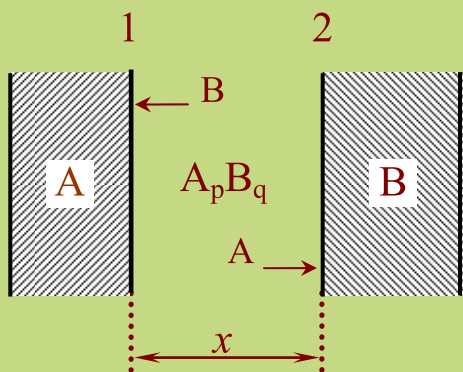
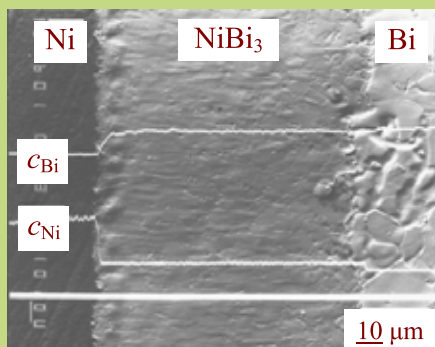




SOLID STATE REACTION KINETICS

V. I. Dybkov



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НАЦІОНАЛЬНА АКАДЕМІЯ НАУК УКРАЇНИ

ІНСТИТУТ ПРОБЛЕМ МАТЕРІАЛОЗНАВСТВА

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Solid State Reaction Kinetics

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Summary

The monograph is largely devoted to the consideration of solid-state growth kinetics of chemical compound layers in heterogeneous systems formed by two solids as well as a solid with a liquid or a gas. It is explained why the number of compound layers growing at the interface between initial phases is usually much less than the number of chemical compounds on the phase diagram of a binary system under given temperature-pressure conditions. For example, of eight intermetallic compounds existing in the aluminium-zirconium binary system, only the ZrAl_3 phase was found to grow as a separate layer at the Al–Zr interface in the course of isothermal annealing. The physico-chemical approach predicts that in most cases the number of compound layers should not exceed two, with the main factor resulting in the occurrence of additional layers being crack formation due to thermal expansion and volume effect.

It is shown that many experimentally observed kinetic dependences of the layer thickness (or mass) upon time can readily be derived from a single theoretical viewpoint based on two almost obvious basic postulates: (i) about the summation of the time of diffusion of reacting species and the time of subsequent chemical transformations with their participation and (ii) about the independency of elementary acts of solid-state chemical reactions. Examples presented include linear growth of Cu_6Sn_5 between Cu and Sn, parabolic growth of NiBi_3 between Ni and Bi, linear-parabolic growth of SiO_2 between Si and oxygen, asymptotic and parilinear growth of two oxides, simultaneous parabolic growth of two layers Al_3Mg_2 and $\text{Al}_{12}\text{Mg}_{17}$ between Al and Mg, and two layers FeB and Fe_2B between Fe–Cr alloys and B.

The reasons for the kinetic instability of the layers of chemical compounds that may result in their gradual degradation (disappearance) with passing time are discussed. An example is the Ti– Ti_3Al –TiAl– TiAl_2 – TiAl_3 –Al reaction system, with the layers Ti_3Al , TiAl and TiAl_2 disappearing during isothermal annealing at temperatures below the melting point of aluminium. This kind of instability is by no means connected with the thermodynamic stability of the compounds under given temperature-pressure conditions.

Comparative analysis of growth kinetics of the same compound layer in various reaction couples consisting of elements A and B and other chemical compounds of a multiphase binary system is presented. Mathematical expressions relating the growth rate of the layer in one of the couples to that in the others are proposed. The formation of duplex structures in these couples is discussed, with the emphasis on the determination of the ratio of the sub-layers of a layer of the same compound, which look like the layers of two quite different chemical compounds. For example, the FeSn layer between Fe and FeSn_2 consists of two sub-layers of equal thickness, differing by the shape of grains. The same applies to the

Co₃O₄ layer between CoO and oxygen and also many others.

The dissolution in the solid-liquid systems as well as the evaporation in the solid-gas systems was shown to play a significant role in determining the layer-growth rate. These effects were taken into account in equations describing the rate of growth of the compound layer under conditions of its simultaneous dissolution in the liquid phase or evaporation into the gaseous phase. Calculations carried out for the Fe₂Al₅, NiBi₃, CoSn₂ and other intermetallic layers growing at the solid-liquid interface showed that theoretical equations fit the available experimental data fairly well.

The reasons for the great difference in values of reaction- and self-diffusion coefficients of the components of a chemical compound are analysed. For example, in the case of Fe₃₋₈O₄ the reaction-diffusion coefficient is two orders of magnitude greater than the self-diffusion coefficient of iron ions. For other compounds (Al₂O₃, Fe₂Al₅, Pd₂Si, AlSb, *etc.*) this difference varies from five to ten orders of magnitude. When normalised to the same vacancy concentration, the values of reaction- and self-diffusion coefficients of the same component become close, if not identical, as it should be from a physical viewpoint. Though conventionally assumed to be the same, the real effect of native (inherent) and newly-formed (reaction-induced) vacancies on the process of layer growth is shown to be quite opposite.

The difference in diffusivities of the components in a growing chemical compound layer is often connected, especially in the literature on physics and metallurgy and especially in relation to intermetallics, with the Kirkendall effect. In many cases, however, this does not seem to be sufficiently substantiated from both historical and scientific viewpoints. In particular, this is so in the case of formation of chemical compound layers at the interface of reacting substances. A brief consideration is presented to show that different diffusional contributions of the components to the growth process of a chemical compound layer can hardly be regarded as a result or manifestation of the Kirkendall effect.

Comparison of the consequences following from the physico-chemical and purely diffusional approaches is given to show that the latter is one of the limiting cases of the former. Theoretical conclusions are illustrated by the available experimental data on the formation of intermetallics, silicides, oxides, salts and other chemical compounds.

The book is addressed to scientific workers, engineers, post-graduates and students (physical, solid-state and inorganic chemists, metal and solid-state physicists, materials and corrosion scientists, metallurgists, *etc.*) involved into the study of solid-state processes and their practical applications including the solid-state synthesis of inorganic substances, protective coating, corrosion, all-in-one joining of dissimilar metals, welding, soldering, brazing and thin-film electronic technology. It can equally be used by theoreticians, experimentalists and technologists to satisfy, to a greater or lesser extent, their specific needs.

Preface to Third Edition

This edition includes all the material of my previous books “Kinetics of Solid State Chemical Reactions” (Naukova Dumka, Kiev, 1992, in Russian), “Growth Kinetics of Chemical Compound Layers” (Cambridge International Science Publishing, Cambridge, 1998) and “Reaction Diffusion and Solid State Chemical Kinetics” (First Edition, IPMS Publications, 2002, in Ukrainian and English; Second Edition, Trans Tech Publications, 2010). As the title of this preface indicates, it can be considered as the third edition of the book “Reaction Diffusion and Solid State Chemical Kinetics.”

As far as I know, previous books happen to be used by students, post-graduates and lecturers as textbooks. To facilitate their work and to show more clearly the similarity and distinctions of the kinetics of homogeneous and heterogeneous reactions, a short section providing an overview of main concepts and laws of homogeneous kinetics was included in Chapter 1. As I myself was unable to make any contribution to the subject of homogeneous reaction kinetics, this consideration is based entirely on the works of our prominent predecessors.

Most drastically revised is Section 1.9 of Chapter 1 devoted to the establishment of interrelation between the self-diffusion coefficients of the components of any chemical compound and their reaction-diffusion coefficients in a growing layer of that compound. Its primary aim is to show the opposite effect of native (inherent) and newly-formed (reaction-induced) vacancies on the process of layer growth.

Experimental results on boriding of Fe–Cr alloys and chromium steels providing evidence for the applicability of theoretical equations to describe the kinetics of physico-chemical processes taking place at phase interfaces, are additionally presented in Chapter 2 of this edition. Also, many figures were added.

To compensate for a noticeable increase in volume of the book, its title was shortened from “Reaction Diffusion and Solid State Chemical Kinetics” to “Solid State Reaction Kinetics”.

V.I. Dybkov, March 2013

Preface to Second Edition

This book has first been published in 2002 in a small amount of copies. Therefore, it soon became a rarity and is now available only from the libraries of largest universities, institutes and companies. Also, a limited number of most curious researchers and students have the book at their bookshelves. I hope that the layer of dust on its cover is not too thick.

To broaden the audience, publication of a revised and amended version of the book has been undertaken. I am grateful to Mr. Thomas Wohlbier, Vice-President of Trans Tech Publications, who kindly agreed to support my intention, in spite of not very favourable economic circumstances.

V.I. Dybkov, January 2009

Preface to First Edition

The main ideas, theoretical concepts, mathematical equations and experimental data laid in the basis of this book have been first presented in a series of papers published in the periodicals *Zhurnal Fizicheskoy Khimii*, *Poroshkovaya Metallurgiya*, *Journal of the Less-Common Metals*, *Journal of Materials Science*, *Journal of Physics and Chemistry of Solids*, *Journal of Materials Science Letters*, *Materials Science Forum*, *Defect and Diffusion Forum*, and *Journal of Alloys and Compounds*. A more generalised consideration of the reaction-diffusion process resulting in the formation of chemical compound layers has been given in my monographs “Kinetics of Solid State Chemical Reactions: Growth of Chemical Compound Layers in Binary Heterogeneous Systems” (Naukova Dumka, Kiev, 1992, in Russian) and “Growth Kinetics of Chemical Compound Layers” (Cambridge International Science Publishing, Cambridge, 1998).

Since the time of publication of my first papers, I have felt an incessant interest (both positive and negative but equally stimulating and therefore valuable to me) of the researchers, who are involved into the investigation of reaction kinetics and compound-layer formation at phase interfaces, to theoretical results presented in those works. Therefore, I decided to write a new book summarising almost all I presumptuously think I know about the fundamentals of this subject.

It should be emphasised that this monograph only deals with the physico-chemical theory of formation of chemical compound layers. The consideration is based mainly upon my own views and results. This does not mean that I am not aware of the theoretical works of other investigators or intentionally ignore them. Simply, my views regarding the theory of the reaction-diffusion process differ, in some cases diametrically, from the views of many researchers in the field. To avoid a compilation, I preferred to give only my interpretation of both theoretical and experimental data on the reaction diffusion and solid-state chemical kinetics, supposing that those investigators, who are unable to agree with this interpretation, will have a strong stimulus to write their own books showing the erroneous character of one or another of my conclusions, and thus will be entirely satisfied.

The book is addressed, in the first place, to the actively working researchers, graduate students and post-graduates. As this part of scientific community has not got sufficient time to read lengthy books, I tried to be concise. Nevertheless, I explained, as far as I could, the main results in word, not relying only upon the clarity of mathematical formulae, their number in the book being probably somewhat greater than in other books written mainly for chemists, physicists and metallurgists. As all the formulae are obtained from very simple assumptions, the reader will doubtless be able to derive, analyse and apply them without any

difficulties, in spite of their seemingly complex look.

The experimental data have been invoked in the minimal necessary amount in order to illustrate theoretical conclusions and consequences. This appears to be sufficiently justified since usually any actively working researcher is aware of the state of affairs with experiment in the field very well. Again, for students and post-graduates, an excess amount of experimental data, often contradictory, seems to be undesirable, producing an impression of the lack of any order in science. Those readers, who wish to know more details, are referred to original works quoted in the list of references, relatively long but of course not exhaustive.

The consideration is only restricted to the case where the layers of initial substances and the layers of growing compounds are parallel-plane. Probably, this does not mean that the results obtained are of no interest to researchers working, for example, in the field of sintering or reaction kinetics in powder mixtures. The processes analysed in the book take place also during the interaction of powders but under more complicated (and in many cases poorly defined) conditions because the influence of the surface curvature and the extent of proximity of reacting particles prove important or may even be decisive in determining the kinetics of layer formation. For the works in this field, it is traditional to try to obtain a formal kinetic description of the reaction rate, the main aim being establishing the time dependence of the extent of transformation of the reactants into the final product(s). This question is not considered in the book at all. It has been analysed in detail in many other books and it is very difficult to add something new and fresh to the well-known data.

It is not accidental that the consideration bears a polemic character. It was not my intention merely to give a number of ready mathematical formulae for the experimentalists to treat their data and to obtain some constants, although such a work is clearly also necessary and useful, and must therefore be welcome. However, it seemed to be far more important to show that, firstly, not all has yet been done in the field of theory of solid-state reaction kinetics and, secondly, some of wide-spread views should be modified or even rejected as contradicting not only the available experimental data but the common sense as well.

The results of this work may in turn seem to be questionable. I would be grateful to those readers, who could draw my attention to the facts necessitating the reconsideration of one or the other of theoretical consequences and conclusions following from the proposed approach.

I express my deep gratitude to colleagues from the Department of Physical Chemistry of Inorganic Materials, who were the first listeners of my works. This department has been organized and headed for more than thirty years by Professor V.N. Yeremenko, now unfortunately late. His contribution to my growth as a researcher in the field of layer growth is very significant. I acknowledge this contribution with sincere gratitude.



V.N. Yeremenko, Member, National Academy of Sciences of Ukraine

(12.08.1911 – 31.10.1992)

My thanks are also due to Professor V.V. Skorokhod for the help with publication of the book "Kinetics of Solid State Chemical Reactions" and many papers. I greatly appreciate the friendly support of my work by Professors F.J.J. van Loo, F.M. d'Heurle, J. Philibert and P. Gas. Numerous stimulating discussions with them in Paris, Aussois and Orsay in 1993, in Marseille during my stay as a visiting professor at Faculte des Sciences St. Jérôme in 1996, in Kyiv and Cherkasy during their visit to Ukraine in 1998, and in Paris during DIMAT'2000 meeting organised by Drs Y. Limoge and J.L. Bocquet were of special value to me. Of course, this does not mean that they necessarily share my views. Helpful discussions with Professors L.N. Larikov, B. Pieraggi, V.O. Lavrenko, G. Blaise, V.P. Kazimirov, V.M. Danilenko, O.I. Raichenko, A.M. Gusak, L.N. Paritskaya, V.R. Sidorko, W. Lengauer, K. Barmak, W.C. Johnson, H. Mehrer and Ch. Herzig are also acknowledged.

I would like to express my gratitude to the researchers, who kindly presented me the reprints of their works. Each of these works has been used, to a greater or lesser extent, during preparation of this and previous books. I hope that the authors will be tolerant in those cases where my and their own interpretations of the results obtained are somewhat different. The future work, the most promising directions of which are tentatively outlined in the book, will show whose interpretation is more substantiated.

I am indebted to the publishers for their permission to reproduce some figures, and especially to the authors (Dr. A.A. Kodentsov, Prof. W. Lengauer, Prof. H. Mehrer, Dr. J. Gülpén and others) who kindly presented original drawings and micrographs. Doubtless, these made the text more vivid and understandable.

V.I. Dybkov, October 2002

Collaborators

Even though only the head is needed to put forward a theory, any experimental work almost always demands more than two hands and therefore can hardly be carried out properly without skilled collaborators. The help of V.R. Sidorko, V.G. Khoruzha, L.V. Goncharuk, A.V. Samelyuk, V.V. Berezutsky, S.V. Bykova, L.A. Duma, I.G. Kondratenko, K.A. Meleshevich, E.S. Rabotina, D.M. Pashko and V.M. Petukh with preliminary work, maintenance of equipment and carrying out experiments is acknowledged with sincere gratitude.



L.A. Duma



V.M. Petukh



E.S. Rabotina



A.V. Samelyuk



L.V. Goncharuk



V.R. Sidorko



V.V. Berezutsky



V.G. Khoruzha

Producers

This book is a result of consolidated efforts of the workers of Dybkov Production Group, Unlimited. The concentration of its members does not reveal any trend to saturation. Further forecast seems to be rather optimistic.



W = wife, M = mother,
GM = grandmother



GS = grandson



S = son,
DL = daughter-in-law



GD = granddaughter



(Executive Producer)

<необмежена продюсерська група **ДИБКОВ** – **DYBKOV** production group, unlimited>

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, and 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 the reaction-diffusion process and solid-state growth kinetics of compound layers 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], P. Sarrazin *et al.* [25], A.M. Gusak *et al.* [26] and others.

Various aspects of compound-layer formation (growth mechanism, sequence of occurrence, phase nucleation, main diffusing species, kinetic laws, *etc.*) were considered in papers by U. Gösele and K.N. Tu [27], R.A. Rapp [28], F.M. d'Heurle and P. Gas [29], G. Ottaviani [30], W.C. Johnson and G. Martin [31], U. Gösele [32], F.M. d'Heurle [33, 34], J. Philibert [35, 36], F.J.J. van Loo [37], E.G. Colgan [38], K. Barmak *et al.* [39], A.M. Gusak and K.P. Gurov [40], L.N. Larikov [41], P. Gas [42], W. Lengauer [43], V.I. Zmiy [44], R. Pretorius [45], V.I. Franchuk *et al.* [46], L.N. Paritskaya *et al.* [47] 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 and solid-state chemists, metal physicists, materials, surface and corrosion scientists, physical and chemical metallurgists, *etc.*) in regards to the mechanism of reaction-diffusion process resulting in the occurrence of compound layers at phase interfaces differ, sometimes very considerably. Meanwhile, the main features of layer-growth kinetics 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, molecules and 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, 48, 49].

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 appreciated 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 (a phase of varying composition) 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, 50]).

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 derive theoretically the parabolic law of growth of a chemical compound layer, established experimentally by G. Tammann [51] 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 [52], G.V. Kidson [53], Ya.E. Geguzin [21], K.P. Gurov *et al.* [22], B. Schröder and V. Leute [54], A.T. Fromhold and N. Sato [55], D.S. Williams *et al.* [56], G.-X. Li and G.W. Powell [57], M. Danielewski [58], A.M. Gusak *et al.* [26] and other researchers. With the passage of time, however, it becomes more and more clear that in the case of formation of chemical compounds and not solid solutions, no improvements of the diffusional approach can lead to satisfactory agreement of the theory with available experimental data, even qualitatively, because of its implicit limitations.

For example, in many systems a thin compound layer (some tens to some hundreds of nanometers thick) is known to grow linearly with passing time [7, 11, 13, 59-67]. However, such a simple kinetic dependence is hardly explainable in the framework of the diffusional approach without additional assumptions.

Besides, from an analysis of the experimental data, for example, of F.J.J. van Loo [68], K.N. Tu *et al.* [69], J.M. Poate and T.C. Tisone [70], W.K. Chu *et al.* [71], S.U. Campisano *et al.* [72], G.J. van Gurp and C. Langereis [73], S.S. Lau *et al.* [74], G.J. van Gurp *et al.* [75], G. Ottaviani and M. Costato [76], A. Thevand *et al.* [77], Y. Fujiwara *et al.* [78], B.Y. Tsaur *et al.* [79], D.M. Scott and M.-A. Nicolet [80], J.E.E. Baglin *et al.* [81], K.N. Tu *et al.* [82, 83], T.G. Finstad [84], H.T.G. Hentzell *et al.* [85], F.M. d'Heurle *et al.* [86], G. Majni *et al.* [87, 88], M. Natan and S.W. Duncan [89], F.M. d'Heurle and C.S. Petersson [90], E.G. Colgan *et al.* [91], Z. Marinković and V. Simić [92, 93], B. Coulman and H. Chen [94], M.V. Belous *et al.* [95], E.G. Colgan [38, 96], X.-A. Zhao *et al.* [97, 98], A.A. Naem [99], E.G. Colgan and J.W. Mayer [100], R.J. Tarento and G. Blaise [101], B. Blanpain *et al.* [102], G.E. White and H. Chen [103], O. Thomas *et al.* [104], K.P. Rodbell *et al.* [105], L. Zhang and D.G. Ivey [106], Yu.N. Makogon [107], A.K. Pant *et al.* [108], K. Radermacher *et al.* [109], M. Millares *et al.* [110], G.P. Vassilev and S. Budurov [111], S.B. Jung *et al.* [112], P.T. Vianco *et al.* [113], S. Bader *et al.* [114], L. Levin *et al.* [115], T.C. Chou and L. Link [116], Yu.E. Ugaste and P.A. Kyarsna [117], D.B. Bergstrom *et al.* [118], K. Bouché *et al.* [119], W. Mayr *et al.* [120], S. Wöhlert and R. Bormann [121] and other researchers (see Refs [6, 11, 13, 122-127]), it can readily 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 available 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.

Inasmuch as two phases (initial substances) always exist in any reaction couple from the very beginning of the experiment, such a conclusion is clearly absurd. 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. These are thus contradictory. 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 its equilibrium state. Therefore, the assumption of local equilibrium should be used with great care. Its too straightforward application may prove to be misleading.

The unjustified neglect of a chemical interaction step in analysing 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 seem to be in contradiction with existing diffusional views. It may happen that, from a physico-chemical viewpoint, such results are quite adequate and therefore might be expected.

1: Formation of a chemical compound layer at the interface of two elementary substances

From the point of view of their kinetics and mechanism, chemical reactions are conventionally divided into two broad groups. The first group is homogeneous chemical reactions taking place entirely within one phase that can be gaseous, liquid or solid. The second is heterogeneous chemical reactions involving two or more phases.

Considered in Chapters 1 to 4 of this book are the common features of solid-solid, solid-liquid and solid-gas heterogeneous reactions resulting in the formation of solid layers of chemical compounds at phase interfaces. The effect of dissolution of a solid in the liquid phase of a solid-liquid system or of its evaporation into the gaseous phase of a solid-gas system on the growth kinetics of a chemical compound layer is then analyzed in Chapter 5. Thus, under conditions of occurrence of a chemical reaction its product will be assumed to be solid and to form a continuous compact layer adherent at least to one of initial phases.

1.1: Distinctions in description of the kinetics of homogeneous and heterogeneous chemical reactions

Before proceeding to a consideration of the kinetics of heterogeneous chemical reactions, it appears relevant to remind the main concepts and laws of the kinetics of homogeneous chemical reactions. As these concepts and laws are considered in detail in numerous texts on physical chemistry, chemical kinetics and metallurgy (see, for example, Refs [128-138]), it is only their short survey that is provided in this section, just for further comparison with the relationships typical of heterogeneous reactions.

1.1.1: Overview of the basic concepts and laws of the kinetics of homogeneous chemical reactions

When considering the kinetics of homogeneous chemical reactions, it is always explicitly or tacitly assumed that, if forward, reverse, parallel, consecutive, chain and other reactions are taking place simultaneously in a given system, their elementary acts are independent of each other. Hence, the rate of each of those reactions can mathematically be described by an individual differential equation. These rates are algebraically combined to yield a kinetic expression for the overall reaction rate.

The *rate* of a *homogeneous chemical reaction* is characterised by the *change in concentration* of its reagents per unit time. The *concentration*, c , is defined as the *amount* of a *reactant* or a *product* of the reaction in *unit volume* and is expressed in moles (or kilograms) per cubic metre, mol m^{-3} (kg m^{-3}). Application of other units such as mass or

atomic percent, mole or volume fraction, *etc.*, must be substantiated in each particular case to avoid errors in calculation of numerical values of reaction rates and some other chemical and physical quantities (for example, diffusion coefficients) because generally different concentration units are not proportional to each other.

The rate of a homogeneous reaction of the type $A + B = AB$ can be expressed in terms of molar concentrations of its reactants A and B or its product AB as follows

$$-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = +\frac{dc_{AB}}{dt}. \quad (1.1)$$

The negative or positive sign indicates that the concentrations of the reactants A and B are decreasing, while the concentration of the product AB is increasing with time as the reaction proceeds. The reaction rate is always considered to be a positive quantity. In the case of more complicated reactions of the type $pA + qB = A_pB_q$, the rate of the reaction can alternatively be written as

$$-\frac{1}{p} \frac{dc_A}{dt} = -\frac{1}{q} \frac{dc_B}{dt} = +\frac{dc_{A_pB_q}}{dt}. \quad (1.2)$$

Note that the use of the term *concentration* implies the availability of a *macroscopic reaction volume*, the size of which in three dimensions far exceeds the size of reacting atoms, ions, molecules or radicals. In this macroscopic volume, the reactants and products are supposed to be mixed together by convection, mechanical agitation or diffusion at the *microscopic (molecular) level*, as shown schematically in Fig. 1.1 for the case of two dimensions. The atoms, ions, molecules or radicals of all the reagents are thus in immediate contact with each other and are able to move more (in the gaseous phase) or less (in the liquid phase) or still less (in the solid phase) freely in any direction within a reaction volume.

