, radicals) across the bulk of a growing layer to the reaction site (a phase interface) and the step of subsequent chemical transformations with the participation of these diffusing particles and the surface atoms (ions) of another component (or "molecules" of the other chemical compound of a binary multiphase system). This is the physico-chemical approach, the main concepts and consequences of which were presented in the most consistent form in the works of V.I. Arkharov [1, 46, 47].

Historically, it dates from the early 1920's. Indeed, in 1924 U.R. Evans [7] proposed an equation showing the comparative influence of chemical and physical phenomena on the growth rate of a chemical compound layer. Unfortunately, its importance for understanding the essence of the reaction-diffusion process was not estimated properly at that time. Moreover, even now many researchers, especially physicists and metallurgists, tend to underestimate its significance.

In the majority of subsequent works, the step of chemical transformations was neglected as such for the seemingly substantiated reason – in most cases it takes a relatively small part of the overall time of the reaction-diffusion process to complete. Actually, no distinction was made between the formation of a solid solution and a chemical compound (a phase of constant composition). As a result, during a long period of time the *diffusional* theory in its different modifications was dominating. This is the second group of approaches that originates from the ideas expressed most consistently by C. Wagner in the 1930's (see Refs [6, 13, 48]).

Based upon Fick's diffusion laws, Wagner's theory helped the chemists to reveal the main features of the kinetics of solid-state heterogeneous reactions which have little in common with the kinetics of homogeneous chemical reactions taking place in solutions or gas mixtures. In particular, from a diffusional viewpoint, C. Wagner was able to theoretically derive the parabolic law of growth of a chemical compound layer, established experimentally by G. Tammann [49] in studying the interaction of metals with halogens (see also Refs [5-8, 20]). It was one of the greatest successes of the diffusional theory since within the framework of purely chemical considerations such a dependence of the layer thickness (or mass) upon time could not be explained.

Further development of the diffusional approach is due to the works by Th. Heumann [50], G.V. Kidson [51], Ya.E. Geguzin [21], K.P. Gurov *et al.* [22], B. Schröder and V. Leute [52], A.T. Fromhold and N. Sato [53], D.S. Williams *et al.* [54], G.-X. Li and G.W. Powell [55], M. Danielewski [56] and other researchers. With time, however, it became quite clear that in the case of formation of chemical compounds, no improvements of the diffusional approach can lead to satisfactory agreement of the theory with available experimental data, even qualitatively.

For example, in many systems thin compound layers (some tens to some hundreds of nanometers thick) are known to grow linearly with passing time [7, 11, 13, 57-65]. However, the diffusional approach does not admit the existence of such a kinetic dependence.

Besides, from an analysis of experimental data of F.J.J. van Loo [66], K.N. Tu *et al.* [67], J.M. Poate and T.C. Tisone [68], W.K. Chu *et al.* [69], S.U. Campisano *et al.* [70], G.J. van

Gurp and C. Langereis [71], S.S. Lau *et al.* [72], G.J. van Gurp *et al.* [73], G. Ottaviani and M. Costato [74], A. Thevand *et al.* [75], Y. Fujiwara *et al.* [76], B.Y. Tsaur *et al.* [77], D.M. Scott and M.-A. Nicolet [78], J.E.E. Baglin *et al.* [79], K.N. Tu *et al.* [80, 81], T.G. Finstad [82], H.T.G. Hentzell *et al.* [83], F.M. d'Heurle *et al.* [84], G. Majni *et al.* [85,86], M. Natan and S.W. Duncan [87], F.M. d'Heurle and C.S. Petersson [88], E.G. Colgan *et al.* [89], Z. Marinkovič and V. Simič [90, 91], B. Coulman and H. Chen [92], M.V. Belous *et al.* [93], E.G. Colgan [36, 94], X.-A. Zhao *et al.* [95, 96], A.A. Naem [97], E.G. Colgan and J.W. Mayer [98], R.J. Tarento and G. Blaise [99], B. Blanpain *et al.* [100], G.E. White and H. Chen [101], O. Thomas *et al.* [102], K.P. Rodbell *et al.* [103], L. Zhang and D.G. Ivey [104], Yu.N. Makogon [105], A.K. Pant *et al.* [106], K. Radermacher *et al.* [107], M. Millares *et al.* [108], G.P. Vassilev and S. Budurov [109], S.B. Jung *et al.* [110], P.T. Vianco *et al.* [111], S. Bader *et al.* [112], L. Levin *et al.* [113], T.C. Chou and L. Link [114], Yu.E. Ugaste and P.A. Kyarsna [115], D.B. Bergstrom *et al.* [116], K. Bouché *et al.* [117], W. Mayr *et al.* [118], S. Wöhlert and R. Bormann [119] and other researchers (see Refs [6, 11, 13, 120-125]), it can be concluded that the simultaneous occurrence and further parabolic growth of more than two compound layers in reaction couples of multiphase binary systems is a rare exception rather than the rule. Contrary to these observations, the diffusional considerations usually start from the quite opposite point of view, assuming that the layers of all chemical compounds present on the equilibrium phase diagram of a multiphase binary system must occur and grow simultaneously from the very beginning of interaction between initial substances (see, for example, Ref. [22]).

Again, the diffusional theory rests on the assumption of local equilibrium or quasi-equilibrium. However, it is clear that no local equilibrium can exist in any diffusion couple in which the layers of some part of thermodynamically stable compounds are missing. Also, if successive layers of reactants and products are in equilibrium with each other, then all the system must be in local equilibrium. Therefore, by applying the Gibbs phase rule, it is easy to come to the "logical" conclusion that under constant temperature and pressure conditions no compound layer can occur at all between two reactants in any binary system since in this case the largest number of co-existing phases at the zero number of degrees of freedom is two.

Such a conclusion is clearly absurd since two phases (initial substances) always exist in any reaction couple from the very beginning of the experiment. Therefore, the assumption of the existence of local equilibrium between all the phases involved into the interaction is incompatible with the assumption of simultaneous growth of compound layers. As pointed out by W. Jost [8], the number of growing layers cannot be restricted by the phase rule because in the course of chemical reactions resulting in their formation the system is too far from equilibrium. Thus, the assumption of local equilibrium should be used with great care. Its too straightforward application may be misleading.

The unjustified neglect of a chemical interaction step in analyzing the process of compound-layer formation appears to be the main source of discrepancies between the diffusional theory and available experimental data. The primary aim of this book is, on the basis of physico-chemical views regarding the reaction-diffusion process and solid-state reaction kinetics,

(*i*) to show the comparative role of diffusion and chemical transformations in the course of growth of a chemical compound layer at the interface between reacting substances;

(*ii*) to explain why all the compound layers of a multiphase binary system not only should not but in most reaction couples cannot occur and grow simultaneously;

(*iii*) to obtain, in the framework of a single theoretical approach, the main experimentally observed kinetic dependences of the layer thickness (or mass) upon time;

(*iv*) to persuade the experimentalist not to hesitate to publish the results that are in conflict with existing diffusional views. It may happen that, from a physico-chemical viewpoint, such results are quite adequate and therefore might be expected.