According to the *law of mass action* established by C.M. Guldberg and P. Waage in 1867, the *rate of a homogeneous chemical reaction* is proportional to the *concentrations* of the reactants, with each reactant concentration raised to a numerical power, n . The value of n defines the *order* of a reaction in regard to a given reactant. The sum of these values for all the reactants is the total order of the reaction.

If any reaction proceeds exactly according to the stoichiometric chemical equation, then the order of this reaction coincides with its molecularity determined from the balancing coefficients in the chemical equation. The *molecularity* of an elementary reaction involving no intermediate steps in its mechanism is the number of atoms, molecules or other species taking part in that reaction. Hence, reactions of the type $A = \text{Products}$ are unimolecular, those of the type $A + B = \text{Products}$ or $2A = \text{Products}$ are bimolecular, those of the type $A + B + C = \text{Products}$ or $2A + B = \text{Products}$ are trimolecular, and so forth. In fact, however, the

order of a reaction coincides with its molecularity only for the limited number of simple chemical reactions.

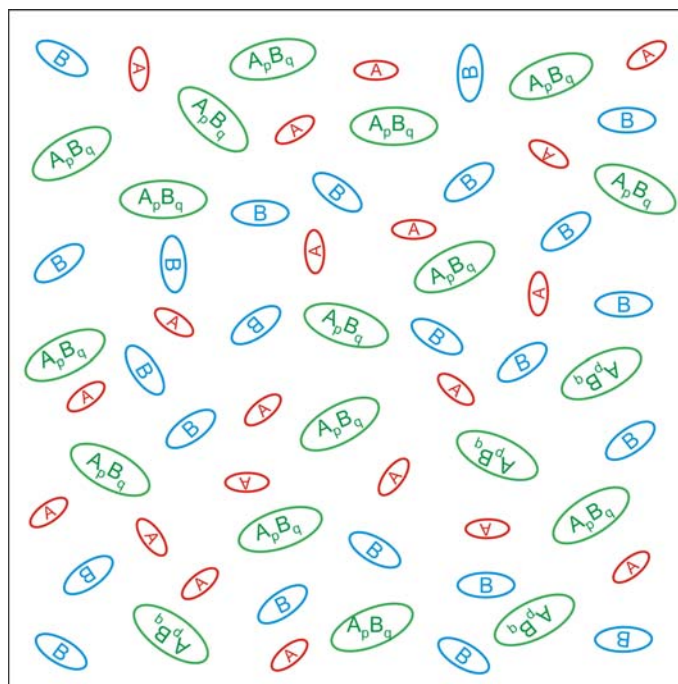


Fig. 1.1. Schematic illustration of a homogeneous chemical reaction of the type $pA + qB = A_p B_q$. Three reacting species are intermixed at the molecular level. The size of the reaction volume far exceeds the size of the particles involved into the reaction.

Note that, unlike the molecularity which is always an integer varying from 1 to 3 (probability of many-particle collisions involving four or more atoms, molecules or other reacting species is quite negligible) and will never be zero, the order of a reaction can be, as established experimentally, zero, an integer, a fraction or a changing and even a negative number, indicative of a complicated reaction mechanism including a few *intermediate stages* (*steps*) with the formation of the *intermediate* products (*intermediates* or *intermediaries*), either detectable or, in most cases, only postulated. The slowest of those steps is the *rate-determining* step for the overall reaction.

If $n = 1$, the reaction is first-order and its rate is proportional to the instantaneous concentration, c , at time, t

$$-\frac{dc}{dt} = k_1 c, \quad (1.3)$$

where k_1 is a rate constant.

After integration with the initial condition $c = c_0$ at $t = 0$, this equation yields

$$c = c_0 \exp(-k_1 t). \quad (1.4)$$

In the case of first-order chemical reactions, a plot of either $\ln c$, or $\ln (c/c_0)$, or $\ln (c_0/c)$ against t is a straight line, the slope of which can be used to determine a value of the reaction constant, k_1 . For this type of reaction, the *half-life period* or simply *half-life*, $\tau_{1/2}$, i.e. the time taken for the reactant concentration to drop from c_0 to $c_0/2$, is seen to be independent of c_0 and is inversely proportional to k_1

$$\tau_{1/2} = \frac{\ln 2}{k_1}. \quad (1.5)$$

The reciprocal of k_1 is often called the *lifetime*, τ_{life} . It is the time necessary for the reactant concentration to diminish from c_0 to c_0/e , with e being the natural logarithm base,

$$\tau_{\text{life}} = \frac{1}{k_1} \ln \frac{c_0 e}{c_0} = \frac{1}{k_1}. \quad (1.6)$$

Second-order reactions are those in which the rate is proportional either to the product of the molar concentrations of two reactants as in the general case of reactions $A + B = \text{Products}$ or to the square of the concentration of one of the reactants, if initially both concentrations are equal or if a reaction involves only one reactant ($2A = \text{Products}$). In the former case,

$$-\frac{dc_A}{dt} = k_{\text{II}} c_A c_B. \quad (1.7)$$

The total order of the reaction is second, while its order in regard to either A or B is first. In the latter case ($c = c_A = c_B$),

$$-\frac{dc}{dt} = k_{\text{II}} c^2. \quad (1.8)$$

The integrated form of this equation ($c = c_0$ at $t = 0$) gives

$$\frac{1}{c} - \frac{1}{c_0} = k_{\Pi} t. \quad (1.9)$$

If a reaction is second-order, a plot of $1/c$ against t must yield a straight line. The slope of this line is equal to the reaction-rate constant, k_{Π} .

The half-life is

$$\tau_{1/2} = \frac{1}{k_{\Pi} c_0}. \quad (1.10)$$

For second-order reactions, it is dependent on both k_{Π} and c_0 .

As any chemical reaction, even the simplest like isomerization or dissociation, involves at least one molecule, zero-order reactions are clearly impossible from the point of view of their molecularity. However, if a given reactant, for example, B in a generic reaction $A + B = \text{Products}$, is taken in large excess, its concentration remains almost unchanged during the time of observation and does not influence the overall reaction rate. Then, the reaction can formally be considered to be zero-order in regard to this reactant: $n = 0$, $c_B^0 = 1$. Hence, its rate is (see equation (1.7))

$$-\frac{dc_A}{dt} = k_{\Pi} c_A c_B^0 = k_{\Pi} c_A. \quad (1.11)$$

The bimolecular second-order reaction thus becomes first-order.

The total order of any other reaction involving a few reactants can similarly be lowered, but obviously not to zero, because all the reactants cannot simultaneously be taken “in large excess”. Therefore, if a reaction is found experimentally to be zero-order in regard to all the reactants, it simply means that this reaction, though otherwise homogeneous, proceeds by a different mechanism under particular conditions of its occurrence. Such are, for example, chemical reactions taking place on solid catalysts. In this case, the reaction proceeds in the diffusion boundary layer at the solid-gas or solid-liquid interface, saturated by all the reagents. Its rate-determining step is independent of their instantaneous concentrations in the bulk of the gaseous or liquid phase. Formally, the total order of the reaction becomes zero and the rate is constant. The reactants are consumed, while the products are accumulated linearly with passing time until the reaction has completed, which case is not typical of homogenous reactions, as seen from the rate equations of this section. In this and similar cases, it appears better not to apply at all the concept *order of reaction* to the overall reaction.

In the particular case of third-order reactions $A + B + C = \text{Products}$, where the initial molar concentrations of all the reactants are equal, the kinetic equation is of the form

$$-\frac{dc}{dt} = k_{\text{III}} c^3. \quad (1.12)$$

After integration ($c = c_0$ at $t = 0$), it becomes

$$\frac{1}{2} \left(\frac{1}{c^2} - \frac{1}{c_0^2} \right) = k_{\text{III}} t. \quad (1.13)$$

The rate constant, k_{III} , is therefore determined from the slope of a plot of $1/c^2$ against t .

Accordingly, the half-life is

$$\tau_{1/2} = \frac{3}{2k_{\text{III}} c_0^2}. \quad (1.14)$$

Again, it depends on both the rate constant, k_{III} , and the initial concentration, c_0 , of the reactants.

For a reaction of order n , whose rate is dependent on the concentration of only one reactant ($nA = \text{Products}$ or $A + A_1 + \dots + A_n = \text{Products}$, with the initial molar concentrations of all the reactants being equal), the rate equation is

$$-\frac{dc}{dt} = k_n c^n. \quad (1.15)$$

Its integrated form ($c = c_0$ at $t = 0$) yields a dependence of c upon t

$$c^{-(n-1)} = c_0^{-(n-1)} + (n-1)k_n t. \quad (1.16)$$

By plotting $c^{-(n-1)}$ against t , a straight line is obtained. Its slope is equal to $(n-1)k_n$, with n being any number (positive, negative, whole or fractional). In the case of $n = 1$, application of l'Hôpital's rule converts an indeterminate form of this equation to the determinate one $\ln c_0 - \ln c = k_1 t$ (see equation (1.4)).

The half-life for reactions of order n is

$$\tau_{1/2} = \frac{2^{n-1} - 1}{(n-1)k_n c_0^{n-1}}. \quad (1.17)$$

Reversible (opposed) reactions proceed simultaneously in both directions. For a reversible first-order reaction $A \leftrightarrow B$, the rate of the forward reaction $A \rightarrow B$ with the constant k_f is

$$\left(\frac{dx}{dt}\right)_{\text{forward}} = k_f(a - x), \quad (1.18)$$

while that of the reverse reaction $B \rightarrow A$ with the constant k_r is

$$\left(\frac{dx}{dt}\right)_{\text{reverse}} = -k_r(b + x), \quad (1.19)$$

where a and b are initial molar concentrations of A and B , respectively, and x is the amount of A in unit volume that has reacted to form B (the decrease in concentration of A or, alternatively, the increase in concentration of B) at time, t .

The overall reaction rate is

$$\frac{dx}{dt} = k_f(a - x) - k_r(b + x). \quad (1.20)$$

At (dynamic) equilibrium, the rate of the forward reaction $A \rightarrow B$ becomes equal to that of the reverse reaction $B \rightarrow A$. Hence, the overall rate is zero ($dx/dt = 0$), and

$$k_f(a - x_\infty) = k_r(b + x_\infty), \quad (1.21)$$

where x_∞ is the decrease in concentration of A or the increase in concentration of B at the position of equilibrium.

Rearrangement gives

$$\frac{b + x_\infty}{a - x_\infty} = \frac{k_f}{k_r} = K_{\text{equil}}, \quad (1.22)$$

where K_{equil} is the equilibrium constant of the reaction, a thermodynamic quantity.

Equation (1.20) can be re-written as follows

$$\frac{dx}{dt} = k_f a - k_f x - k_r b + k_r x = (k_f + k_r) \left(\frac{k_f a - k_r b}{k_f + k_r} - x \right). \quad (1.23)$$

From equation (1.22),

$$\frac{k_f a - k_r b}{k_f + k_r} = x_\infty. \quad (1.24)$$

By inserting this relation into equation (1.23), one obtains

$$\frac{dx}{dt} = (k_f + k_r)(x_\infty - x) \quad (1.25)$$

or, after integration from 0 to t and from 0 to x ,

$$\ln \frac{x_\infty}{x_\infty - x} = (k_f + k_r)t. \quad (1.26)$$

By plotting $\ln [x_\infty / (x_\infty - x)]$ against t , the sum of k_f and k_r is obtained. Their ratio and then separate values are found, using equation (1.22) and an experimental value of x_∞ .

Parallel (competitive) reactions are those in which a reactant or a few reactants yield two or more different sets of products. For reactions $A \rightarrow B$ and $A \rightarrow C$ taking place simultaneously, the rate equations are

$$-\frac{dc_A}{dt} = k_A c_A, \quad \frac{dc_B}{dt} = k_B c_A, \quad \frac{dc_C}{dt} = k_C c_A, \quad (1.27)$$

where $k_A = k_B + k_C$.

If the products B and C are missing initially,

$$c_A = c_{A0} \exp(-k_A t) = c_{A0} \exp[-(k_B + k_C)t], \quad (1.28)$$

$$c_B = c_{A0} \frac{k_B}{k_B + k_C} \{1 - \exp[-(k_B + k_C)t]\}, \quad (1.29)$$

$$c_C = c_{A0} \frac{k_C}{k_B + k_C} \{1 - \exp[-(k_B + k_C)t]\}. \quad (1.30)$$

The concentration of the reactant A decreases with time from its initial value, c_{A0} , to zero, while the concentrations of the products B and C increase exponentially until A has consumed completely, the ratio of the concentration of B to that of C being constant during the whole course of the reaction,

$$\frac{c_B}{c_C} = \frac{k_B}{k_C}. \quad (1.31)$$

Equation (1.28) is similar to (1.4). The sum of k_B and k_C is determined from the slope of a plot of $\ln c_A$ against t . Then, by using the ratio of these constants found from the experimental values of the concentrations of B and C at any fixed time, the values of k_B and k_C can be calculated separately.

Consecutive reactions involve a sequence of a few reactions following one another. In the case of consecutive reactions of the type $A \rightarrow B \rightarrow C$, if initially ($t = 0$) the concentration of A is a and the substances B and C are missing, while at any moment of time, t , the concentrations are $a - x$ for A , $x - y$ for B and y for C , the rate equations are

$$\frac{dx}{dt} = k_A(a - x) \quad (1.32)$$

for the transformation of A into B with the rate constant k_A and

$$\frac{dy}{dt} = k_B(x - y) \quad (1.33)$$

for the subsequent transformation of B into C with the rate constant k_B .

The integrated equations are

$$x = a[1 - \exp-(k_A t)] \quad (1.34)$$

for A and

$$y = a \left\{ 1 + \left[\frac{k_A}{k_B - k_A} \exp(-k_B t) \right] - \left[\frac{k_B}{k_B - k_A} \exp(-k_A t) \right] \right\} \quad (1.35)$$

for C .

By subtracting equation (1.35) from (1.34), an expression for the intermediate product B is obtained

$$x - y = a \frac{k_A}{k_B - k_A} \{ [\exp(-k_A t)] - [\exp(-k_B t)] \}. \quad (1.36)$$

The determinate forms

$$x - y = a k t [\exp(-k t)] \quad (1.37)$$

and

$$y = a \{ 1 - [\exp(-k t)] - [k t \exp(-k t)] \} \quad (1.38)$$

of equations (1.35) and (1.36) in the case of equal values, $k_A = k_B = k$, of both constants are found, using l'Hôpital's rule.

As seen from equation (1.37), the function $(x - y)$ describing the time dependence of the concentration of B must have a maximum because initially ($t = 0$) it is zero, then increases almost linearly ($\exp(-k t)$ is close to unity at small t) and finally again tends to zero ($[t \exp(-k t)] \rightarrow 0$, as $t \rightarrow \infty$). The time when the maximum is reached can readily be found by differentiating equation (1.37) with respect to time and further equating the first derivative to zero, giving

$$t_{\max} = \frac{1}{k}. \quad (1.39)$$

In this particular case of equal rate constants, the maximum value of the concentration of B is

$$(x - y)_{\max} = a / e, \quad (1.40)$$

where e is the natural logarithm base.

The kinetic dependences for A , B and C in the general case of commensurate values of both constants k_A and k_B are shown schematically in Fig. 1.2. As equations (1.34)-(1.36) contain a on their right-hand parts, the reduced concentrations of the reagents are provided on the ordinate (in fractions relative to the initial concentration of A).

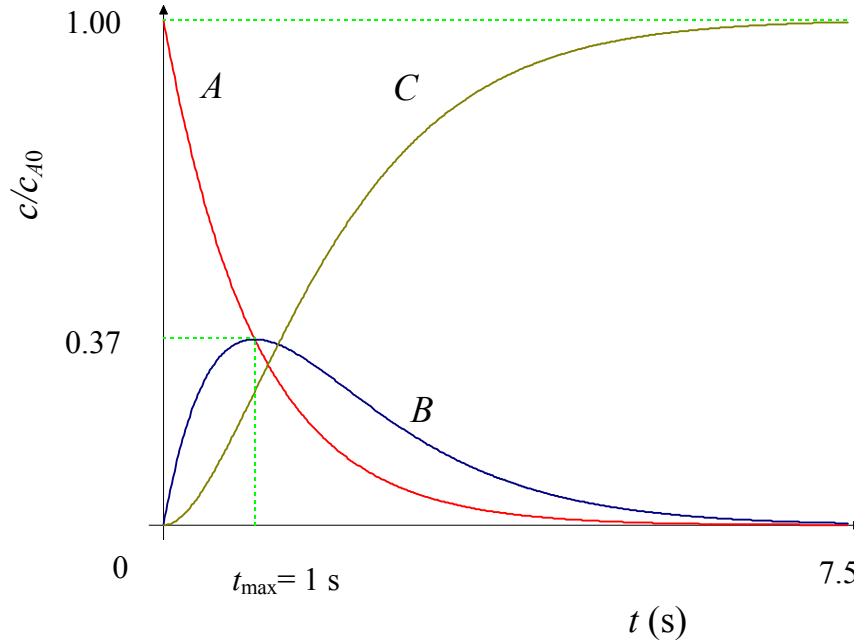


Fig. 1.2. Typical plots of the concentrations, c , of the reagents A , B and C against time, t , in the consecutive reaction $A \rightarrow B \rightarrow C$ in the general case of equal values of both constants k_A and k_B ($k_A = k_B = 1 \text{ s}^{-1}$).

The concentration of A is seen to decrease exponentially from unity to zero with passing time (ordinary first-order reaction). The concentration-time relationship for B again goes through a maximum that is attained at the time

$$t_{\max} = \frac{\ln(k_B / k_A)}{k_B - k_A}. \quad (1.41)$$

Its height is found by inserting $t_{\max}$ into equation (1.36). Hence,

$$(x - y)_{\max} = \frac{a}{r - 1} [r^{-1/(r-1)} - r^{-r/(r-1)}], \quad (1.42)$$

where $r = k_B / k_A$. The maximum value, $(x - y)_{\max}$, of the concentration of B is seen to depend only on the ratio of the rate constants and not on their absolute values.

The concentration-time relationship for C is sigmoid in shape and exhibits a point of inflection, whose position coincides with $t_{\max}$. Initially, the rate of formation of the final product C is very low. The initial stage when the product C is hardly detectable is often called the *induction* period of the consecutive reaction. Then, the reaction $A \rightarrow C$ accelerates and after the inflection point has reached it again becomes progressively slow. Finally, the concentration of C attains the initial concentration of A , whereas the latter drops to zero.

Consider two extreme cases. If $k_A \gg k_B$ and hence r is very small, then its value can be neglected in comparison with unity, and equation (1.42) yields

$$(x - y)_{\max} \approx \frac{a}{-1} (r^{+1} - r^{-r}) \approx a. \quad (1.43)$$

The concentration-time relationships for this case are shown schematically in Fig. 1.3. The concentration of A drops very rapidly from its initial value a (or unity in relative fractions) to almost zero, so that the concentration curve for A practically coincides with the plot axes and is readily distinguishable only if drawn in colour.

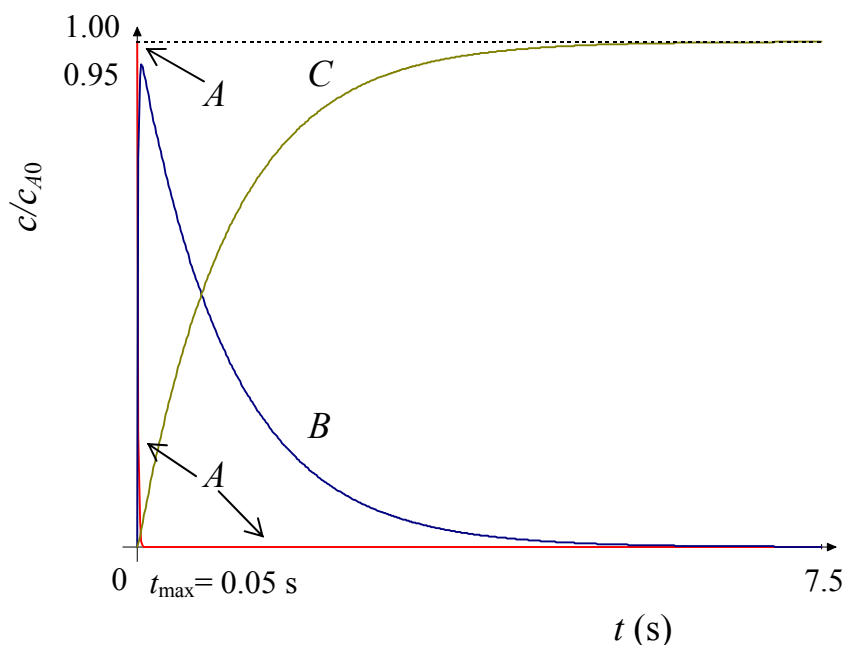


Fig. 1.3. Typical plots of the concentrations, c , of the reagents A , B and C against time, t , in the consecutive reaction $A \rightarrow B \rightarrow C$ in the case where $k_A \gg k_B$ ($k_A = 100 \text{ s}^{-1}$, $k_B = 1 \text{ s}^{-1}$).

At the same time, the concentration of B increases from zero to values close to a (unity). In other words, A rapidly transforms into B . Accordingly, the maximum on the concentration curve for B becomes higher (0.95 in Fig. 1.3 instead of 0.37 in Fig. 1.2) and displaces towards the origin ($t_{\max} = 0.05$ s). Further reaction actually consists in the consumption of the accumulated substance B in the subsequent slow transformation $B \rightarrow C$. The reaction $B \rightarrow C$ thus becomes *rate-determining* for the whole series of consecutive transformations $A \rightarrow B \rightarrow C$.

If $k_A \ll k_B$ and hence r is very large, then in equation (1.42) unity can be neglected in comparison with its value. Therefore,

$$(x - y)_{\max} \approx \frac{a}{r} (r^{-1/r} - r^{-1}) \approx \frac{a}{r} \quad . \quad (1.44)$$

In this case, the first transformation $A \rightarrow B$ is very slow and therefore is rate-determining for the overall reaction $A \rightarrow B \rightarrow C$. The height of the maximum for B is extremely small.

It should be noted that in both extreme cases none of the reactions ceases entirely. They all are continuing, though at very different rates, until A is consumed completely.

The case in which $k_B > k_A$ and the ratio, k_B/k_A , of the rate constants remains unchanged, while the difference $k_B - k_A$ varies appreciably, deserves further consideration. If $k_B / k_A = \text{const}$, the height of the maximum for B determined from equation (1.42) is the same, whatever the difference $k_B - k_A$, as illustrated schematically in Fig. 1.4 for the hypothetical reaction with $k_B/k_A = 10$ and four values of the difference $k_B - k_A$.

However, as evidenced from equation (1.41), the position of this maximum is dependent upon the difference $k_B - k_A$, so that the smaller the difference $k_B - k_A$, the greater is $t_{\max}$. Also, as seen from Fig. 1.4, the maximum broadens significantly, as the value of $k_B - k_A$ decreases. It means that at $t > t_{\max}$ the rate of formation of B remains close to zero during a rather long period of time. Hence, the *quasi-stationary* regime is established when the rate of formation of B in the first reaction $A \rightarrow B$ of their series $A \rightarrow B \rightarrow C$ is almost equal to the rate of its consumption in the second $B \rightarrow C$.

It is also worth mentioning that, if $k_B > k_A$, the term $\exp(-k_B t)$ of equation (1.36) becomes negligibly small at sufficiently long times in comparison with the term $\exp(-k_A t)$, and this equation takes the simpler form

$$x - y = a \frac{k_A}{k_B - k_A} \exp(-k_A t) \quad . \quad (1.45)$$

Dividing this expression by $a - x = a \exp(-k_A t)$ determined from equation (1.34) yields

$$\frac{c_B}{c_A} = \frac{x-y}{a-x} = \frac{k_A}{k_B - k_A}. \quad (1.46)$$

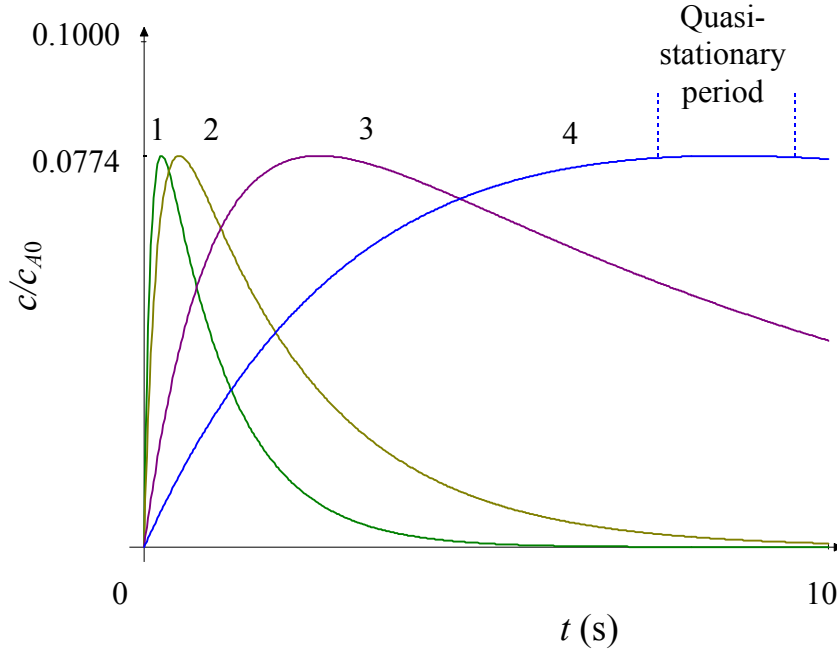


Fig. 1.4. Plots of the concentration, c , of the intermediate product B formed in the consecutive reaction $A \rightarrow B \rightarrow C$ against time, t , in the case where $k_B/k_A = 10$ and $k_B = 10.0 \text{ s}^{-1}$, $k_A = 1.0 \text{ s}^{-1}$ (line 1); $k_B = 5.0 \text{ s}^{-1}$, $k_A = 0.5 \text{ s}^{-1}$ (line 2); $k_B = 1.0 \text{ s}^{-1}$, $k_A = 0.1 \text{ s}^{-1}$ (line 3) and $k_B = 0.3 \text{ s}^{-1}$, $k_A = 0.03 \text{ s}^{-1}$ (line 4).

Hence, the *quasi-stationary* state (sometimes also called the *transition equilibrium*) is established when the ratio of the concentration of the intermediate product B to that of the reactant A remains constant.

If $k_B \gg k_A$, then $(k_B - k_A) \approx k_B$ and equation (1.46) becomes

$$\frac{c_B}{c_A} = \frac{k_A}{k_B} = \frac{(\tau_{1/2})_B}{(\tau_{1/2})_A} = \frac{(\tau_{\text{life}})_B}{(\tau_{\text{life}})_A}. \quad (1.47)$$

In this particular case, the reactant A and the intermediate product B are said to be in *secular equilibrium* with each other, even though it is only the quasi-stationary state and not a real equilibrium.

1.1.2: Description of the kinetics of solid-state heterogeneous reactions

Let us begin an analysis of the process of formation of chemical compounds in heterogeneous systems with the simplest case of growth of a solid layer between elementary substances A and B which form, according to the equilibrium phase diagram of the A – B binary system, only one chemical compound A_pB_q , p and q being positive numbers (Fig. 1.5). The substances A and B are considered to be solid at reaction temperature T_1 and mutually insoluble.

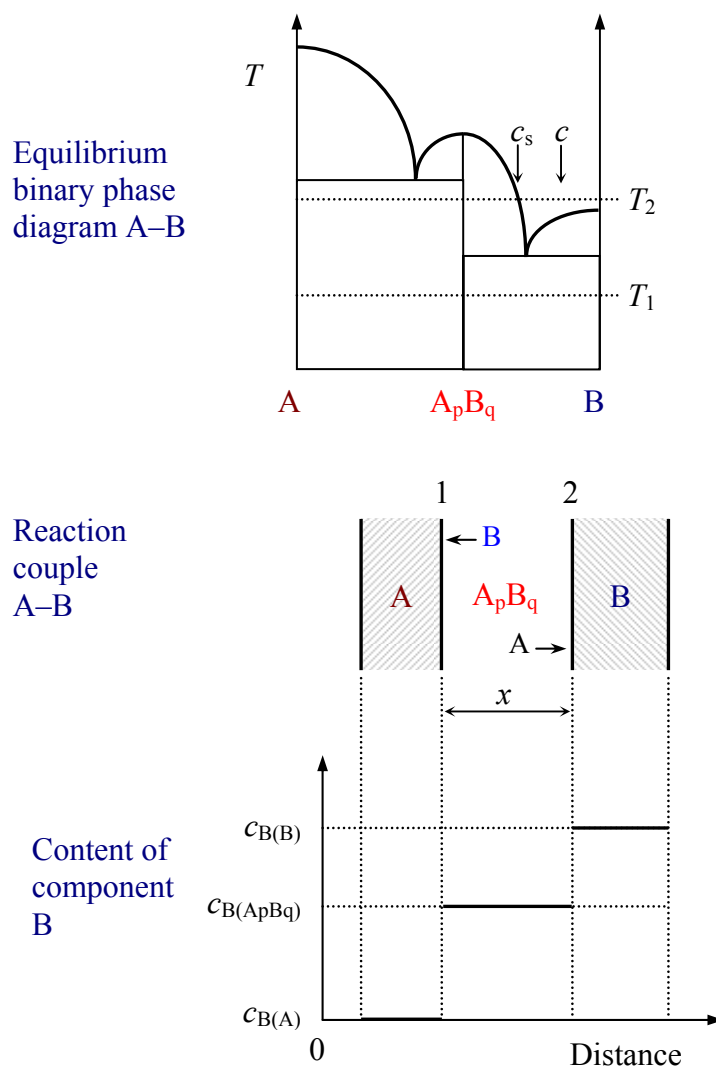


Fig. 1.5. Schematic diagram to illustrate the heterogeneous process of growth of the A_pB_q chemical compound layer at the interface between mutually insoluble elementary substances A and B .

It is easy to notice that the basic concepts and laws of the kinetics of homogeneous chemical reactions surveyed in the preceding section can hardly be used in considering the examined *heterogeneous* process. Indeed, difficulties already arise when employing the main concepts of chemical kinetics, namely, the *concentration* of a reactant or a product in the system and the *rate* of a chemical reaction.

In the case of any homogeneous system in which all reacting substances are mixed at the atomic or molecular level, the definition of the concentration as the amount of a substance in unit volume is applicable to the entire system consisting of initial substances and reaction products as a whole. By contrast, in the case of any heterogeneous system, it is only rational for components A and B within each of its homogeneous parts (phases).

In the examined case of the $A-A_pB_q-B$ system, it is clearly possible to define the concentration (content) of component, for example A , in initial phases A and B or in a growing layer of the compound A_pB_q . However, it is quite irrational to consider the concentration of substance A , A_pB_q or B in the entire heterogeneous system consisting of non-mixing phases A , A_pB_q and B . In contrast to any homogeneous system in which the concentration of a given substance at any moment of time is the same at all points or at least changes continuously from point to point, in any heterogeneous system the concentration of the components is in general different at different points, and at the phase interfaces its value changes abruptly (see Fig. 1. 5). Therefore, in heterogeneous systems the distribution of the concentrations of components A and B with distance becomes important.

By definition, the chemical compound is an ordered phase of constant composition. Ordering means that in the crystal lattice of any compound each component forms its own sublattice in which all the sites are only occupied by atoms or ions of this component. The constancy of composition is a consequence of the valency rule as, for example, in the case of oxides (Al_2O_3 , CuO , TiO_2 , Fe_3O_4), or of more complicated (and still poorly understood) laws as in the case of intermetallics where compounds of somewhat surprising composition (NiBi_3 , Fe_2Al_5 , CoSn_2 , IrMo) are formed. Though the solids contain no molecules, for example, of Al_2O_3 or NiBi_3 as such, the composition of the Al_2O_3 or NiBi_3 phases is on average described by these chemical formulae. Stoichiometry resulting from the chemist's laws of definite (J.L. Proust, 1794) and multiple (J. Dalton, 1804) proportions is a characteristic feature of chemical compounds that distinguishes them from solid solutions, *i.e.* disordered phases of varying composition. As will be clear from further considerations, it is just the *stoichiometry* of a chemical compound and not the presence of *inherent structure defects*, as usually assumed, that determines the growth kinetics of the solid layer of that compound at the interface of initial substances.

Obviously, such a measure of the rate of a chemical reaction taking place in any homogeneous system as the change in *concentration* of reacting substances or its products per unit time at constant reaction volume [128-138] cannot be applied to the heterogeneous systems. In any heterogeneous system, the concentration (content) of components A and B in initial phases and in a growing layer of the A_pB_q compound having no homogeneity range

remains constant, in spite of the occurrence of any chemical reaction. Therefore, a quantitative characteristic of the rate of a chemical reaction in any heterogeneous system is the change of the *thickness* or *mass* of a solid layer per unit time. Choice of the method of following the growth process of any compound layer (either by its thickness or by mass) depends entirely upon the efficiency of experimental techniques available for the investigation of interaction of initial substances in a particular heterogeneous system.

In this book, attention will only be paid to the parallel-plane layers whose thickness is the same over the entire surface of contact of the reactants. In addition, the length of the layer in the direction normal to the direction of diffusion of components *A* and *B* (see Fig. 1.5) is assumed to be considerably greater than its thickness. In this case, the edge effects on the process of layer growth can be neglected.

It should be noted that the compound layers observed in practice seldom have an ideal appearance. Firstly, one or both boundaries of a layer with initial phases may be uneven. As an example, Fig. 1.6 shows optical micrographs of the Fe_2Al_5 intermetallic-compound layer formed at the interface between aluminium and commercial iron or steels of differing carbon content [139]. Bimetallic specimens were prepared under similar conditions by interaction of solid iron or steel with molten aluminium at 700 °C, followed by their subsequent joint cooling in water until the solidification of the melt. As seen in Fig. 1. 6, the interface of the Fe_2Al_5 layer with aluminium is relatively flat, while that with iron or steel is irregular, with the irregularity becoming progressively less, the higher the carbon content of steel. Secondly, the compound layers formed often contain cracks, pores and other macroscopic defects. Undoubtedly, this exerts a considerable (sometimes, even controlling) effect on the kinetics of their growth.

Hereafter, attention will only be paid to the growth of a compound layer that is ideal both in the chemical (constant composition) and physical (ordered structure, no macroscopic defects) sense. Influence of secondary factors such as stress, strain, specimen geometry, *etc.*, will be neglected.

1.2: Reaction-diffusion process

As its name indicates, the reaction-diffusion process includes two alternate steps (reaction and diffusion) and results in the occurrence of a continuous solid compound layer between initial substances [140]. Unlike homogeneous reactions, in this case the reaction product necessarily stays in place at the interface and is not carried away from the reaction site, thus separating the reacting phases from each other.

Note that the term *reaction diffusion* is often used in the more broad sense designating any phenomenon in which a chemical reaction is coupled with diffusion, motion or migration. Such *reaction-diffusion* phenomena are considered in detail, for example, in the book by B.A. Grzybowski [141].

The term *reaction diffusion* reflects the most important feature of the layer-formation mechanism, namely, that the layer growth is due to a continuous alternation of two consecutive steps:

- (1) *diffusion* of atoms (ions) of the reactants across its bulk in the opposite directions;
- (2) *subsequent chemical transformations* taking place at the layer interfaces with the participation of diffusing atoms of one of the components and the surface atoms of another component (*chemical reaction* as such).

In the present case, reaction-diffusion process may thus concisely be defined as chemical transformations after diffusion or *vice versa*, both being inseparably linked to one another.

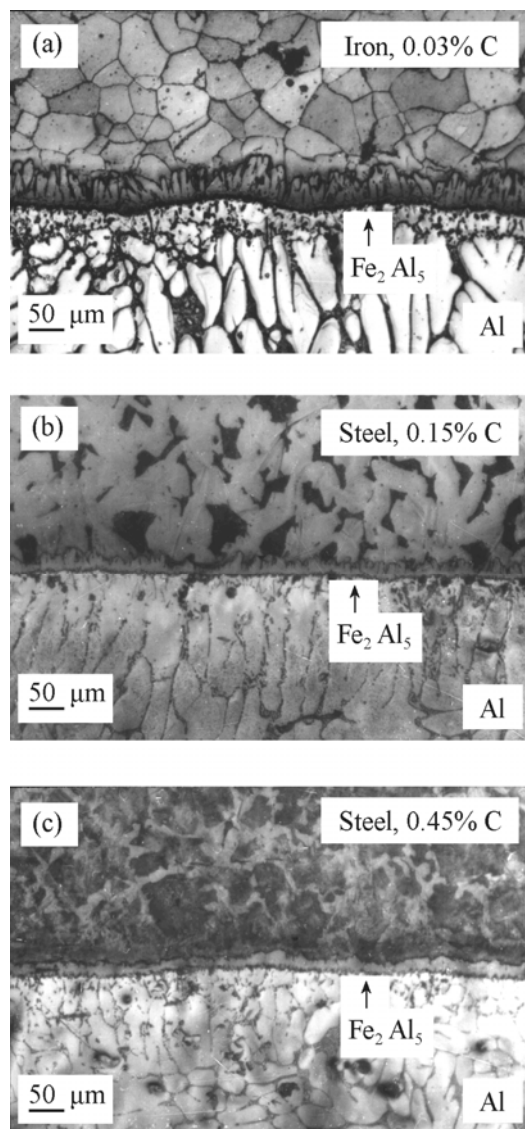


Fig. 1.6. Optical micrographs of the transition zone between commercial purity iron or steel and aluminium. The Fe_2Al_5 intermetallic compound layer becomes progressively flatter and thinner with increasing carbon content of steel. The “Al + an intermetallic compound” eutectic is distributed at grain boundaries of aluminium solid solutions.

It should be emphasised that the term *diffusional* (or *diffusion-controlled*) *growth* (*formation*) of chemical compound layers, used largely by physicists and metallurgists, only reflects one of the two aspects of the layer-growth mechanism, namely, atomic diffusion. The inadequacy of terminology is not so unimportant as it may seem at first sight. If employed solely to mask the attempt to neglect the step of *chemical transformations* inherent in the reaction-diffusion process, it results, as will be seen later, in a chain of misleading consequences and views, even though the treatment of the kinetics of solid-state formation of *chemical compounds* can formally be declared.

In the case under consideration, the concept *chemical transformations* (synonyms: *chemical reaction*, *chemical interaction*) unites the following processes.

- (1) Transition of the atoms (ions) of a given kind through the interface from one phase into the other. This is *external* diffusion, according to the terminology proposed by B.Ya. Pines [9, 142].
- (2) Redistribution of the electronic density of atomic orbitals resulting in the formation of molecules, ions, radicals or other stable groupings of atoms included in a growing compound layer.
- (3) Rearrangement of the crystal lattice of an initial phase into the crystal lattice of a chemical compound formed.

It should be noted that something like the elementary act of external diffusion also occurs in homogeneous reactions taking place in solutions or gases. Indeed, in order to be combined into a molecule, the reacting particles must move (diffuse) towards each other. The second of these processes in a liquid-phase or a gas homogeneous system results in the formation of an individual molecule that is able to travel relatively freely within the reaction volume. In the examined solid-state heterogeneous system, however, the “molecule” formed is rigidly fixed in the crystal lattice of a chemical compound together with a number of other similar “molecules”, thus lost their individuality. What is only possible in this case is the substitution of atoms of any of the “molecules” comprising the layer for equivalent atoms, not violating the stoichiometry of a compound and the total balance of atoms in the entire system.

In the general case of comparable mobility of components *A* and *B* within the A_pB_q crystal lattice, the A_pB_q compound layer grows at the expense of diffusion of the *B* atoms to interface 1 (see Fig. 1.5) where a *partial* chemical reaction then takes place in accordance with the equation

$$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q \quad (1.48)$$

and also at the expense of diffusion of the *A* atoms to interface 2 followed by another *partial* chemical reaction

$$pA_{\text{dif}} + qB_{\text{surf}} = A_pB_q. \quad (1.49)$$

Clearly, the rates of these reactions are different. Indeed, before entering reaction (1.48), the B atoms must lose any contact with the main mass of substance B and be transferred across the A_pB_q layer from interface 2 to interface 1. On the contrary, component A enters reaction (1.48) in the form of particles (atoms or ions) located onto the surface of phase A and therefore bonded chemically with the bulk of substance A . The A atoms diffusing across the A_pB_q layer from interface 1 to interface 2 and the surface B atoms enter reaction (1.49). In addition, reactions (1.48) and (1.49) take place at different interfaces of the A_pB_q layer and are therefore separated in space. Hence, the equality of their rates is a rare exception rather than the rule. Kinetically, these are two different parallel chemical reactions.

Note that parallel reactions (1.48) and (1.49) have nothing in common with parallel homogeneous chemical reactions treated in Section 1.1 of this chapter, except for the word *parallel*. In the former case, two parallel reactions proceeding at two layer interfaces yield a single compound layer. In the latter, one reactant produces two or a few products. Their kinetics are described by quite different mathematical equations.

It should be emphasised that in any heterogeneous system that attained constant temperature-pressure conditions from below (from smaller to higher values), no reaction ever proceeds within the bulk of the A_pB_q layer. Inside the A_pB_q layer, the A and B atoms (or ions) can and do exchange of their positions but these acts of natural diffusion by no means represent any chemical reaction.

It is also worth mentioning that some (very short) initial period of interaction of elementary substances when there is still no compound layer and consequently there is only one common interface at which substances A and B are able to react directly, is outside the scope of the proposed macroscopic consideration. The stage of nucleation of a chemical compound between initial phases is to be the subject of examination within the framework of a microscopic theory that would indicate, amongst other parameters of the process, a minimal thickness sufficient to identify the interaction product formed at the A – B interface as a layer of the chemical compound A_pB_q possessing its typical physical and chemical properties. However, it can already now be said with confidence that this value is very small in comparison with really measured thicknesses of compound layers and therefore can hardly exert any noticeable influence on the layer thickness-time kinetic dependences observed in practice.

Indeed, refined experiments carried out using modern techniques of investigation including various kinds of electron microscopy, X-ray diffraction, Rutherford backscattering of light ions, electron probe microanalysis, ion mass spectrometry, *etc.*, showed the layers of chemical compounds, a few nanometers thick, to possess all the properties of bulk phases. For example, in the nickel-aluminium reaction couple R.J. Tarento and G. Blaise [101] were able not only to identify the nickel aluminides NiAl_3 , Ni_2Al_3 , NiAl and Ni_3Al in the layers 5 nm thick, but also to determine the ranges of homogeneity of the aluminides having such ranges (Ni_2Al_3 and NiAl). It should be noted that the homogeneity ranges determined by those authors were in good agreement with the values indicated on the equilibrium phase

diagram of the Ni–Al binary system. The same applies to the transition metal-silicon systems that have been studied sufficiently well as the objects of primary importance for microelectronics [126, 127].

As the values of lattice spacing of chemical compounds are usually of the order of 0.5 nm or more, it follows that any compound layer 5 nm thick can contain at most 10 crystal-lattice units. Therefore, the results of an analysis of the nucleation process, obtained by F.M. d'Heurle [33] for transition-metal silicides, appear to be quite reasonable.

F.M. d'Heurle evaluated a specific thickness of the layers (an analogue of the critical radius of nuclei in a homogeneous system; for more detail, see Ref. [33]) for compounds of the Ni–Si binary system. For Ni₂Si, its value was found to be 0.15 nm, *i.e.* the “nucleus” does not contain even one lattice unit. Although higher values were obtained for other nickel silicides, they never exceeded 1 nm. Therefore, the nucleation process can hardly play any significant role in the formation of most transition-metal silicides, except in some special cases [29, 33]. This conclusion is likely to be valid for any other chemical compound layer. It should be noted, however, that there is also a different viewpoint [26, 40, 143].

Chemical treatment of the nucleation process in heterogeneous systems can be found, for example, in the book edited by W.E. Garner [144]. It might be interesting for the reader to compare it with physical considerations of A.M. Gusak *et al.* [26].

1.3: Growth of the A_pB_q layer at the expense of diffusion of component B

Let us assume that reaction (1.48) is the only one in the A – A_pB_q – B system, *i.e.* the diffusivity of component A in the crystal lattice of the A_pB_q compound is negligible in comparison with that of component B . The kinetic equation expressing the growth rate of the A_pB_q layer as a result of diffusion of the B atoms and subsequent reaction (1.48) can readily be found using the following three assumptions (postulates) [145-155].

(1) The time, dt , required for increasing the thickness of the A_pB_q layer by dx_{B1} (from x to $x + dx_{B1}$, Fig. 1.7) is the sum of the time, $dt_{\text{dif}}^{(B)}$, of diffusion of the B atoms across its bulk to the reaction site (interface 1) and the time, $dt_{\text{chem}}^{(B)}$, of their subsequent chemical interaction with the surface A atoms at interface 1:

$$dt = dt_{\text{dif}}^{(B)} + dt_{\text{chem}}^{(B)}. \quad (1.50)$$

(2) The time, $dt_{\text{dif}}^{(B)}$, of diffusion of the B atoms is directly proportional to both the increase, dx_{B1} , of the thickness of the A_pB_q layer and its total thickness, x :

$$dt_{\text{dif}}^{(B)} = \frac{x}{k_{1B1}} dx_{B1}, \quad (1.51)$$

where k_{1B1} is a physical (diffusional) constant ($\text{m}^2 \text{s}^{-1}$).

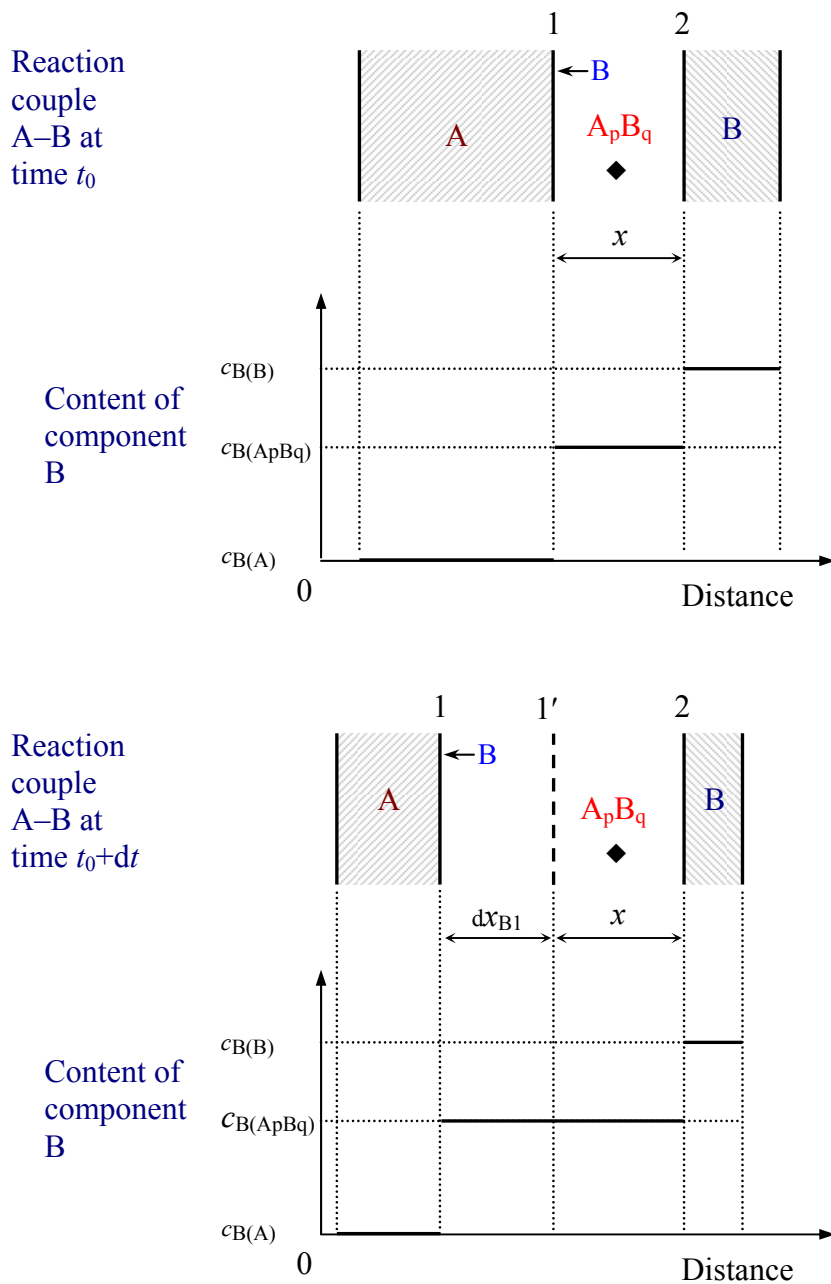


Fig. 1.7. Schematic diagram to illustrate the growth process of the A_pB_q layer between elementary substances A and B at the expense of diffusion of the B atoms and their subsequent chemical interaction with the surface A atoms. The symbol $\blacklozenge$ designates an inert marker inside the A_pB_q layer. An increase in layer thickness takes place only at the A – A_pB_q interface. Not to scale; in fact, $dx_{B1} \ll x$.

(3) The time, $dt_{\text{chem}}^{(B)}$, of chemical transformations at interface 1 with the participation of diffusing B atoms (chemical reaction as such) is directly proportional to the increase, dx_{B1} , of the thickness of the A_pB_q layer and is independent of its total thickness, x :

$$dt_{\text{chem}}^{(B)} = \frac{1}{k_{0B1}} dx_{B1}, \quad (1.52)$$

where k_{0B1} is a chemical constant (m s^{-1}).

The subscript $B1$ at dx indicates that the increase in thickness the A_pB_q layer is a result of diffusion of the B atoms and takes place at interface 1. In the subscripts $0B1$ at the chemical constant k_{0B1} and $1B1$ at the physical (diffusional) constant k_{1B1} , the first digit shows that $dt_{\text{chem}}^{(B)}$ is proportional to x^0 , while $dt_{\text{dif}}^{(B)}$ is proportional to x^1 ; the letter B and the last digit 1 have the former meaning.

Basic assumptions 1 to 3 were put forward [145, 146] as a result of analysis (i) of the reaction-diffusion mechanism described in detail by V.I. Arkharov [1, 48, 49] and (ii) of a linear-parabolic equation derived for the first time by U.R. Evans from somewhat different considerations [7]. It should be noted that similar assumptions were used earlier by B.Ya. Pines [9, 142], who, when deriving differential forms of kinetic equations, summed up the duration of *external* and *internal* diffusion.

Physicist B.Ya. Pines appeared to be unaware of chemical studies of U.R. Evans. He never referred to his works and perhaps re-discovered independently the kinetic equation that had already been known for decades, at least to chemists. It is instructive to note that Ya.E. Geguzin, who worked together with B.Ya. Pines for a long period of time and evidently knew of his approach to the problems of solid-state reaction kinetics, did not appreciate, for some obscure reasons, the importance of the results obtained by B.Ya. Pines. Ya.E. Geguzin was therefore unable to advance beyond the incomplete analysis of the growth kinetics of a single-phase compound layer [21].

Substituting the expressions for $dt_{\text{dif}}^{(B)}$ and $dt_{\text{chem}}^{(B)}$ from equations (1.51) and (1.52) into equation (1.50) yields a differential form of the required kinetic equation describing the growth rate of the A_pB_q compound layer due to partial chemical reaction (1.48):

$$dt = \left(\frac{x}{k_{1B1}} + \frac{1}{k_{0B1}} \right) dx_{B1} \quad (1.53)$$

or

$$\frac{dx_{B1}}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}}. \quad (1.54)$$

Integration of equation (1.53) (initial condition $x = 0$ at $t = 0$) gives an expression relating the time of growth of the A_pB_q layer to its total thickness:

$$t = \frac{x^2}{2k_{1B1}} + \frac{x}{k_{0B1}}. \quad (1.55)$$

These equations represent differential (equations (1.53) and (1.54)) and integrated (equation (1.55)) forms of Evans' equation. In fact, their distinction from the original Evans equation only consists in the lesser amount of constants. After eliminating excessive constants, it is easy to appreciate the significance and importance of Evans' equation that is not merely one of a number of known kinetic dependences.

Obviously, in an initial period of interaction of substances A and B when the A_pB_q layer is very thin, the number of the B atoms which could have diffused to interface 1 per unit time is considerably greater than the number of those atoms which could be combined in the A_pB_q compound by the surface A atoms. It should be noted that, in spite of the displacement of interface 1 in the course of reaction (1.48), the number of the A atoms per unit area of the surface of substance A adjacent to the A_pB_q layer remains constant. As seen in Fig. 1.8, the number of the A atoms is the same in all sections of phase A by the vertical plane passing through the atomic sites.

For real crystalline substances, this only holds with the accuracy to the lattice spacing. Since the lattice spacing is much less than the layer thickness, initial substances can be considered as macroscopically isotropic, at least in the direction of layer growth.

Each surface A atom is able to chemically bond a certain number of diffusing B atoms. For the AB compound (see Fig. 1.8), this number is equal to unity, while for the A_pB_q compound to q/p . Since the number of the A atoms onto the surface of phase A , which are ready to immediately react with the diffusing B atoms, is finite, it is obvious that the reactivity of the A surface towards these atoms is also finite.

The *reactivity* (or *combining ability*) of the *surface* of substance A towards the B atoms is equal to the largest number of diffusing B atoms that can be combined per unit time by the surface A atoms into a compound of certain composition. For example, if each of the four surface A atoms shown in Fig. 1.8 combines per second one diffusing B atom into the AB compound at interface 1, the reactivity of the A surface towards the B atoms is four B atoms per second.

Initially, when the A_pB_q layer is very thin, the reactivity of the A surface is realized to the full extent because the supply of the B atoms is almost instantaneous due to the negligibly short diffusion path. In such a case, the condition $k_{0B1} \ll k_{1B1}/x$ is satisfied. Therefore, if the surface area of contact of reacting phases A and A_pB_q remains constant, chemical reaction (1.48) takes place at an almost constant rate. In practice, this regime of layer growth is

usually referred to as *reaction controlled*. Though much less suited, the terms *interface controlled regime* and *kinetic regime* are also used.

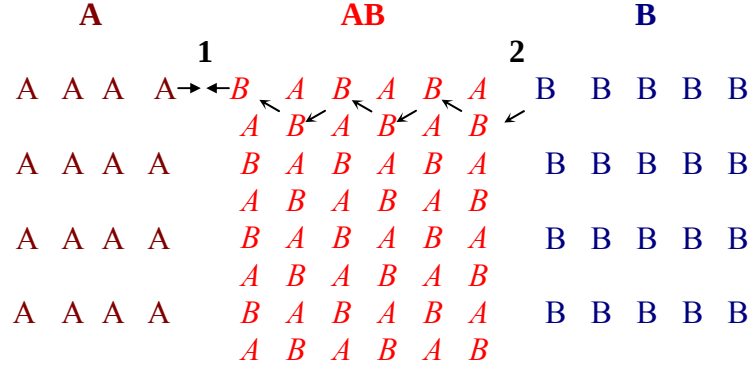


Fig. 1.8. Schematic diagram to illustrate the mechanism of growth of the AB compound layer between elementary substances A and B at the expense of diffusion of component B . Arrows indicate only one of the four shortest paths of supply of the B atoms from substance B to interface 1 where subsequently chemical transformations with their participation take place.

In the reaction controlled regime, the overall rate of layer formation is only limited by the rate of chemical transformations (chemical reaction as such). Therefore, the A_pB_q layer grows at the highest rate possible under given temperature-pressure conditions:

$$\left(\frac{dx_{B1}}{dt} \right)_{\text{reaction controlled regime}} = k_{0B1}. \quad (1.56)$$

Equation (1.56) results from equations (1.53) and (1.54) if $k_{0B1} \ll k_{1B1}/x$. In this case, the first term on the right-hand side of equation (1.55) is negligibly small compared to the second one. Hence, initial growth of the A_pB_q layer is linear:

$$x = k_{0B1}t. \quad (1.57)$$

The chemical constant k_{0B1} can readily be determined from the experimental dependence of the A_pB_q layer thickness upon time plotted in coordinates $x - t$ (Fig. 1.9a). The slope of its initial linear portion gives a value of k_{0B1} .

It is easy to understand that the reaction controlled regime of growth of the A_pB_q layer is one of the two extremes. Another is its growth in the *diffusion controlled* (or simply *diffusional*) regime. Indeed, as long as the A_pB_q layer steadily thickens, the transport of the B

atoms across its bulk from interface 2 to interface 1 (see Fig. 1.7) becomes increasingly slow. Therefore, with passing time the overall rate of layer formation becomes more and more dependent on the rate of diffusion of the B atoms, whereas the effect of the rate of chemical transformations gradually decreases and eventually becomes negligible by comparison.

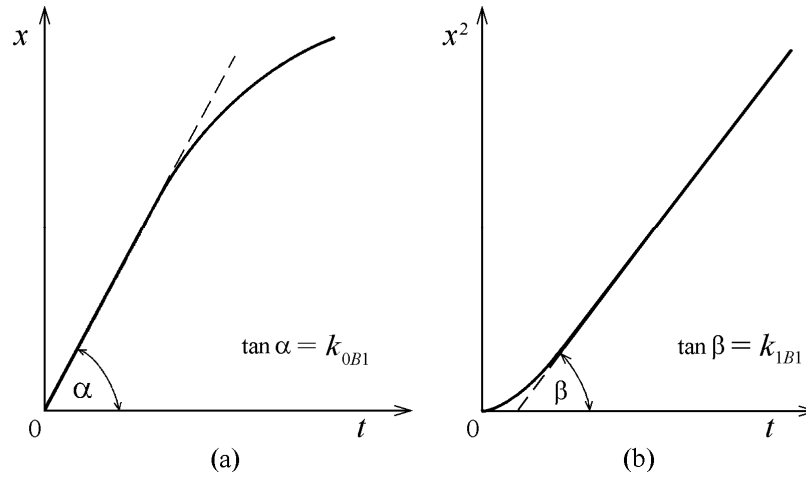


Fig. 1.9. Experimental determination of reaction-diffusion constants from a linear-parabolic dependence between the layer thickness, x , and time, t , of interaction of initial substances: $\tan \alpha = k_{0B1}$ (a), $\tan \beta = k_{1B1}$ (b). Not to scale. In fact, linear region of Fig. 1.9a corresponds to the beginning of non-linear region of Fig. 1.9b.

During growth of the A_pB_q layer in the diffusion controlled regime, the condition $k_{0B1} \gg k_{1B1}/x$ is satisfied in equations (1.53) to (1.55). In this case, the rate of growth of the layer is inversely proportional to its total thickness, x , existing at a time, t :

$$\left(\frac{dx_{B1}}{dt} \right)_{\text{diffusion controlled regime}} = \frac{k_{0B1}}{x}. \quad (1.58)$$

The time dependence of the A_pB_q layer thickness is therefore described by a parabolic equation of the form

$$x^2 = 2k_{1B1}t. \quad (1.59)$$

The physical (diffusional) constant k_{1B1} can readily be found from a long-time portion of the same A_pB_q layer thickness-time dependence but now plotted in coordinates x^2-t (Fig. 1.9b). The slope of a plot of the squared thickness of the A_pB_q layer against time yields a value of

k_{1B1} . If reaction times and accordingly layer thicknesses are insufficiently large to neglect a linear portion of the A_pB_q layer thickness-time dependence without any noticeable error, equation (1.58) must be integrated with the use of initial condition $x = x_0$ at $t = 0$ or $x = x_0$ at $t = t_0$, giving

$$x^2 - x_0^2 = 2k_{1B1}t \quad (1.60)$$

or

$$x^2 - x_0^2 = 2k_{1B1}(t - t_0). \quad (1.61)$$

Thus, both constants (chemical and physical) are determined from different portions of one and the same kinetic dependence of Evans' type.

It should be noted that if one reaction (1.52) takes place in the $A-A_pB_q-B$ system, not only the differential time, dt , is the sum of two terms, $dt_{\text{dif}}^{(B)}$ and $dt_{\text{chem}}^{(B)}$, but the integral time, t , required for the A_pB_q layer to grow from 0 to x also consists of two terms, namely, the time, $t_{\text{dif}}^{(B)}$, of diffusion of the B atoms from interface 2 to interface 1

$$t_{\text{dif}}^{(B)} = \frac{x^2}{2k_{1B1}} \quad (1.62)$$

and the time, $t_{\text{chem}}^{(B)}$, of chemical transformations with their participation at interface 1

$$t_{\text{chem}}^{(B)} = \frac{x}{k_{0B1}}. \quad (1.63)$$

As the steps of diffusion and chemical transformations are consecutive and alternate, this result appears to be quite obvious.

The idea about the summation of the times of consecutive steps of the examined solid-state process is of primary importance for understanding the peculiarities of multiple formation of compound layers in heterogeneous systems. Moreover, even in the case of growth of a single compound layer, this idea makes it possible to reveal a few aspects of the reaction-diffusion process, which remained overlooked until the year 1982 [145, 146].

1.3.1: Critical thickness of the A_pB_q layer with regard to component B

While the reactivity of the A surface towards the B atoms remains constant, the flux of the B atoms across the A_pB_q layer gradually decreases from infinitely high to infinitely small values, as the layer thickness increases with passing time from zero to infinitely high values. Hence, there is a single *critical* thickness of the A_pB_q layer [145, 147, 151, 153-155]

$$x_{1/2}^{(B)} = \frac{k_{1B1}}{k_{0B1}} \quad (1.64)$$

at which these quantities are equal. Equation (1.64) is obtained from equations (1.50)-(1.53) by putting $dt_{\text{dif}}^{(B)} = dt_{\text{chem}}^{(B)}$.

The equality $dt_{\text{dif}}^{(B)} = dt_{\text{chem}}^{(B)}$ means that half the differential time, dt , is spent on the transport of the B atoms to the reaction site, while another half is spent on further chemical transformations in which those atoms take part. This is denoted by the index 1/2 at x .

At $x < x_{1/2}^{(B)}$, the reactivity of the A surface towards the B atoms is less than the flux of these atoms across the A_pB_q layer. Therefore, there are “excessive” B atoms which may be used in the formation of either other chemical compounds (enriched in component A in comparison with the A_pB_q compound) of a multiphase binary system or a solid solution of B in A .

On the contrary, at $x > x_{1/2}^{(B)}$, there is a deficit of the B atoms because the reactivity of the A surface exceeds the flux of these atoms across the A_pB_q layer. Therefore, on reaching interface 1, each B atom is combined at this interface into the A_pB_q compound. In this case, there are no “excessive” B atoms for the formation of other compounds enriched in component A . Thus, none of compound layers located between A and A_pB_q can grow at the expense of diffusion of component B . This almost obvious result following in a natural way from the proposed physico-chemical considerations is crucial for understanding the mechanism of formation of multiple compound layers. Perhaps, just its evident character is the main reason, firstly, why it was overlooked by other investigators and, secondly, why it was met with prejudice by many university professors and members of different academies, but fortunately not by students and active researchers whose minds are flexible enough to readily accept obvious facts.

It should be emphasised that in the examined case of growth of a single layer of the A_pB_q compound, there is only the *possibility* of occurrence of an “excess” of the B atoms at $x < x_{1/2}^{(B)}$, but not this excess as such in the form of a build-up of those atoms at interface 1. In the solid-state reactions, there is simply no free space for this to take place. Therefore, the word *excess* was inserted in the commas, in contrast to the word *deficit*. At $x > x_{1/2}^{(B)}$, a relative deficit of the B atoms is the severe reality even for the A_pB_q layer itself, which could otherwise have grown at a much higher rate.

The thickness, $x_{1/2}^{(B)}$, of the A_pB_q layer is referred to as *critical* because the growth conditions for the layers of other compounds of a given multiphase system become indeed critical, if $x > x_{1/2}^{(B)}$. At this thickness, all other compound layers lose a source of the B atoms (only substance B is actually such a source) and their growth at the expense of diffusion of the B atoms proves impossible. This problem will be examined in more detail when analysing the process of formation of two and multiple chemical compound layers.

The existence of a critical thickness of any growing layer can easily be understood without any complicated mathematical equations from a schematic diagram shown in Fig. 1.10. This diagram explains the mechanism of physico-chemical processes taking place in the $A-AB-B$ system. Only one of the diffusion paths, along which the B atoms can move (see Fig. 1.8), is shown in Fig. 1.10. To simplify the diagram, the number of “molecular” AB units was halved in comparison with their number in Fig. 1.8.

Time	Process	A	AB	B
			1	2
0 s	Initial state	A A A A	B A B A B A	B B B B B
1 s	External diffusion of atom B from AB towards A	A A A A	← B A B A B A	B B B B B
6 s	Chemical reaction resulting in the formation of a new “molecule” AB and a vacancy V_B	A A A	A V_B A B B A B A	B B B B B
7 s	Internal diffusion of atom B in AB via the vacancy mechanism	A A A	A B A B B A V_B A	B B B B B
8 s	External diffusion of atom B from B into AB	A A A	A B A V_B ← B B A B A	B B B B B
9 s	New initial state, with the thicker AB layer	A A A	A B A B B A B A	B B B B

Fig. 1.10. Physico-chemical processes taking place in the $A-AB-B$ system during growth of the AB layer at the expense of diffusion of component B (see also Fig. 1.8).

Let us assume that the chemical transformations resulting in the formation of an additional “molecule” AB require six seconds, of which the diffusion of a B atom through interface 1 to phase A takes one second, whereas the redistribution of electrons and the rearrangement of the A lattice into the AB lattice take five seconds in total. It is also assumed that the transition of each B atom to the adjacent vacant site of the AB lattice takes place

within one second. The time of external diffusion of a B atom from phase B through interface 2 into the AB lattice is considered to be one second as well.

It is obvious that a new AB plane will form at the end of the sixth second. This plane corresponds to an additional “molecule” AB , while a vacancy occurs in the previous plane instead of the B atom that has reacted with the surface A atom. This vacancy is step-by-step filled with adjacent B atoms, and at the end of the eighth second it will be located onto the surface of phase AB from the side of interface 2. Finally, it is filled with another B atom from substance B .

Thus, at the end of ninth second the system $A-AB-B$ returns to a new initial state which differs from the previous one only by the lesser number of atoms (atomic planes in two dimensions) in initial phases A and B and the greater number of “molecular” AB units in the growing AB layer. The reaction-diffusion process is repeated again and again, with the diffusion path of the B atoms from interface 2 to interface 1 becoming progressively longer, until either A or B is consumed completely.

It is easy to notice that during the same nine seconds three B atoms could have displaced from substance B across the AB layer to interface 1, if the chemical transformations at interface 1 (including also external diffusion of the B atoms to phase A through interface 1) would occur instantaneously or if the “excessive” B atoms (there are two such atoms in the case under consideration) would be used in the formation of the layers of other compounds of the same binary system. In the examined case of a single compound, this possibility of diffusion of “excessive” B atoms from interface 2 to interface 1 is not realized because the diffusion path is closed up until chemical transformations at interface 1 have completed. However, the existence of such a possibility must be borne in mind when considering the multiple layer growth.

Obviously, the critical thickness of the AB layer at which all the B atoms, capable of reaching interface 1 by a given moment of time, will be combined into the AB compound is six atomic planes corresponding to AB “molecules” (see Fig. 1.8). Indeed, in this case the reactivity of the A surface towards the B atoms is equal to one-sixth of B atom per second (one B atom per six seconds). The flux of the B atoms across the bulk of the AB layer is also equal to the same value (six consecutive displacements of the B atoms to adjacent sites within the AB lattice plus the transition of one of them through interface 2 last 6 seconds, so that one B atom crosses interface 1 as a result of these movements). At a greater thickness of the AB layer the rate of diffusion of the B atoms across its bulk is already insufficient to satisfy to the full extent the reactivity (combining ability) of the surface of phase A towards these atoms.

1.3.2: Growth regime of the A_pB_q layer with regard to component B : theoretical definition

The existence of the critical thickness, $x_{1/2}^{(B)}$, of the A_pB_q layer makes it possible to give a strict *theoretical* definition of its growth regime. Namely, the regime of growth of the A_pB_q layer is *reaction controlled with regard to component B* at

$$x < x_{1/2}^{(B)}$$

and is *diffusion controlled with regard to this component* at

$$x > x_{1/2}^{(B)}.$$

If the A_pB_q layer grows in the reaction controlled regime with regard to component B , then

$$dt_{\text{chem}}^{(B)} > dt_{\text{dif}}^{(B)}.$$

If growth of the A_pB_q layer is diffusion controlled with regard to component B , then

$$dt_{\text{chem}}^{(B)} < dt_{\text{dif}}^{(B)}.$$

From a theoretical viewpoint, the layer thickness-time dependence can therefore be divided into two distinct regions: reaction controlled at $0 < x < x_{1/2}^{(B)}$ and diffusion controlled at $x > x_{1/2}^{(B)}$ (Fig. 1.11a).

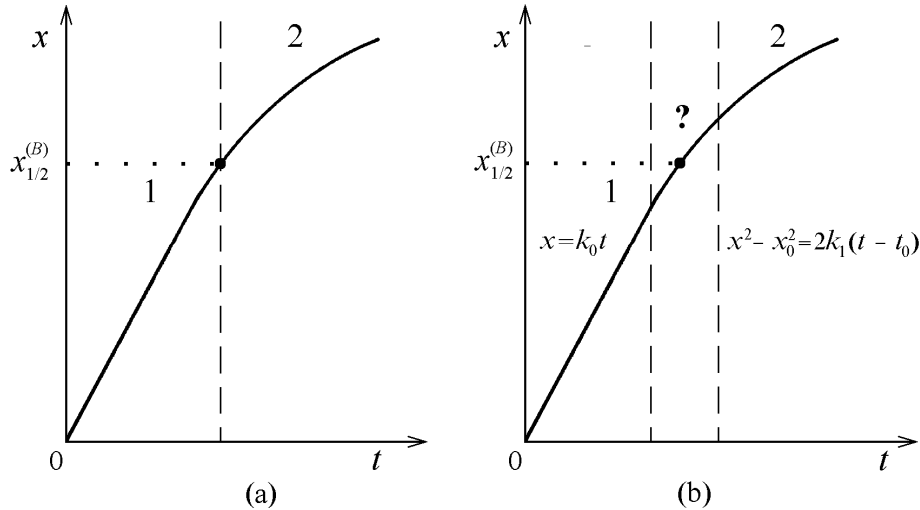


Fig. 1.11. Schematic diagram explaining (a) the theoretical definition of the concept of the growth regime of the A_pB_q layer and (b) the ‘practical’ one. 1, region of reaction control; 2, region of diffusion control.

It is easy to notice a principal difference between the proposed theoretical definition of the concept of the growth regime of any compound layer and the previous ‘practical’ one. In practice, the reaction controlled regime is in fact associated with the linear stage of layer growth ($k_{0B1} \ll k_{1B1}/x$), while the diffusion controlled regime with the parabolic stage ($k_{0B1} \gg k_{1B1}/x$). Hence, the first stage corresponds to layer thicknesses much less than $x_{1/2}^{(B)}$:

$$x \ll x_{1/2}^{(B)},$$

whereas the second stage corresponds to layer thicknesses much greater than $x_{1/2}^{(B)}$:

$$x \gg x_{1/2}^{(B)}.$$

Therefore, instead of the definite point, $x_{1/2}^{(B)}$, of change of the growth regime of the A_pB_q layer, there occurs a transition region of uncertain width. In Fig. 1.11b, this region is designated by the question mark to underline its uncertainty.

1.3.3: Stationary point

Although the validity of equation (1.55) as one of basic kinetic dependences has been verified by numerous experiments (see Refs [6,7,13,59-64,123,124]) and is now beyond any doubt, its derivation given originally by U.R. Evans and then repeated in many papers, monographs and textbooks is unfortunately misleading. Firstly, it is quite inapplicable to chemical compounds without any range of homogeneity. Secondly, it is based on the separate description of the rates of the reaction and diffusion controlled stages of any solid-state chemical reaction by some functions $(dx/dt)_{\text{reaction stage}} = f_1$ and $(dx/dt)_{\text{diffusion stage}} = f_2$ which are assumed to be equal in some “stationary” or “equilibrium” state (for more detail, see, for example, Ref. [7]).

It is obvious, however, that neither the diffusion of atoms nor their chemical transformations, even if they would happen to take place in isolation from each other, can result in increase of the layer thickness by dx . Therefore, both the rate of diffusional supply of atoms and the rate of chemical transformations cannot in general be expressed in the form of any derivative dx/dt , with x being the thickness of the A_pB_q layer at time t .

This misunderstanding is likely to arise from the unjustified application of the concept of stationary or steady state, which proved to be helpful in analysing the kinetics of a few *consecutive chemical reactions* ($A_1 \rightarrow A_2 \rightarrow A_3$) in a homogeneous system, to the case of a single solid-state process taking place in a heterogeneous system in a few *consecutive steps* which are often also referred to as *stages*. It is probably the last word that leads to confusion. In fact, kinetics of consecutive homogeneous chemical reactions briefly considered in Section 1.1.1 have nothing in common with the examined reaction-diffusion process resulting in the solid-state growth of a chemical compound layer.

Indeed, in the former case it is possible to indicate for each substance A_1 , A_2 and A_3 the appropriate mass, m_i , or concentration, c_i , and to characterise the rate of their formation by three derivatives dm_i/dt or dc_i/dt ($i = 1, 2, 3$), whereas in the latter case it is only possible to indicate that part, dt_i , of the differential time, dt , which is necessary for the i -th step of the process to complete. In general, each dt_i is a function of both x and dx . The sum of dt_i is equal to the time, dt , during which the thickness of a growing layer increases by dx (or its mass by dm) since, of a chain of successive steps in a solid-state heterogeneous system, any next step can only start after the preceding step has completed.

It should be emphasised that, although there are several such steps, they can readily be divided into two groups on the basis of their dependence on dx and x .

- (1) The steps that depend on dx but are independent of x . These were united under the term *chemical transformations* (see Section 1.1.2).
- (2) The steps that depend on both dx and x , with the only representative being the diffusion of atoms (ions or other particles) across a growing chemical compound layer.

Therefore, equations (1.50) and (1.53) contain only two terms on their right-hand sides. In regards to the stationary state of the reaction-diffusion process, it should be noted that the number of the B atoms diffusing across the A_pB_q layer is always equal to their number combined by the A surface into the A_pB_q compound at interface 1, provided that the growth of this layer is not accompanied by the formation of other compounds or solid solutions. This is a *forced stationary state* due to (i) the impossibility of any build-up of atoms at interfaces between the solids, (ii) the limited number of diffusion paths in the A_pB_q layer for the B atoms to travel from interface 2 to interface 1 and (iii) the finite value of the reactivity of the A surface towards the B atoms. It is clear that the real stationary state would only be observed at $x = x_{1/2}^{(B)}$.

Actually, in the case under consideration there is a single stationary point and not the steady state. If it were possible to maintain the thickness of the A_pB_q layer equal to $x_{1/2}^{(B)}$ by continuous removing the product of reaction (1.48), which is accumulating above this value, such growth conditions would indeed correspond to the stationary state in which the number of the B atoms diffusing to interface 1 per unit time is equal to their number which the A surface is able to combine into the A_pB_q compound. The time at which the A_pB_q layer reaches the thickness $x_{1/2}^{(B)}$ is the only moment of full harmony between reaction and diffusion. At smaller times reaction predominates, whereas at greater times diffusion becomes dominant. In any heterogeneous $A-A_pB_q-B$ system given to itself, no steady state is clearly possible.

In the general case of varying thickness of the A_pB_q layer, the summation of $dt_{\text{dif}}^{(B)}$ and $dt_{\text{chem}}^{(B)}$ makes it possible to match the diffusional flux of the atoms across its bulk with the flux of the same atoms combined at the corresponding interface into the chemical compound. Actually, it is employed instead of any kind of the continuity equation that can hardly be applied directly in the case under consideration.

1.4: Growth of the A_pB_q layer at the expense of diffusion of components A and B

If components A and B have comparable mobilities in the A_pB_q lattice, then reactions (1.48) and (1.49) proceed simultaneously. In fact, these are two parallel reactions each of which takes place in two consecutive steps.

Note that, in application to any $A-A_pB_q-B$ system, the word *reaction* may be and is used in the following three senses. Most broadly, it merely means that A and B react forming A_pB_q . In the less broad sense, it is used to designate reactions (1.48) and (1.49) resulting in the formation of A_pB_q at interfaces 1 and 2. Actually, this word unites reaction as such and diffusion supplying atoms for it to proceed. Also, it is employed as a synonym of the terms *chemical interaction* and *chemical transformations* (see Section 1.1.2).

During the time dt , the thickness of the A_pB_q layer increases from x to $x + dx_{B1}$ at interface 1 due to reaction (1.48) and from x to $x + dx_{A2}$ at interface 2 due to reaction (1.49), as shown in Fig. 1.12. Using the results of Section 1.3, it is easy to find an equation relating dt to dx_{A2} . Again, the following three assumptions are employed.

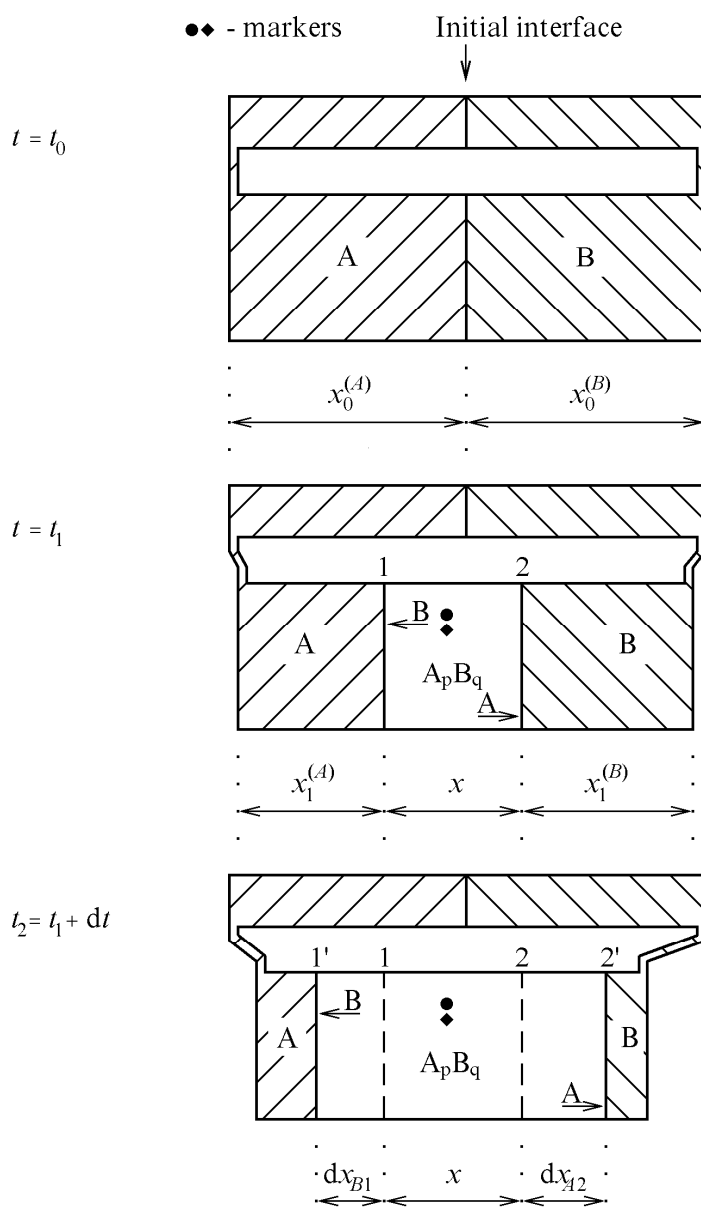


Fig. 1.12. Schematic representation of the growth process of the A_pB_q layer between elementary substances A and B due to the simultaneous diffusion of both components. Formation of the A_pB_q compound is accompanied by a decrease in volume of that part of the couple where the components A and B are able to react with each other (negative volume effect). Positive volume effect (an increase in volume of the couple) can also be observed.

(1) The differential time, dt , necessary to increase the thickness of the A_pB_q layer by dx_{A2} (from x to $x + dx_{A2}$) is the sum of the time, $dt_{\text{dif}}^{(A)}$, of diffusion of the A atoms across its bulk to interface 2 where reaction (1.49) takes place and the time, $dt_{\text{chem}}^{(A)}$, of their subsequent chemical interaction with the surface B atoms at this interface:

$$dt = dt_{\text{dif}}^{(A)} + dt_{\text{chem}}^{(A)}. \quad (1.65)$$

This equation differs from equation (1.50) only by the values of the terms on the right-hand side.

(2) The time, $dt_{\text{dif}}^{(A)}$, of diffusion of the A atoms is directly proportional to both the increase, dx_{A2} , of the thickness of the A_pB_q layer and its total thickness, x :

$$dt_{\text{dif}}^{(A)} = \frac{x}{k_{1A2}} dx_{A2}, \quad (1.66)$$

where k_{1A2} is another physical (diffusional) constant. The values of the constants k_{1B1} and k_{1A2} are in general different.

(3) The time, $dt_{\text{chem}}^{(A)}$, of their chemical interaction with the surface B atoms is directly proportional to the increase, dx_{A2} , of the thickness of the A_pB_q layer and is independent of its total thickness, x :

$$dt_{\text{chem}}^{(A)} = \frac{1}{k_{0A2}} dx_{A2}, \quad (1.67)$$

where k_{0A2} is another chemical constant different from k_{0B1} .

Substituting the expressions for $dt_{\text{dif}}^{(A)}$ and $dt_{\text{chem}}^{(A)}$ from equations (1.66) and (1.67) into equation (1.65) yields the required differential equation

$$dt = \left(\frac{x}{k_{1A2}} + \frac{1}{k_{0A2}} \right) dx_{A2}. \quad (1.68)$$

It is analogous to equation (1.53).

1.4.1: Critical thickness and growth regime of the A_pB_q layer with regard to component A

It seems obvious that, in addition to $x_{1/2}^{(B)}$, there is another critical value, $x_{1/2}^{(A)}$, of the thickness of the A_pB_q layer, at which all the A atoms capable of reaching interface 2 (see Figs 1.8 and 1.12) by a given moment of time are combined at this interface by the surface B atoms into the A_pB_q compound. To find out this value, it is sufficient to put $dt_{\text{dif}}^{(A)} = dt_{\text{chem}}^{(A)}$ in equations (1.65)-(1.68). Hence,

$$x_{1/2}^{(A)} = \frac{k_{1A2}}{k_{0A2}}. \quad (1.69)$$

At $x < x_{1/2}^{(A)}$, there is an “excess” of diffusing A atoms since the reactivity of the B surface towards these atoms is less than their flux across the A_pB_q layer. The “excessive” A atoms can be consumed in the formation of the layers of other chemical compounds of a given binary system enriched in component B in comparison with A_pB_q , if present on the equilibrium phase diagram.

On the contrary, if $x > x_{1/2}^{(A)}$, there is a deficit of the A atoms even for the growth of the A_pB_q layer because the reactivity of the B surface towards the A atoms is greater than the flux of these atoms across its bulk. On reaching interface 2, each A atom is combined at this interface into the A_pB_q compound. Therefore, there are no “excessive” A atoms for the growth of other compounds enriched in component B in comparison with A_pB_q .

Like the case of component B , it is possible to theoretically define the concept of the regime of growth of the A_pB_q layer with regard to component A as well. The growth regime of the A_pB_q layer is *reaction controlled with regard to component A* at

$$x < x_{1/2}^{(A)}$$

and *diffusion controlled with regard to this component* at

$$x > x_{1/2}^{(A)}.$$

If the layer of the A_pB_q chemical compound grows in the reaction controlled regime with regard to component A , then

$$dt_{\text{chem}}^{(A)} > dt_{\text{dif}}^{(A)}.$$

During its growth in the diffusion controlled regime with regard to component A ,

$$dt_{\text{chem}}^{(A)} < dt_{\text{dif}}^{(A)}.$$

Critical thicknesses, $x_{1/2}^{(B)}$ and $x_{1/2}^{(A)}$, of the A_pB_q layer are in general different. Therefore, from a theoretical viewpoint, the layer thickness-time dependence (see Fig. 1.11a) can once again be divided into the following two regions: reaction controlled with regard to component A at $0 < x < x_{1/2}^{(A)}$ and diffusion controlled with regard to this component at $x > x_{1/2}^{(A)}$. In most reaction couples, such a division with regard to components A and B does not coincide (Fig. 1.13). Hence, during some period of time (at $x_{1/2}^{(B)} < x < x_{1/2}^{(A)}$) the A_pB_q layer

grows in the reaction controlled regime with regard to component A and in the diffusion controlled regime with regard to component B .

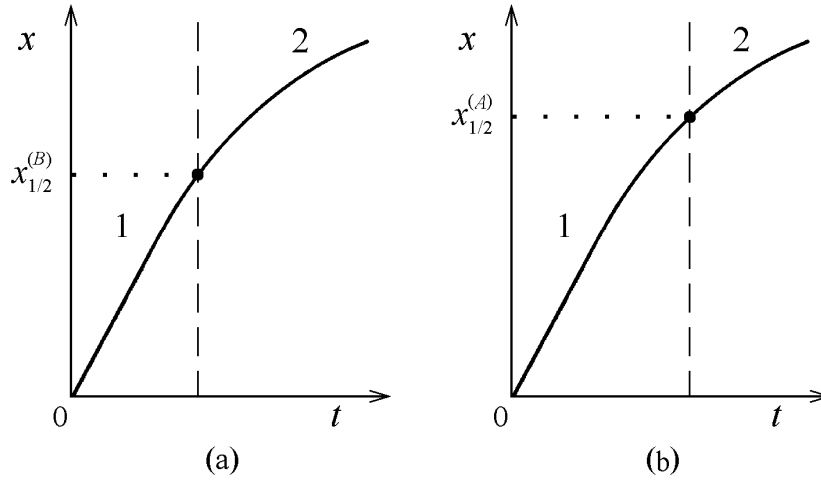


Fig. 1.13. Schematic diagram to explain the theoretical definition of the concept of the growth regime of the A_pB_q layer with regard to components A and B . (a): 1, region of *reaction* (or, more precisely, *chemical*) control with regard to component B ; 2, region of *diffusion* control with regard to component B . (b): 1, region of *reaction* (*chemical*) control with regard to component A ; 2, region of *diffusion* control with regard to component A .

Since the “practical” definition of the concept of the layer growth regime is based on the conditions $k_{0B1} \ll k_{1B1}/x$ and $k_{0A2} \ll k_{1A2}/x$ for the reaction controlled regime and $k_{0B1} \gg k_{1B1}/x$ and $k_{0A2} \gg k_{1A2}/x$ for the diffusion controlled regime (see Section 1.3.2), it is clear that in this case there is no need to indicate the component with regard to which the growth regime is defined. Indeed, according to the “practical” definition of this concept, $x \ll x_{1/2}^{(B)}$ and $x \ll x_{1/2}^{(A)}$ during growth of the A_pB_q layer in the reaction controlled regime and $x \gg x_{1/2}^{(B)}$ and $x \gg x_{1/2}^{(A)}$ during its growth in the diffusion controlled regime. Thus, the width of the transition region between the two “practical” growth regimes of the layer becomes even more uncertain than in the case of diffusion of only one component B . In contrast, the theoretical definition gives two definite points of change of the growth regime of the A_pB_q layer, namely, $x_{1/2}^{(A)}$ with regard to component A and $x_{1/2}^{(B)}$ with regard to component B [145, 147, 151, 153-155].

Note that, to be most precise and to avoid any confusion with terminology, it would be more relevant to use the term *chemical control* instead of *reaction control*. Then, the A_pB_q layer formation could be specified as its growth under conditions of either *chemical control* or *diffusion control*.

It should be noted that in the absence of stress the position of the A_pB_q layer as a whole relative to the initial interface between the phases A and B (see Fig. 1.12) only depends on

the stoichiometry of the A_pB_q chemical compound but by no means on the speed of movement of diffusing species in the crystal lattice of this compound. The initial interface cannot therefore serve as a marker to identify the faster diffusing component of the compound.

Most chemical reactions are in fact accompanied by the occurrence of stress due to (i) the difference in the coefficients of thermal expansion of the phases involved into the interaction and (ii) the volume effect associated with the formation of a chemical compound, the volume of the reactants consumed being in general not equal to the volume of the product(s) formed. As the stresses arisen at both layer interfaces are different, the layer displacement relative to the initial interface may also depend on their magnitudes.

1.4.2: Single compound layer: general kinetic equation

Equations (1.53) and (1.68) relating the time, dt , to the increases, dx_{B1} and dx_{A2} , of the thickness of the A_pB_q layer are assumed to be independent of each other. Here, the principle of independency of the rates of elementary chemical processes taking place in a given system is used. This principle was successfully employed as a basis for examining the kinetics of homogeneous reactions (see, for example, Refs [128, 130]). Also, in the case of solid-state heterogeneous reactions, the results obtained using this principle are, as will become clear later, in good agreement with the available experimental data, indicative of the fundamental nature of this postulate of chemical kinetics.

The counter-fluxes, j_A and j_B , of the A and B atoms across the bulk of the growing A_pB_q layer are assumed to be independent of each other as well. Indeed, in the ordered lattice of any chemical compound the atoms of each of its components can readily move on the sites of their own sublattice, thus not hindering the movement of the atoms of another component.

Regrouping the terms of equation (1.68) gives an expression for the growth rate of the A_pB_q layer at interface 2 at the expense of diffusion of the A atoms and subsequent partial chemical reaction (1.49):

$$\frac{dx_{A2}}{dt} = \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}}. \quad (1.70)$$

Summation of the right-hand parts of equations (1.54) and (1.70) yields a general kinetic equation describing the rate of growth of the A_pB_q layer between initial substances A and B due to the simultaneous occurrence of partial chemical reactions (1.48) and (1.49):

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}}. \quad (1.71)$$

This type of equation appears to have been proposed first to treat the experimental data on solid-state kinetics by B.Ya. Pines in 1959 [9, 142]. The solution to equation (1.71) with the initial condition $x = 0$ at $t = 0$ is

$$R_1 x^2 + R_2 x - R_3 \ln(1 + R_4 x) = t, \quad (1.72)$$

where

$$\begin{aligned} R_1 &= \frac{1}{2(k_{1B1} + k_{1A2})}, \\ R_2 &= \frac{k_{1B1}^2 k_{0A2} + k_{0B1} k_{1A2}^2}{k_{0B1} k_{0A2} (k_{1B1} + k_{1A2})}, \\ R_3 &= \frac{k_{1B1} k_{1A2} |k_{0B1} k_{1A2} - k_{1B1} k_{0A2}|^2}{k_{0B1}^2 k_{0A2}^2 (k_{1B1} + k_{1A2})^3}, \\ R_4 &= \frac{k_{0B1} k_{0A2} (k_{1B1} + k_{1A2})}{k_{1B1} k_{1A2} (k_{0B1} + k_{0A2})}. \end{aligned}$$

Equation (1.72) is much more complicated than equation (1.55) because in general the values of the chemical constants k_{0B1} and k_{0A2} as well as those of the diffusional constants k_{1B1} and k_{1A2} are not equal. Even the proportionality of the diffusional and chemical constants, so that $x_{1/2}^{(A)} = x_{1/2}^{(B)}$, is probably a rare occasion. In the particular case where $k_{0B1} = k_{0A2} = k_0$ and $k_{1B1} = k_{1A2} = k_1$, equations (1.71) and (1.72) are simplified to

$$\frac{dx}{dt} = \frac{2k_0}{1 + \frac{k_0 x}{k_1}} \quad (1.73)$$

and

$$t = \frac{x^2}{4k_1} + \frac{x}{2k_0}, \quad (1.74)$$

respectively.

Equation (1.74) produces a layer thickness-time dependence that at low values of x is close to the straight line $x = 2k_0 t$, while at high values of x it tends to the parabola $x^2 = 4k_1 t$. In this case, the increases of the thickness of the $A_p B_q$ layer at both interfaces with initial phases A and B are equal. Again, the duration of the steps of chemical transformations at interface 1 with the participation of diffusing B atoms is equal to the duration of the steps of chemical transformations at interface 2 with the participation of diffusing A atoms. The

durations of diffusion of the A and B atoms across the bulk of the A_pB_q layer are also equal. Therefore, equation (1.74) assumes the same simple form as equation (1.55). Its right-hand side consists of the time of diffusion of the A and B atoms respectively to interfaces 2 and 1 during growth of the A_pB_q layer from 0 to x :

$$t_{\text{dif}} = \frac{x^2}{4k_{1B1}} \quad (1.75)$$

and the time of chemical transformations with the participation of these atoms

$$t_{\text{chem}} = \frac{x}{2k_{0B1}}. \quad (1.76)$$

It can be seen that, if the contributions of diffusing A and B atoms to the process of formation of the A_pB_q layer are equal, the time necessary for the layer to reach any given thickness x is two times less compared to the case where only one component is diffusing (compare equations (1.55), (1.63) and (1.64) on the one hand with equations (1.74)-(1.76) on the other).

In the general case where these contributions are different, some initial portion of the dependence of the layer thickness upon time is also linear. Indeed, if $k_{0B1} \ll k_{1B1}/x$ and $k_{0A2} \ll k_{1A2}/x$ ($x \ll x_{1/2}^{(B)}$ and $x \ll x_{1/2}^{(A)}$), then

$$\frac{dx}{dt} = k_{0B1} + k_{0A2} \quad (1.77)$$

and therefore

$$x = (k_{0B1} + k_{0A2})t. \quad (1.78)$$

At sufficiently high x , the conditions $k_{0B1} \gg k_{1B1}/x$ and $k_{0A2} \gg k_{1A2}/x$ ($x \gg x_{1/2}^{(B)}$ and $x \gg x_{1/2}^{(A)}$) are satisfied. Hence,

$$\frac{dx}{dt} = \frac{k_{1B1} + k_{1A2}}{x}. \quad (1.79)$$

Thus, at long times the layer thickness-time dependence is almost parabolic

$$x^2 = 2(k_{1B1} + k_{1A2})t. \quad (1.80)$$

If integration of equation (1.79) with the initial condition $x = 0$ at $t = 0$ produces unsatisfactory results, it must be carried out using the initial condition $x = x_0$ at $t = 0$ or $x = x_0$ at $t = t_0$ (see equations (1.60) and (1.61)).

It should be noted that in the majority of experimental investigations carried out with reaction couples formed by two metals, a metal and silicon, a metal and oxygen, two salts, *etc.*, growth kinetics of compound layers were found to be parabolic (see, for example, Refs [5, 6, 8, 38, 41, 126, 127]). However, this does not necessarily mean that the linear growth is not characteristic of those systems. Until recently, metallographic and other relatively low-sensitive methods have mainly been used for investigations, not allowing the examination of compound layers thinner than about 1 μm . Since the lattice spacing of chemical compounds is usually of the order of several tenths of a nanometre, it is clear that any layer having a thickness of 1 μm is too thick for the diffusion across its bulk not to play a significant role in determining the overall rate of the growth process. On the contrary, in such layers just the diffusion appears to be the rate-controlling step.

Examination of thin compound layers, strongly stimulated by the application of thin-film technology in microelectronics [126, 127], showed that in many reaction couples some initial portion of the layer thickness-time dependence is in fact linear. Metallic systems are no exception, though in the monograph by K.P. Gurov *et al.* [22] dealing with the interaction in such systems the possibility of linear growth was not even mentioned. Meanwhile, in most reaction couples consisting of two metals forming at least one intermetallic compound, the linear growth kinetics can readily be observed, if sufficiently thin layers (about 10 to 500 nm thick) are investigated.

In most cases, the temperature dependence of the chemical and physical (diffusional) constants is likely to be described by an equation of the Arrhenius type (see Refs [126-128]):

$$K = K_0 \exp\left(-\frac{E}{RT}\right), \quad (1.81)$$

where K stands for any of the two constants, K_0 is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

Since the activation energy, E_{chem} , of chemical transformations is known to be a few times higher than the activation energy, E_{dif} , of diffusion (see, for example, Refs [126, 127]), from equation (1.81) it follows that the rate of chemical transformations decreases with decreasing temperature far more rapidly than the rate of atomic diffusion. Therefore, just at low temperatures the rate of chemical transformations at phase interfaces limits the observed rate of layer formation. Clearly, in this case the growth rate of the layer of any chemical compound is low but the linear region of its growth becomes wider in time and therefore can more easily be studied experimentally. On the contrary, at high temperatures the time of

linear growth may even be shorter than the time of heating of the examined reaction couple up to the required temperature.

Note that within the framework of phenomenological considerations it is impossible to predict the shape of the layer thickness-time dependence for any particular binary system, since the values of the chemical and physical (diffusional) constants are not known *a priori* and must be found from experimental studies. For different systems, these can vary over a wide range. For this reason, under close experimental conditions in one binary system the layer growth can proceed in the reaction controlled regime, in the second in the diffusion controlled regime, and in the third in the transition (mixed) regime (see Section 1.3.2 and Fig. 1.11b).

Even with similar systems, different time dependences of the layer thickness may be observed. For example, according to the data of C.-D. Lien *et al.* [67], at 400-505 °C the CrSi₂ layer grows between chromium and silicon linearly, whereas even at lower temperatures (230-335 °C) the Ni₂Si layer grows in the nickel-silicon reaction couple over almost the same time range parabolically (Fig. 1.14). The linear growth of the CrSi₂ layer then gradually changes to the parabolic one [89]. It takes place at a layer thickness greater than approximately 650 nm. Deviation from the straight line can readily be noticed on curve 5 of Fig. 1.14a.

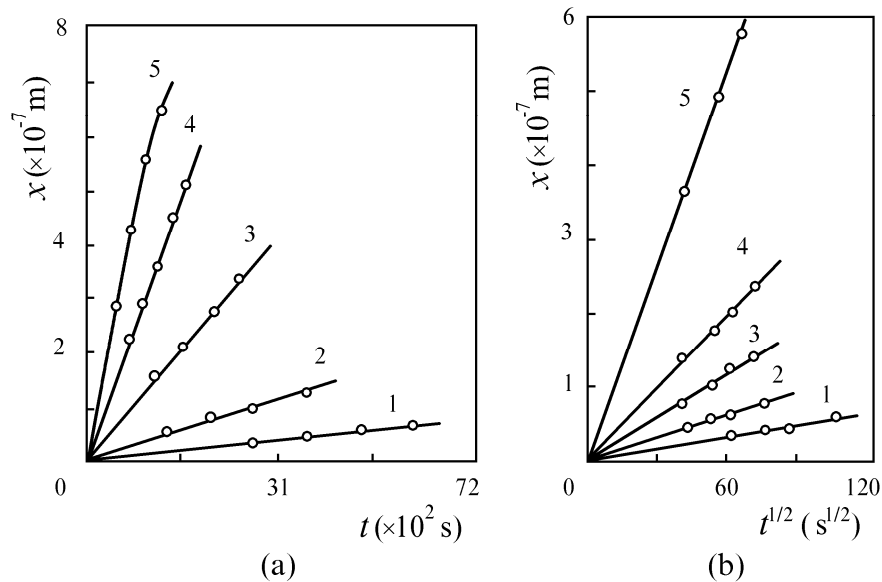


Fig. 1.14. Linear growth of the CrSi₂ layer between chromium and silicon (a) and parabolic growth of the Ni₂Si layer between nickel and silicon (b) according to the experimental data by C.-D. Lien *et al.* [67]. (a) 1, 400 °C; 2, 425; 3, 450; 4, 475; 5, 490. (b) 1, 230 °C; 2, 250; 3, 265; 4, 295; 5, 335.

1.4.3: Separate determination of reaction-diffusion constants

It is obvious that from any experimental dependence of the total layer thickness upon time it is only possible to determine the sum of the chemical constants as well as the sum of physical (diffusional) constants. The former sum is to be found from an initial portion of this dependence plotted in coordinates $x - t$, while the latter from its long-time portion plotted in coordinates $x^2 - t$ or $x - t^{1/2}$. For their separate determination, it is necessary to measure the increases in thickness of the A_pB_q layer at its both interfaces with initial substances A and B .

The specimen, most suitable for such measurements, is shown schematically in Fig. 1.12. The upper part of the specimen is used as reference. To prevent the interaction of components A and B in this part, a thin barrier layer of some substance which does not react with both A and B under chosen experimental conditions is deposited. The position of the layer interfaces is measured at certain moments of time relative to the inert markers located at the initial interface between substances A and B and/or inside the A_pB_q layer. Microhardness indentations onto the specimen cross-section surface, thin wires or strips of chemically inert materials, bubbles of inert gases, *etc.*, can serve as the markers (for more detail, see for example Refs [37, 126]).

As already pointed out earlier, in most cases the formation of chemical compounds is accompanied by considerable changes of the volume of reaction couples. Figure 1.12 represents the case where the layer occurrence reduces the total volume of the $A-A_pB_q-B$ reaction system. This causes the displacement of that part of the specimen, where initial substances interact, relative to the other where they do not react with each other. A thin cut made throughout the entire depth of the specimen almost up to its ends makes it possible to reduce the mechanical stresses between the reference and measurement parts.

Separate determination of the chemical constants k_{0B1} and k_{0A2} can be carried out in practice using the following procedure. First, it is necessary to reveal a temperature-time range in which the time dependence of the total thickness of the A_pB_q layer is linear. Then, by measuring the position of its interfaces 1 and 2 relative to the markers at some moments of time t_1 and $t_2 = t_1 + \Delta t$, the increases, Δx_{B1} and Δx_{A2} , in thickness of the A_pB_q layer during the time Δt must be determined (see Fig. 1.12 in which dt should be replaced by Δt , dx_{B1} by Δx_{B1} , and dx_{A2} by Δx_{A2}). The chemical constants k_{0B1} and k_{0A2} are found from the equations

$$k_{0B1} = \frac{\Delta x_{B1}}{\Delta t} \quad (1.82)$$

and

$$k_{0A2} = \frac{\Delta x_{A2}}{\Delta t}, \quad (1.83)$$

respectively.

To determine the physical (diffusional) constants k_{1B1} and k_{1A2} , it is necessary to establish the conditions under which the total thickness of the A_pB_q layer increases with time parabolically. Then, like the previous case, the increases, Δx_{B1} and Δx_{A2} , in thickness of the layer at its interfaces 1 and 2 are to be measured. The values of the physical (diffusional) constants k_{1B1} and k_{1A2} are calculated from the equations

$$k_{1B1} = x_{\text{mean}} \frac{\Delta x_{B1}}{\Delta t} \quad (1.84)$$

and

$$k_{1A2} = x_{\text{mean}} \frac{\Delta x_{A2}}{\Delta t} \quad (1.85)$$

where x_{mean} is the mean value of the total thickness of the A_pB_q layer in the time range Δt .

It should be emphasised that in determining the chemical constants k_{0B1} and k_{0A2} the time range Δt can be chosen arbitrarily. It is only important to remain within the linear region of layer growth. When determining the physical (diffusional) constants, however, the increases, Δx_{B1} and Δx_{A2} , should be sufficiently small, so that during the time Δt there were no large change of the total thickness of the A_pB_q layer. If this condition is not satisfied, the constants k_{1B1} and k_{1A2} obtained will clearly be time-dependent.

It is evident that the separate determination of the chemical and physical (diffusional) constants is much more difficult in comparison with conventional experiments where only the total thickness of the growing A_pB_q layer is measured, with the further search for its growth law by means of mathematical treatment of the results using linear, parabolic, logarithmic and other dependences (see, for example, Refs [6, 7, 13]). However, the former procedure ultimately gives a more complete and adequate description of the interaction in the examined reaction couple $A-B$ compared to the latter.

It should be noted that the value of each of the chemical constants k_{0B1} and k_{0A2} depends on the physical and chemical properties of two reacting phases. The value of k_{0B1} depends on the nature of substance A and the compound A_pB_q , while the value of k_{0A2} depends on the nature of substance B and the compound A_pB_q . Both physical (diffusional) constants depend only on the nature of the chemical compound A_pB_q and are therefore characteristic of this compound layer wherever it grows. However, as will be demonstrated in the next chapters, the stoichiometry of adjacent phases must also be taken into account when estimating the growth rate of the A_pB_q layer in various reaction couples of the $A-B$ binary system.

The sum of the chemical constants k_{0B1} and k_{0A2} as well as the sum of the physical (diffusional) constants k_{1B1} and k_{1A2} can also be determined from the decrease in thickness of the layers of initial substances A and B [156]. Indeed, using equations (1.48) and (1.49), it can readily be shown that the decrease, $\Delta x^{(A)}$, in thickness of the layer of substance A and

that, $\Delta x^{(B)}$, of the layer of substance B during the time Δt is related to the increases, Δx_{B1} and Δx_{A2} , in thickness of the $A_p B_q$ layer during this time through the relationships

$$\Delta x^{(A)} = \frac{pV_A}{V_{A_p B_q}} (\Delta x_{B1} + \Delta x_{A2}) \quad (1.86)$$

and

$$\Delta x^{(B)} = \frac{qV_B}{V_{A_p B_q}} (\Delta x_{B1} + \Delta x_{A2}) \quad (1.87)$$

where V is the molar volume of appropriate substances.

Therefore, in the region of linear growth of the $A_p B_q$ layer

$$\Delta x^{(A)} = \frac{pV_A}{V_{A_p B_q}} (k_{0B1} + k_{0A2}) \Delta t \quad (1.88)$$

and

$$\Delta x^{(B)} = \frac{qV_B}{V_{A_p B_q}} (k_{0B1} + k_{0A2}) \Delta t, \quad (1.89)$$

while in the parabolic region

$$\Delta x^{(A)} = \frac{pV_A}{V_{A_p B_q}} \left(\frac{k_{1B1} + k_{1A2}}{x_{\text{mean}}} \right) \Delta t \quad (1.90)$$

and

$$\Delta x^{(B)} = \frac{qV_B}{V_{A_p B_q}} \left(\frac{k_{1B1} + k_{1A2}}{x_{\text{mean}}} \right) \Delta t. \quad (1.91)$$

It can easily be seen that this method has practically no advantages in comparison with direct measuring the thickness of the growing $A_p B_q$ layer. Its disadvantages are obvious. Firstly, the diffusional constants are calculated using the differential forms of kinetic equations. This usually produces a larger computational error than the calculations with the use of the integrated equations. Secondly, the amount of initial substances A and B consumed in the reaction of compound formation is in most cases much less than their total amount present. Therefore, the decrease, $\Delta x^{(A)}$ or $\Delta x^{(B)}$, is the difference of two large magnitudes, each of which is determined at some error. The procedure where a small

magnitude is determined as the difference of two large figures is known to yield insufficiently accurate results.

1.5: Linear growth of the Cu₆Sn₅ layer in the copper-tin reaction couple

As an example of linear growth, consider the results by K.N. Tu and R.D. Thompson [66] on the formation of the Cu₆Sn₅ intermetallic layer in thin-film Cu–Sn specimens. It should be noted that the example with the intermetallic compound was chosen not accidentally. In many works, the linear growth of intermetallic compounds is regarded as a deviation from the parabolic one that is regarded as normal. In fact, both growth laws are the limiting cases of the same dependence of Evans' type and therefore can equally be expected to hold in any binary system, though the linear growth is doubtless much more difficult to observe experimentally in view of the necessity to deal with very thin layers in the nanometre range.

The Cu₆Sn₅ intermetallic compound contains 54.55 at.% (39.11 %) of copper and 45.45 at.% (60.89 %) of tin [157]. The sign % will be used throughout for mass %. The solubility of tin in the solid copper does not exceed 0.4 at.% (0.74 %) at 170 °C and is almost equal to zero at 100 °C. The solubility of copper in tin in the solid state is only 0.01 at.% (0.006 %) at the eutectic temperature 227 °C [157]. Therefore, at 20 °C tin and copper can be regarded as practically insoluble in each other.

The Cu–Sn specimens for experiments were prepared by sequential deposition of copper (560 nm) and tin (200 or 560 nm) films on quartz discs under vacuum. To prevent any reaction during the specimen preparation, a tin film was deposited after cooling the substrate with an already deposited copper film down to the liquid nitrogen temperature (for more detail, see Ref. [66]).

At room temperature, a tin film 200 nm thick was consumed completely in the formation of the Cu₆Sn₅ intermetallic compound in 35 days. The dependence of the thickness of the Cu₆Sn₅ layer on the duration of interaction of copper with tin at 20 °C for a 560 nm Cu–500 nm Sn specimen, obtained by K.N. Tu and R.D. Thompson, is shown in Fig. 1.15. It is seen that the experimental points produce a straight line in coordinates $x - t$, indicative of linear growth kinetics.

The formation of the Cu₆Sn₅ intermetallic layer is due to partial chemical reaction between the diffusing tin atoms and the surface copper atoms at interface 1 (Fig. 1.16)



and also to partial chemical reaction between the diffusing copper atoms and the surface tin atoms at interface 2



From the data in Fig. 1.15 (see also Ref. [66]), it follows that $k_{0\text{Sn}1} + k_{0\text{Cu}2} = 4 \times 10^{-14} \text{ m s}^{-1}$.

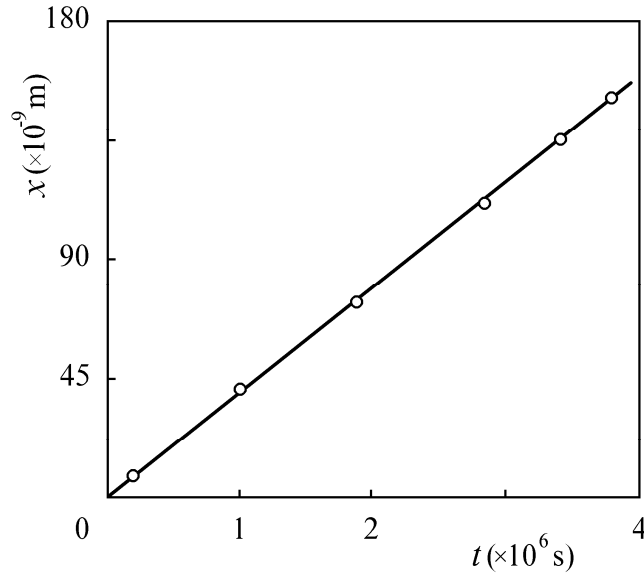


Fig. 1.15. Linear growth kinetics of the Cu_6Sn_5 intermetallic layer in a 560 nm Cu–500 nm Sn thin-film specimen at 20 °C according to the experimental data of K.N. Tu and R.D. Thompson [66].

Besides measuring the total thickness of the Cu_6Sn_5 layer, K.N. Tu and R.D. Thompson have also determined the distance from inert markers located inside the intermetallic layer to its interfaces with the copper and tin phases (see Fig. 1.16). Discontinuous tungsten stripes deposited onto the copper surface prior to the deposition of tin served as the markers.

In one series of experiments, the distance, $x_{\text{Sn}1}$, from the Cu– Cu_6Sn_5 interface to a tungsten marker was found to be around 60 nm, while the distance, $x_{\text{Cu}2}$, from this marker to the Cu_6Sn_5 –Sn interface was equal to 185 nm. Hence,

$$\frac{k_{0\text{Sn}1}}{k_{0\text{Cu}2}} = \frac{1}{3}$$

and

$$k_{0\text{Sn}1} = 1 \times 10^{-14} \text{ m s}^{-1}, \quad k_{0\text{Cu}2} = 3 \times 10^{-14} \text{ m s}^{-1}.$$

Note that these quantities characterise the rate of chemical transformations at the interfaces of the Cu_6Sn_5 intermetallic layer with the initial phases Cu and Sn, but by no means the rate of diffusion of the tin and copper atoms across the bulk of the layer [151, 152, 155]. In the linear region of growth of any chemical compound layer, the rates of diffusion of its both components, even if far different, are quite sufficient to fully satisfy the reactivities (combining abilities) of the surfaces of the reactants.

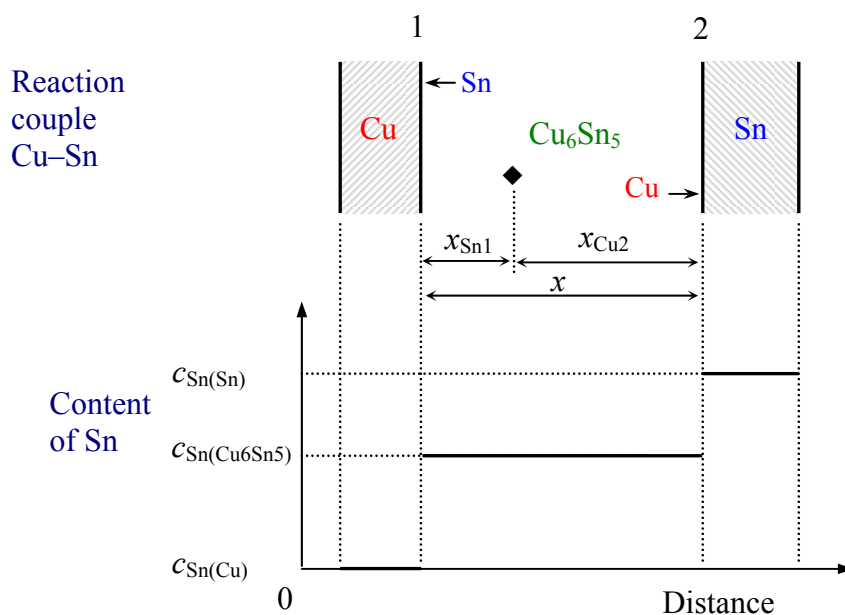


Fig. 1.16. Schematic representation of the growth process of the Cu_6Sn_5 intermetallic layer in the copper-tin reaction couple.

Though the faster diffusing component may reasonably be expected to react faster, this does not necessarily mean that the ratio of the chemical constants should be equal to the ratio of the physical (diffusional) constants. Therefore, it would be interesting to determine the ratio of the volume diffusivities of the components in the Cu_6Sn_5 intermetallic layer from the parabolic region of its growth and then to compare their ratio with the ratio of the chemical constants $k_{0\text{Sn}1}$ and $k_{0\text{Cu}2}$. This type of work still awaits further experimentation.

It should be noted that the concept *chemical transformations* is used here in the rather broad sense. When analyzing the process of formation of the Cu_6Sn_5 intermetallic compound layer in greater detail, it would be desirable to reveal the comparative influence on its course of the rate of external diffusion of the atoms through the phase interfaces and the rates of crystallographic transformations resulting in the rearrangement of the lattices of the initial substances into the lattice of the intermetallic compound. However, on the basis of the kinetic data alone, it is clearly impossible to make any substantiated conclusion regarding the contribution of these processes to the observed overall rate of formation of the Cu_6Sn_5 layer because from the point of view of formal kinetics they are equivalent in the sense that, whatever is rate-determining, the layer thickness-time dependence will be the same, namely, linear. To distinguish between them, it is necessary to carry out additional investigations employing more refined techniques.

1.6: Parabolic growth of the AlSb layer in the aluminium-antimony diffusion couple

Schematic diagram illustrating the growth process of the AlSb layer at the aluminium-antimony interface is shown in Fig. 1.17. The kinetics of interaction in this system have been studied by B.Ya. Pines and E.F. Chaikovskiy [158] (see also Ref. [9]) using X-ray patterns obtained from the rotating cross-sections of “aluminium foil, 15 μm thick + polished antimony disc, 3-4 mm high” specimens in a cylindrical self-focusing chamber.

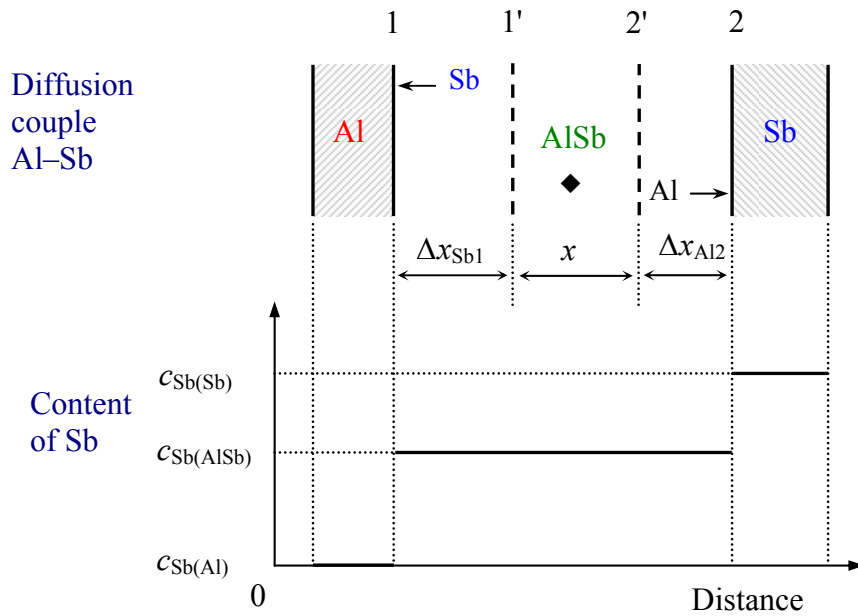


Fig. 1.17. Schematic representation of the growth process of the AlSb layer in the Al–Sb diffusion couple.

The AlSb compound is the only one to exist in the binary Al–Sb system and probably has a very narrow range of homogeneity, if any [157, 159]. The mutual solubility of the components in the solid state (below 645 $^{\circ}\text{C}$) is less than 0.1 % [157, 158].

About one-eighth of the antimony disc was left free. When taking X-ray patterns, a silver standard was placed onto this part of the specimen. B.Ya. Pines and E.F. Chaikovskiy were able to obtain on one and the same X-ray pattern the following diffraction lines: (220) for aluminium, (321) for antimony, (331) for the AlSb compound and (220) for silver.

The change in thickness of the phases involved into the interaction after consecutive anneals of the specimen was followed by the photometric examination of the X-ray patterns (for more detail of the experimental procedure, see Ref. [158]). Using this technique, B.Ya. Pines and E.F. Chaikovskiy were able to determine both the total thickness of the AlSb layer at any given moment of time and the increases in thickness of the layer at its

interfaces. Their data obtained at a temperature of 620 °C are represented in first four columns of Table 1.1, where x_{Sb1} is the distance from a marker to the Al–AlSb interface and x_{Al2} is that to the AlSb–Sb interface.

Table 1.1. Evaluation of diffusional constants for the AlSb layer of the Al–Sb binary system [156] using the experimental data of B.Ya. Pines and E.F. Chaikovskiy [9, 158]

t ($\times 10^2$ s)	x ($\times 10^{-6}$ m)	x_{Sb1} ($\times 10^{-6}$ m)	x_{Al2} ($\times 10^{-6}$ m)	k_{1Sb1} ($\times 10^{-14}$ m ² s ⁻¹)	k_{1Al2} ($\times 10^{-14}$ m ² s ⁻¹)	$k_{\text{1Sb1}} + k_{\text{1Al2}}$ ($\times 10^{-14}$ m ² s ⁻¹)	k_1 ($\times 10^{-14}$ m ² s ⁻¹)
36	20.5	17	3.5	4.8	1.0	5.8	5.8
72	29.5	24	5	4.9	1.0	5.9	6.0
108	37.0	31	6	6.4	0.9	7.3	6.3
144	42.5	35	7.5	4.4	1.7	6.1	6.3

Mean values with 0.95 confidence limits:

$$k_{\text{1Sb1}} = (5.1 \pm 1.4) \times 10^{-14} \text{ m}^2 \text{ s}^{-1}; k_{\text{1Al2}} = (1.2 \pm 0.6) \times 10^{-14} \text{ m}^2 \text{ s}^{-1};$$

$$k_{\text{1Sb1}} + k_{\text{1Al2}} = (6.3 \pm 1.1) \times 10^{-14} \text{ m}^2 \text{ s}^{-1};$$

$$k_1 = (6.1 \pm 0.4) \times 10^{-14} \text{ m}^2 \text{ s}^{-1}.$$

Solid-state growth of the AlSb layer between aluminium and antimony is due to the occurrence of the following partial chemical reactions (see Fig. 1.17):



and



Reaction (1.94) between the antimony atoms diffusing across the bulk of the AlSb layer and the surface aluminium atoms takes place at the Al–AlSb interface (interface 1), whereas reaction (1.95) between the aluminium atoms diffusing across the bulk of the AlSb layer in the opposite direction and the surface antimony atoms proceeds at the AlSb–Sb interface (interface 2).

Clearly, when calculating the physical (diffusional) constants, first of all it is necessary to check out whether the layer indeed grows in the diffusion controlled regime where the conditions $k_{0\text{Sb1}} \gg k_{\text{1Sb1}}/x$ and $k_{0\text{Al2}} \gg k_{\text{1Al2}}/x$ must be satisfied. For this, the experimental data should be treated using the parabolic dependence (see equation (1.80))

$$x^2 = 2(k_{1Sb1} + k_{1Al2})t. \quad (1.96)$$

In the case under consideration, the total thickness, 20.5 to 42.5 μm , of the AlSb layer is comparatively large. It is therefore reasonable to assume that the initial condition can be taken as $x = 0$ at $t = 0$ without any noticeable loss of accuracy.

Using the experimental value $x = 20.5 \times 10^{-6} \text{ m}$ at $t = 3600 \text{ s}$, one obtains from equation (1.96)

$$k_1 = k_{1Sb1} + k_{1Al2} = x^2/2t = 5.8 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}.$$

The other values of k_1 thus obtained are presented in the last column of Table 1.1. The mean value of k_1 found from the time dependence of the total thickness of the AlSb layer by the least-squares fit method is equal to $6.1 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. The confidence limits are $\pm 0.4 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ at a probability level of 0.95.

Hence, possible deviations from the mean value do not exceed 7%. This accuracy is fairly good because in most cases the thickness of any compound layer can hardly be measured more accurately in view of its irregularity. Therefore, integration of equation (1.79) with the initial condition $x = 0$ at $t = 0$ is quite acceptable. This means that the linear stage of growth of the AlSb layer is relatively short and can be neglected. In cases where such an integration does not produce satisfactory results, *i.e.* influence of the linear stage of layer growth is considerable, it is advisable to integrate equation (1.79), using the experimentally determined thickness, x_0 , of the layer at some time, t_0 , as an initial condition.

Let us now calculate the values of k_{1Sb1} and k_{1Al2} separately [156]. The value of k_{1Sb1} is found from the equation

$$k_{1Sb1} = x_{\text{mean}} \frac{\Delta x_{Sb1}}{\Delta t} \quad (1.97)$$

where $x_{\text{mean}} = (1/2)[x(t_i) + x(t_{i-1})]$, $\Delta x_{Sb1} = x_{Sb1}(t_i) - x_{Sb1}(t_{i-1})$ and $\Delta t = t_i - t_{i-1}$ ($i = 1, 2, \dots, n$, n being the serial number of an experimental point). Similarly,

$$k_{1Al2} = x_{\text{mean}} \frac{\Delta x_{Al2}}{\Delta t} \quad (1.98)$$

where $\Delta x_{Al2} = x_{Al2}(t_i) - x_{Al2}(t_{i-1})$, with both x_{mean} and Δt remaining the former. Calculations for the first two pairs of the experimental points including $x = 0$ at $t = 0$ yield:

$$1. \ i=1, \ x_{\text{mean}} = \frac{(20.5+0) \times 10^{-6}}{2} = 10.25 \times 10^{-6} \text{ m},$$

$$\Delta x_{\text{Sb1}} = (17 - 0) \times 10^{-6} = 17 \times 10^{-6} \text{ m},$$

$$\Delta x_{\text{Al2}} = (3.5 - 0) \times 10^{-6} = 3.5 \times 10^{-6} \text{ m},$$

$$k_{\text{1Sb1}} = 10.25 \times 10^{-6} \frac{17 \times 10^{-6}}{3600} = 4.8 \times 10^{-14} \text{ m}^2 \text{ s}^{-1},$$

$$k_{\text{1Al2}} = 10.25 \times 10^{-6} \frac{3.5 \times 10^{-6}}{3600} = 1.0 \times 10^{-14} \text{ m}^2 \text{ s}^{-1};$$

$$2. \ i=2, \ x_{\text{mean}} = \frac{(29.5+20.5) \times 10^{-6}}{2} = 25 \times 10^{-6} \text{ m},$$

$$\Delta x_{\text{Sb1}} = (24 - 17) \times 10^{-6} = 7 \times 10^{-6} \text{ m},$$

$$\Delta x_{\text{Al2}} = (5 - 3.5) \times 10^{-6} = 1.5 \times 10^{-6} \text{ m},$$

$$k_{\text{1Sb1}} = 25 \times 10^{-6} \frac{7 \times 10^{-6}}{3600} = 4.9 \times 10^{-14} \text{ m}^2 \text{ s}^{-1},$$

$$k_{\text{1Al2}} = 25 \times 10^{-6} \frac{1.5 \times 10^{-6}}{3600} = 1.0 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}.$$

Further calculations were carried out for each subsequent pair of the experimental points at a step of 3600 s. The final results are presented in Table 1.1.

It is seen that the scatter in values of k_{1Sb1} and k_{1Al2} is somewhat greater than that in values of k_1 . This is not surprising because the accuracy of measuring the increases of the layer thickness is always lower than the accuracy of measuring its total thickness. Besides, the step of 3600 s is insufficiently small and therefore the mean value of the thickness of the AlSb layer differs considerably from the lower and upper limits. Nevertheless, the values of k_1 are seen to be in quite satisfactory agreement with the sum of $k_{\text{1Sb1}} + k_{\text{1Al2}}$ (compare the last two columns in Table 1.1). The self-consistent character of the results obtained provides evidence for the validity of the proposed physico-chemical approach to examining the process of diffusional growth of a chemical compound layer.

1.7: Linear-parabolic growth of the SiO₂ layer between silicon and oxygen

Linear and parabolic relations are two asymptotic forms of a more general layer thickness-time dependence described by equations (1.71) and (1.72). If the growing layer had ideal parallel-plane geometry and its thickness could be measured with absolute accuracy, it would always be possible to reveal the deviations from both a straight line and a parabola. Evidently, these conditions are never fulfilled in practice. The layer thickness is rarely identical in all sections across its bulk by a plane normal to the interface between reacting phases. In most cases, the difference in thickness of the layer at its different places is 5 to 25% of the mean value, and sometimes even more. The deviation from a straight line or a parabola can only be noticed when its value becomes comparable with an error of measuring the thickness of a chemical compound layer. Therefore, the greater the scatter of experimental points, the wider the regions of both linear and parabolic growth of any layer.

It should be emphasised that in any binary system the linear growth region is much more narrow than the parabolic growth region. Indeed, the linear growth region corresponds to layer thicknesses from 0 to the x values much less than the critical values with regard to components A and B . Thus, this region is restricted from both sides, although its upper limit is uncertain. In contrast, the parabolic region of layer growth, where the x values far exceed the critical ones, has no upper time and thickness limit.

Experimentally, the interaction of initial substances is always examined over a certain finite period of time. For solid-solid systems, this period usually varies from a few minutes to a few hours and seldom is longer. This time range is in most cases too narrow to enable the transition from linear to parabolic kinetics to be established, especially if the number of experimental points is restricted to 3-6. Therefore, one of the two extremes (a straight line or a parabola) is observed, or neither a straight line nor a parabola. The latter case is treated as “mixed” kinetics.

In this respect, the situation is more favourable with solid-gas systems where one of the main techniques of investigation is the thermogravimetric one (see Refs [1, 4, 11, 13, 123-125]) that enables the course of interaction of initial substances to be followed continuously at a high accuracy almost from its very beginning over a time range varying from a few seconds to a few hundreds of hours. It is therefore not surprising that the researchers investigating the formation of chemical compounds in solid-gas systems accept the existence of the linear region of layer growth as an indisputable experimental fact, whereas those involved in the investigation of interaction in solid-solid and solid-liquid systems tend to consider it as an “anomaly” and from time to time put forward its different (quite unconvincing and unnecessary) explanations.

Clearly, the thermogravimetric technique does not allow by itself the separate determination of the increases in layer thickness at its both interfaces. However, if diffusion of one of two components prevails in a growing chemical compound layer, the reaction-diffusion constants can be determined very accurately, using this technique. As an example, consider the process of oxidation of silicon by oxygen or water vapour, resulting in the formation of a solid adherent layer of silicon oxide SiO_2 in which oxygen is known to be the main diffusing species [17, 59-64, 160]. Using radioactive markers, M.P. Murell *et al.* [160] established that the thickness of the SiO_2 layer increases only at the Si– SiO_2 interface.

As a rule, a SiO_2 layer of some thickness x_0 is present onto the surface of any silicon specimen prior to the start of the experiment. Therefore, depending on the form of representing the integration constant, the integrated equation describing its further growth during oxidation can be written either as

$$\frac{x^2}{2k_1} + \frac{x}{k_0} = t + \tau \quad (1.99)$$

or as

$$\frac{x^2 - x_0^2}{2k_1} + \frac{x - x_0}{k_0} = t \quad (1.100)$$

where x is the total thickness of the SiO_2 layer at time t .

Dividing both sides of equation (1.99) by x yields an equation of the straight line

$$x = 2k_1 \left(\frac{t + \tau}{x} - \frac{1}{k_0} \right) \quad (1.101)$$

in coordinates $x - (t + \tau)/x$. Figure 1.18 shows the kinetic data obtained by B.E. Deal and A.S. Grove [61] in the oxidation of silicon by dry oxygen at 920-1200 °C. It is seen that the $x - (t + \tau)/x$ dependence is indeed linear. The physical (diffusional) constant can be found from the slope of the straight line, while the chemical constant from its intercept on the ordinate axis.

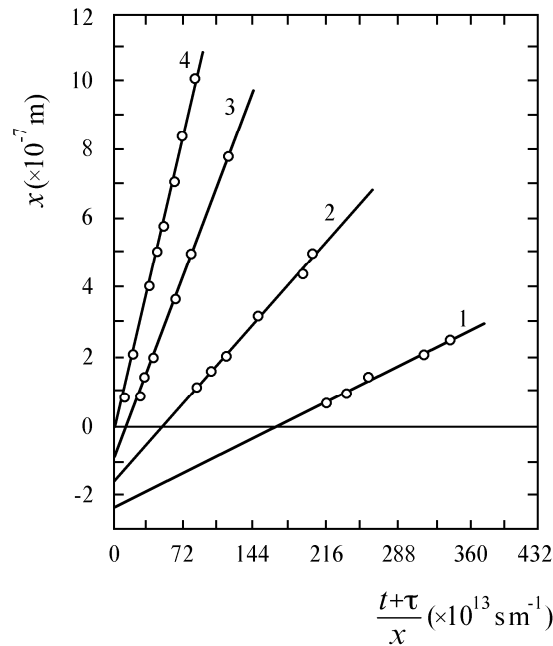


Fig. 1.18. Kinetics of oxidation of silicon in dry oxygen according to the experimental data of B.E. Deal and A.S. Grove [61]. Temperature: 1, 920 °C; 2, 1000; 3, 1100; 4, 1200.

It should be noted that equation (1.99) or similar is often referred to as Deal and Grove's relation. However, these authors themselves point out [61] that this type of equation has been proposed for the first time by U.R. Evans.

Dividing all the terms of equation (1.100) by $(x - x_0)$ gives

$$x + x_0 = 2k_1 \left(\frac{t}{x - x_0} - \frac{1}{k_0} \right). \quad (1.102)$$

As x_0 can be taken with the plus or minus sign, the experimental data should produce a straight line in the coordinates either $(x + x_0) - t/(x - x_0)$ or $(x - x_0) - t/(x + x_0)$. This form of presenting the experimental results was used by N.A. Kolobov and M.M. Samokhvalov [17], who found the values of the reaction-diffusion constants for the SiO_2 layer in the oxidation of silicon by oxygen, listed in Table 1.2. The temperature dependence of both the chemical constant k_0 and the physical (diffusional) constant k_1 is well described by the Arrhenius relation (see equation (1.81)) with an activation energy of 155 and 120 kJ mol^{-1} , respectively.

Table 1.2. Reaction-diffusion constants for the SiO_2 layer in the oxidation of silicon by oxygen [17]

Temperature (°C)	900	1000	1100	1200
$k_1 (\text{m}^2 \text{s}^{-1})$	5.2×10^{-17}	1.3×10^{-16}	3.1×10^{-16}	6.0×10^{-16}
$k_0 (\text{m s}^{-1})$	1.4×10^{-11}	4.8×10^{-11}	1.3×10^{-10}	3.3×10^{-10}

It should be noted that the chemical constant depends on the surface density of the atoms of a reacting substance. Therefore, the values of the chemical constant are different for various crystallographic faces of a single crystal. In the case of silicon, the packing density of the atoms decreases in the series $(110) > (111) > (100)$, with the ratio of the densities being 1:0.82:0.71. According to J.R. Ligenza [59, 60], E.A. Irene [62], Y. Kamigaki and Y. Itoh [63], and N.A. Kolobov and M.M. Samokhvalov [17], the values of the chemical constant in the oxidation of different faces of a silicon single crystal change in about the same proportion but in general this dependence appears to be a weak correlation rather than the strict relation. Clearly, in addition to the packing density of the single-crystal faces, the rate of chemical transformations also depends on (i) the interplanar distances in single crystals of different crystallographic orientations and (ii) the nature of the chemical bond between the atoms onto a given crystallographic face.

1.8: Growth kinetics of the NiBi_3 layer at the nickel-bismuth interface

G. Voss [161] found two intermetallic compounds, NiBi (50 at.% or 78.08 % Bi) and NiBi_3 (75 at.% or 91.45 % Bi), to exist in the nickel-bismuth binary system (see also Ref. [157]). P. Feschotte and J.-M. Rosset [162] have thoroughly re-investigated the phase diagram of this system and confirmed the existence of those two intermetallics (Fig. 1.19).

However, contrary to the expectations of G. Voss [147] and M. Hansen [157], they have not revealed a wide range of homogeneity of the NiBi compound. The composition of this compound was found to be 51.0 ± 0.3 at.% Bi. Thus, its range of homogeneity is very narrow, if any. The NiBi₃ intermetallic compound is stoichiometric. Both compounds melt incongruently: NiBi at 646 °C and NiBi₃ at 467 °C.

Consider characteristic features of compound-layer formation at the Ni–Bi interface, with particular emphasis on the determination of (i) the main diffusing species in the growth process and (ii) the values of the reaction-diffusion constants [163, 164].

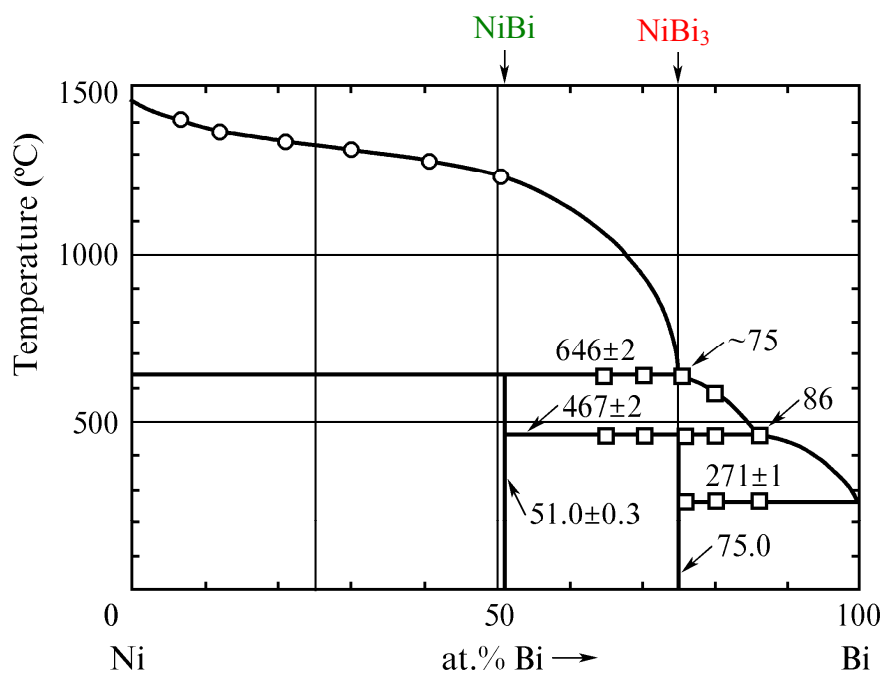


Fig. 1.19. Equilibrium phase diagram of the Ni–Bi binary system according to the work of P. Feschotte and J.-M. Rosset [162]. Reprinted with permission from Elsevier Science.

1.8.1: Experimental details

Electrolytic-grade nickel (99.98 % Ni) was used in the form of polished plates $3 \times 9 \times 14$ mm³. Their final treatment involved electrolytic polishing, both to remove the surface contaminations and to reduce mechanical stresses.

The plates were mounted into graphite crucibles, 11 mm inner diameter, and heated to about 350 °C under a previously dried low-melting flux consisting of the eutectic mixture 82 % ZnCl₂ – 18 % NaCl (melting temperature 280 °C). The crucibles were then filled with molten bismuth (>99.999 % Bi) at 350 °C and allowed to cool until its crystallisation.

The time of contact of a Ni plate with liquid bismuth was 60 s, while that of cooling from 350 °C down to room temperature was around 180 s.

A continuous, coherent intermetallic layer, $1.5 \pm 0.5 \mu\text{m}$ thick, was found to form during the specimen preparation. Hence, this technique ensured intimate contact between the nickel and bismuth phases, so that the reaction started simultaneously anywhere along the entire Ni–Bi interface. Therefore, both intermetallics, NiBi and NiBi₃, had favourable nucleation conditions.

Each bimetallic specimen thus obtained was cut into two pieces using an electric-spark machine. The surface of the Ni–Bi couples was first ground mechanically and then polished electrolytically using a “Elypovist” apparatus and a special electrolyte [139].

The Ni–Bi couples were annealed in sealed glass ampoules, filled with high-purity helium (0.25 atm), at 150, 200 and 250 °C for 1 to 300 h. Each couple was annealed successively a few times. After each anneal, the specimen surface was examined in the as-received conditions and after mechanical or electrolytic polishing.

The compound layer formed in the transition zone between nickel and bismuth was investigated metallographically, by X-ray diffraction and electron probe microanalysis (EPMA). X-ray patterns were taken both from the cross-sections in the planes parallel to the initial Ni–Bi interface (after successive removal of the specimen material and polishing its surface) and the powdered phases, using Cu K α radiation.

The nickel and bismuth contents of the phases and their concentration profiles within the Ni–Bi transition zone were determined with the help of a JEOL Superprobe-733 microanalyser. The spot diameter and the phase volume analysed at each point were estimated to be 1.5–2 μm and 2–3 μm^3 , respectively. The Ni and Bi phases were used as standards. Measurements could be made as close to the phase interfaces as 2–3 μm .

The compound layer thickness was determined using a conventional microhardness tester and an optical microscope. The microhardness tester was also used to put inert markers onto the surfaces of the phases involved in the interaction before each anneal of the Ni–Bi couples, except the first one when the intermetallic layer was still too thin. The microhardness indentations are known to possess advantages over other markers (inert wires, particles, *etc.*). Their main advantage is that the microhardness indentations do not hinder the growth process. It should be noted, however, that in some systems a possible disadvantage of this method may arise from the surface effect, surface diffusivities of the components usually being greater than volume ones.

Five to ten rows of microhardness indentations, typically at a load of 0.196 N (20 g), were put onto the surface of any Ni–Bi cross-section in the direction of diffusion at different places of the Ni–Bi interface. The layer thickness at each annealing time was thus taken as the average of five to ten measurements. The experimental results were treated using standard statistical methods.

1.8.2: Phase identity and chemical composition of the intermetallic layer

Only the NiBi_3 intermetallic compound has formed as a compact layer, up to $230\text{ }\mu\text{m}$ thick, between nickel and bismuth (Fig. 1.20). Its interplanar distances (d-spacing) found experimentally coincided with those calculated using the lattice parameters reported by V.P. Glagoleva and G.S. Zhdanov [165]: $a = 0.8875 \pm 0.0006\text{ nm}$, $b = 0.4112 \pm 0.0004\text{ nm}$, $c = 1.1477 \pm 0.0008\text{ nm}$. The orthorhombic unit cell of this compound contains four NiBi_3 molecules.

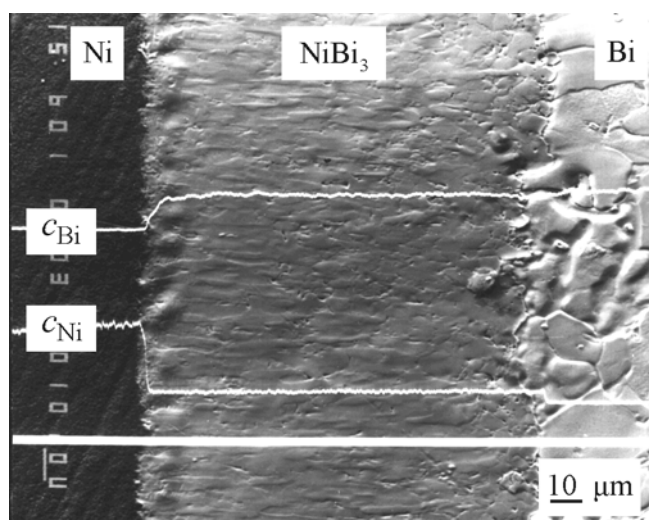


Fig. 1.20. Secondary electron image of the Ni–Bi transition zone and the concentration profiles of both components within the phases involved into the interaction [163]. Temperature $250\text{ }^{\circ}\text{C}$, annealing time $9 \times 10^4\text{ s}$ (25 h). Electrolytic polishing.

No indication of the presence of the NiBi intermetallic compound was found. The reasons for its absence from the Ni–Bi couple will be discussed in the next chapters. Here, it suffices to underline that those are of kinetic rather than thermodynamic nature.

The chemical composition of the intermetallic compound layer grown and also of the adjacent phases was determined by EPMA on a few specimens annealed under different conditions. Point-to-point measurements, 10 to 25 on each specimen, across the intermetallic layer at a step of $3\text{--}10\text{ }\mu\text{m}$ showed its Ni ($25.0 \pm 0.5\text{ at.}\%$) and Bi ($75.0 \pm 0.5\text{ at.}\%$) contents to correspond to the stoichiometry of the NiBi_3 intermetallic compound.

In all the cases, the scatter of experimental values was purely statistical whilst, in the case of existence of a noticeable homogeneity range, a gradual decrease of the Ni content and accordingly an increase of the Bi content in the layer from the Ni– NiBi_3 interface to the NiBi_3 –Bi interface would clearly be revealed. Evidence for the lack of the NiBi_3 homogeneity range also follows from the Ni and Bi concentration profiles shown in Fig.

1.20. These are parallel to one another. It should be emphasised that, when investigating the Ni–Bi equilibrium phase diagram, P. Feschotte and J.-M. Rosset [162] also did not reveal the existence of any appreciable homogeneity range of the NiBi₃ intermetallic compound.

1.8.3: Predominant diffusing component in the NiBi₃ layer

From a general viewpoint, the NiBi₃ compound layer growth (except at the very beginning of the Ni–Bi interaction) is due to two partial chemical reactions. Firstly, the Bi atoms may diffuse across the layer bulk from interface 2 to interface 1 (Fig. 1.21) and then react with the surface Ni atoms to form NiBi₃ at the Ni–NiBi₃ interface:



Secondly, the Ni atoms may diffuse across the layer bulk in the opposite direction and then react with the surface Bi atoms to form more NiBi₃ at the NiBi₃–Bi interface:

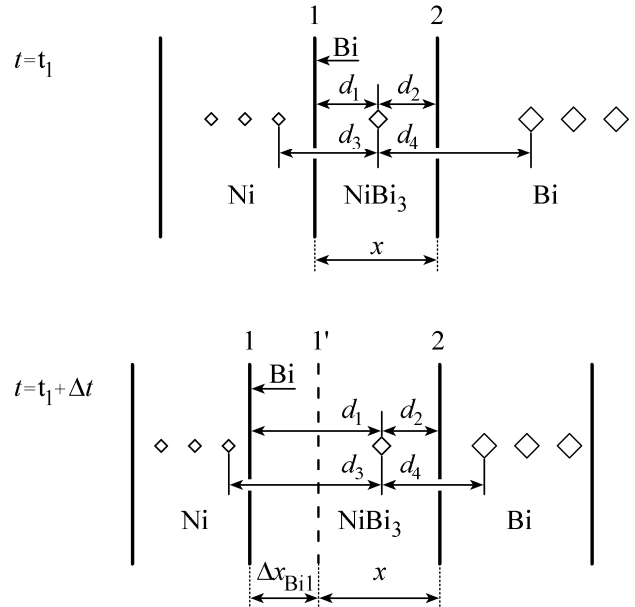


Fig. 1.21. Schematic illustration of the NiBi₃ growth process at the nickel-bismuth interface.

In view of the different size of the Ni and Bi atoms and the great difference in melting points of the components, the contributions of these reactions to the layer growth process can hardly be expected to be equal. On the one hand, the atomic radius of nickel (0.124 nm) is much less than that of bismuth (0.182 nm) [166]. Smaller atoms may reasonably be expected to diffuse faster. On the other hand, however, bismuth has the much lower melting point 271 °C compared to that (1451 °C) of nickel [167]. From this viewpoint, bismuth may be expected to diffuse predominantly in the NiBi₃ layer as its atoms are evidently more mobile at 150-250 °C than the nickel atoms. Microhardness indentation markers allowed these contributions to be visualised unambiguously.

The distances between the markers at the same place of the Ni–Bi interface were measured three times:

- (1) before each successive anneal, except the first one of an as-received Ni–Bi specimen;
- (2) after each anneal, without any polishing of the cross-section surface;
- (3) after the electrolytic re-polishing of the cross-section to remove some amount of the cross-section material from its surface, so that the craters of the microhardness indentations remained visible under optical microscope.

In the latter two cases, no noticeable differences were observed in measured values of the distance between the appropriate markers (compare the numbers in the last two rows of Table 1.3), indicative of the lack of any surface effect.

Table 1.3. Typical changes in distance between the microhardness indentation markers onto the surface of a Ni–Bi cross-section (see also Figs 1.21-1.23). Temperature 250 °C. Time of the first anneal is 18×10^4 s (50 h), while that of the second is 9×10^4 s (25 h); 27×10^4 s or 75 h in total [164]

Measurements made	Distance (μm)											
	Between five markers in Ni phase				d_1	d_2	d_3	d_4	Between five markers in Bi phase			
(1) before second anneal	80	79	77	80	88	104	142	158	76	76	77	78
(2) after second anneal, without polishing	81	79	78	79	122	104	174	121	77	75	78	77
(3) after second anneal, with slight electrolytic polishing	80	78	77	79	121	105	174	120	76	75	77	78

Additional proof for the absence of any significant surface effect was obtained by comparing the layer thickness existing, say, after the second anneal and before the third one. Namely, before the third anneal the Ni–Bi specimen was ground to remove 0.3 to 0.5 mm of its surface material and again polished electrolytically. Comparison of the layer thickness in both cases did not reveal any perceptible difference.

The lack of a noticeable surface effect in the Ni–Bi couples was in all probability due to the presence onto the specimen surface of a very thin protective layer occurred at the end of electrolytic polishing when the current was already switched off, while the specimen surface still continued to contact with the electrolyte. Though transparent and undetectable by EPMA, this layer consisting presumably of bismuth oxide was nonetheless sufficient to prevent surface diffusion.

The distance d_2 between a marker located initially in the middle part of the NiBi_3 layer and interface 2 (see Fig. 1.21) did not change during annealing. Hence, no appreciable diffusion of the Ni atoms across the growing NiBi_3 layer took place. In contrast, the distance d_1 between this marker and interface 1 was found to increase with increasing annealing time. Therefore, at temperatures of 150–250 °C the NiBi_3 layer growth is due to partial chemical reaction (1.103), the contribution of partial chemical reaction (1.104) being quite negligible, if any. The newly-grown NiBi_3 phase occurs entirely at the Ni– NiBi_3 interface (see Figs 1.22 and 1.23). Hence, the Bi atoms appear to be the only diffusing species in the course of layer formation.

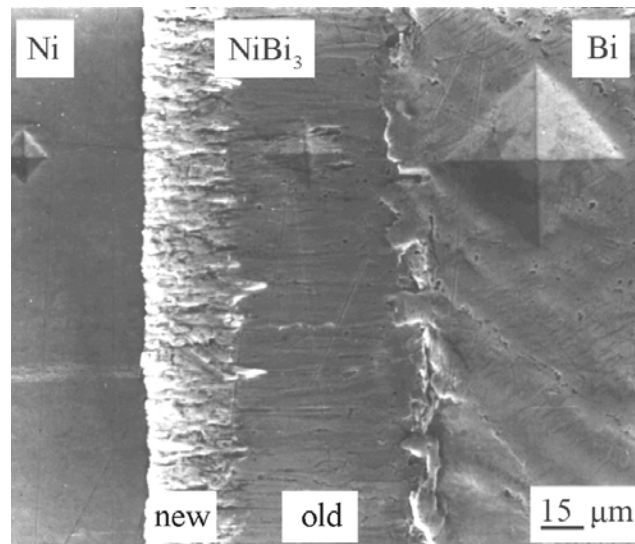


Fig. 1.22. Secondary electron image of the Ni–Bi transition zone after the second anneal in the as-received condition [164]. Temperature 250 °C. Time of the first anneal is 14400 s (4 h), while that of the second is 12600 s (3.5 h); 27000 s or 7.5 h in total. Microhardness indentations were put onto the electropolished surface of the cross-section after the first anneal at a load of 0.196 N (20 g).

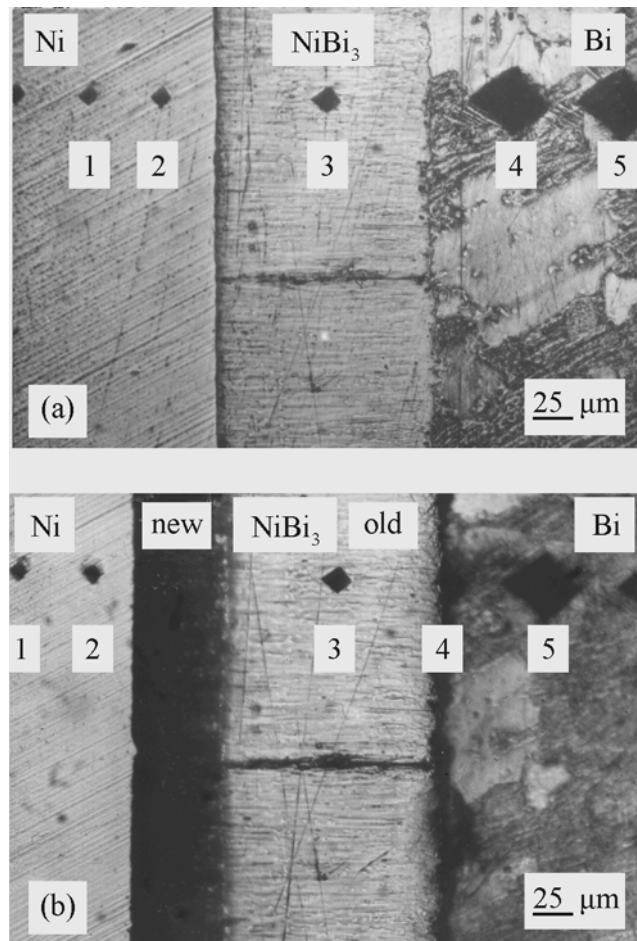


Fig. 1.23. Optical micrographs of the Ni–Bi transition zone (a) before and (b) after the third anneal. Temperature 200 °C, (a) annealed two times 18×10^4 s + 18×10^4 s (50 h + 50 h), (b) the same place after the third anneal for 36×10^4 s (100 h) in the as-received condition. Microhardness indentations were put onto the electropolished surface of the Ni–Bi cross-section after the second anneal at a load of 0.196 N (20 g).

It is worth noting that the sum of the distances d_3 and d_4 slightly diminished during annealing. This is due to a decrease in volume of any Ni–NiBi₃–Bi specimen, connected with the formation of the NiBi₃ intermetallic compound. The ratio of the decrease in $(d_3 + d_4)$ value to the corresponding increase in thickness of the NiBi₃ layer was experimentally found to be 0.20 ± 0.05 .

Note that the distances between the markers located in the Ni phase did not change in the course of annealing, indicative of no formation of a solid solution of bismuth in nickel. The distances between the markers located in the Bi phase remained unchanged as well. Also, no changes in size or configuration of the microhardness indentations were observed in either phase. Hence, the components are indeed mutually insoluble in the temperature range of 150–250 °C.

Microstructures of Fig. 1.23 deserve a more detailed discussion. Shown in Fig. 1.23a is the microstructure of the Ni–Bi transition zone after the second anneal at 200 °C for 100 h in two steps of 50 h. As this cross-section was polished electrolytically after annealing, the NiBi₃ layer is quite homogeneous in appearance. Then, the specimen was annealed for the third time at 200 °C for 100 h (200 h in total). Figure 1.23b shows its microstructure in the as-received condition (without any polishing). The newly-grown NiBi₃ phase is much darker than the old one and therefore is easily distinguishable.

Before the third anneal, microhardness indentation markers were put onto the electropolished cross-section surface in the Ni phase (five markers, about 50 μm from each other), in the middle of the NiBi₃ layer (one marker) and in the Bi phase (five markers, about 75 μm from each other). Only part of them are shown in Fig. 1.23.

After the third anneal, the distance d_1 between the marker 3 and the Ni–NiBi₃ interface increased from 76 to 137 μm, whereas the distance d_2 between this marker and the NiBi₃–Bi interface remained unchanged (70 μm). Marker 4 almost disappeared as a result of consumption of the Bi phase. Distance between the markers 3 and 5 decreased by 61 μm (from 202 to 141 μm). In terms of thickness, the consumption of nickel (around 6 μm) is seen to be much less than that of bismuth (61 μm). These values agree very well with the stoichiometry of the NiBi₃ intermetallic compound, as it must be from a chemical viewpoint.

Indeed,

$$\frac{x_{\text{Ni}}}{x_{\text{Bi}}} = \frac{c_{\text{Ni}}\rho_{\text{Bi}}}{c_{\text{Bi}}\rho_{\text{Ni}}} \quad (1.105)$$

where x , c and ρ are respectively the thickness consumed, the content in NiBi₃ and the density of nickel or bismuth. As $c_{\text{Ni}} = 8.55$ mass %, $c_{\text{Bi}} = 91.45$ mass %, $\rho_{\text{Ni}} = 8.9 \times 10^3 \text{ kg m}^{-3}$ and $\rho_{\text{Bi}} = 9.8 \times 10^3 \text{ kg m}^{-3}$, equation (1.105) yields $x_{\text{Ni}} = 0.1 x_{\text{Bi}}$. Hence, the thickness of the consumed bismuth phase is ten times greater than that of the consumed nickel phase. Therefore, relative to the initial Ni–Bi interface, the growing NiBi₃ layer mostly displaces as a whole into the side of bismuth, though its increase takes place entirely at the opposite side (near nickel).

1.8.4: NiBi₃ layer growth kinetics

As only the Bi atoms are diffusing and experimental values of the NiBi₃ layer thickness are large enough, its growth kinetics at the Ni–Bi interface is described by simplified equations (1.79) and (1.80):

$$\frac{dx}{dt} = \frac{k_{\text{1Bi1}}}{x} \quad (1.106)$$

and

$$x^2 = 2k_{\text{BiI}}t \quad (1.107)$$

where x is the total layer thickness at time t and k_{BiI} is a physical (diffusional) constant.

The latter equation can also be rewritten as follows:

$$x = (2k_{\text{BiI}}t)^{1/2}. \quad (1.108)$$

If the layer thickness-time dependence is described by these equations, then the growth process is undoubtedly diffusion controlled. A plot of the layer thickness against the square root of the annealing time is shown in Fig. 1.24. The experimental points are seen to yield three straight lines. Thus, the NiBi_3 layer growth is indeed diffusion controlled.

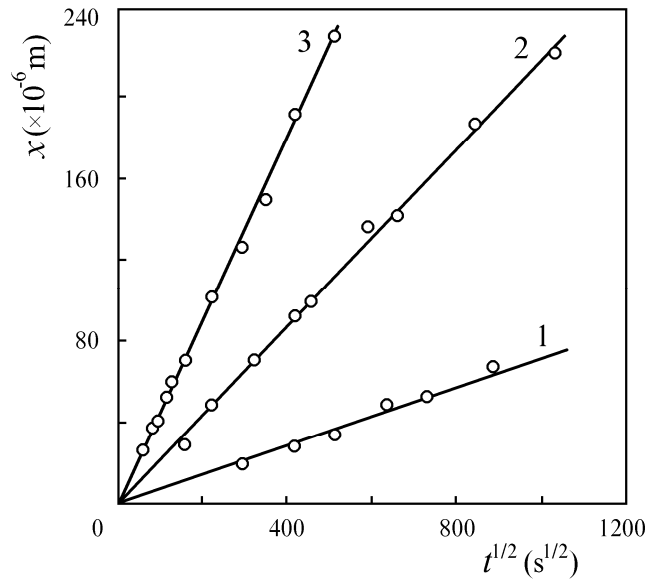


Fig. 1.24. Thickness of the NiBi_3 intermetallic layer plotted against the square root of the annealing time [164]. Temperature: 1, 150 °C; 2, 200; 3, 250.

The value of the physical (diffusional) constant $k_{\text{BiI}}^{(\text{integral})}$ can be calculated using integrated equations (1.107) or (1.108). The superscript *integral* is used to distinguish between the value of the constant calculated from the integrated equation and that found from the differential equation. The latter is denoted $k_{\text{BiI}}^{(\text{differential})}$.

The experimental values of $k_{\text{BiI}}^{(\text{integral})}$ at 150, 200 and 250 °C are listed in Table 1.4, together with their 0.95 confidence limits. These values represent the volume diffusivities of the Bi atoms in the NiBi_3 lattice in the course of the reaction-diffusion process or, in other

words, the *reaction-diffusion coefficients* of bismuth. The interconnection between the reaction- and self-diffusion coefficients of any component of a chemical compound will be discussed in the next section.

Table 1.4. Experimental values of the diffusional constants for the NiBi₃ layer growing between nickel and bismuth [164]

Temperature (°C)	$k_{\text{BiI}}^{(\text{integral})}$ (m ² s ⁻¹)	0.95 confidence limits for $k_{\text{BiI}}^{(\text{integral})}$ (m ² s ⁻¹)	$k_{\text{BiI}}^{(\text{differential})}$ (m ² s ⁻¹)	0.95 confidence limits for $k_{\text{BiI}}^{(\text{differential})}$ (m ² s ⁻¹)
150	2.4×10^{-15}	$\pm 0.4 \times 10^{-15}$	2.6×10^{-15}	$\pm 0.3 \times 10^{-15}$
200	2.2×10^{-14}	$\pm 0.2 \times 10^{-14}$	2.1×10^{-14}	$\pm 0.2 \times 10^{-14}$
250	9.5×10^{-14}	$\pm 0.3 \times 10^{-14}$	9.5×10^{-14}	$\pm 0.5 \times 10^{-14}$

The diffusional constant can also be calculated from a differential equation similar to equation (1.84) [163]. The values of $k_{\text{BiI}}^{(\text{differential})}$ obtained are also given in Table 1.4. If the NiBi₃ layer growth is indeed diffusion controlled and follows the parabolic law, then $k_{\text{BiI}}^{(\text{integral})}$ and $k_{\text{BiI}}^{(\text{differential})}$ must clearly coincide at each annealing temperature. As seen in Table 1.4, this is in fact the case.

Note that $k_{\text{BiI}}^{(\text{integral})}$ is identical to $k_{\text{BiI}}^{(\text{differential})}$ only in this particular case where one component (bismuth) is diffusing across the growing layer. In the general case, where two components A and B are diffusing at comparable rates, $k_{\text{BiI}}^{(\text{integral})}$ is equal to the sum of $k_{\text{BiI}}^{(\text{differential})}$ for A and $k_{\text{BiI}}^{(\text{differential})}$ for B. The latter quantities should be determined from the partial increases in layer thickness at its both interfaces with initial phases (see Section 1.4.3).

The temperature dependence of the reaction-diffusion coefficient (diffusional constant) of bismuth atoms in (or, rather, across) the growing NiBi₃ layer is described by the Arrhenius relation (see equation (1.81)). As seen in Fig. 1.25, a graph of the logarithm of the diffusional constant, $\ln k_1$, plotted against the reciprocal temperature, $1/T$, yields a straight line.

Using the average values of the reaction-diffusion coefficient given in Table 1.5, the equation

$$\ln k_1 = (0.49 \pm 0.05) \times 10^{-6} \exp [-(67.1 \pm 0.7) \text{ kJ mol}^{-1}/RT] \text{ m}^2 \text{ s}^{-1}$$

was obtained by the least-squares fit method. The value, $E = 67.1 \text{ kJ mol}^{-1}$, of the energy of activation falls within a range typical of diffusion controlled processes [1-9].

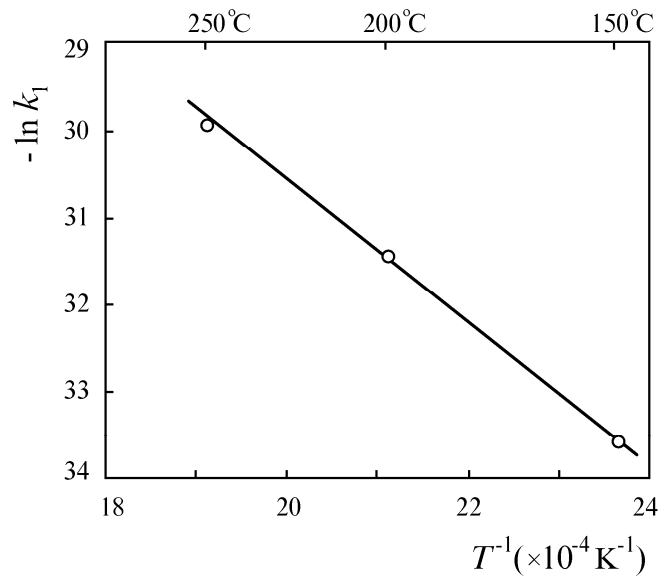


Fig. 1.25. Temperature dependence of the reaction-diffusion coefficient of the bismuth atoms in the growing NiBi₃ layer [164].

Table 1.5. Temperature dependence of the reaction-diffusion coefficient of the bismuth atoms in the growing NiBi₃ layer (see equation (1.81)) [164]

Temperature (°C)	T^{-1} (×10 ⁻³ K ⁻¹)	k_1 (m ² s ⁻¹)	ln k_1	Pre-exponential factor (×10 ⁻⁶ m ² s ⁻¹)	Activation energy (kJ mol ⁻¹)
150	423	2.5×10 ⁻¹⁵	-33.622	0.49±0.05	67.1±0.7
200	473	2.1×10 ⁻¹⁴	-31.494		
250	523	9.5×10 ⁻¹⁴	-29.985		

1.9: Interrelation between the reaction-diffusion coefficients of the components of a chemical compound and their self-diffusion coefficients

Experimental data available in the literature show large, if not to say huge, differences between the values of diffusion coefficients of the elements A and B in the A_pB_q chemical compound layer growing at the A – B interface and the values of diffusion coefficients of the same elements in a separate specimen of the same chemical compound. In other words, for the same component of the same compound the value of the reaction-diffusion coefficient is

quite different from the value of the self-diffusion coefficient, with the difference amounting to a few orders of magnitudes. Note that the reaction-diffusion coefficient is always greater than the appropriate self-diffusion coefficient. Consider a few examples.

According to the data by L.N. Larikov *et al.* [168] (see also Ref. [169]), the self-diffusion coefficients of iron and aluminum in the Fe₂Al₅ phase at 520 °C are equal to $1.9 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ and $8.7 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$, respectively. On the other hand, when investigating the growth kinetics of the Fe₂Al₅ layer at the interface between iron and aluminum, T. Heumann and S. Dittrich [170] found that the growth process is due mainly to the diffusion of aluminium, while the temperature dependence of the reaction-diffusion coefficient of the aluminium atoms in the growing Fe₂Al₅ layer is described by the equation

$$D_{\text{Al}} = 3.3 \times 10^{-6} \exp(-54.8 \text{ kJ mol}^{-1} / RT) \text{ m}^2 \text{ s}^{-1}.$$

Extrapolation produces a value of $7.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 520 °C, five orders of magnitude greater than that determined using radioactive tracers in the Fe₂Al₅ phase taken alone [168, 169].

The same also applies to α -Al₂O₃. According to the data by E. Bergsmark *et al.* [171], M. Le Gall *et al.* [172] and J.D. Cawley *et al.* [173], the experimental values of the parabolic growth-rate constant of oxide films at the interface between aluminum and oxygen are 10^7 - 10^{10} higher than those expected from the values of the self-diffusion coefficients of aluminum and oxygen in this phase.

In the case of Fe_{3- δ} O₄, the difference in cation diffusion coefficients in the growing compound on the one hand and in the non-growing one on the other was found by S. Tinkler and R. Dieckmann [174] to be approximately two orders of magnitude. A.C.S. Sabioni *et al.* [175] (see also Refs [176-178]) showed that the values of self-diffusion coefficients of chromium and oxygen in Cr₂O₃ are considerably lower than the previously reported ones and are insufficient to account for the observed growth rate of the chromium oxide layer.

Diffusion behavior of silicon atoms in the growing Pd₂Si layer was shown by C.M. Comrie and J.M. Egan [179, 180] to be different from that in the absence of growth. According to the data by J.C. Ciccariello *et al.* [181] and T. Barge *et al.* [182], the values of diffusion coefficients of the components in Ni₂Si and CoSi₂ determined with the use of radioactive tracers are a few orders of magnitude lower than those calculated from the rate of formation of the Ni₂Si and CoSi₂ layers. The values of diffusion coefficients of aluminum and antimony in AlSb found from reaction kinetics are much higher than those measured using radioactive tracers [9, 169].

1.9.1: Reasons for the difference in reaction- and self-diffusion coefficients

In the case of the reaction-diffusion process, of all conceivable diffusion mechanisms [3, 5, 17, 183-190], most probable ones are vacancy, grain-boundary and interstitial. What is diffusing (molecule, atom or ion) depends on the structure of a chemical compound and the

physical and chemical properties of its components, in particular of the radius of their atoms or ions.

Diffusion of a reacting substance across the bulk of a growing compound layer in the form of molecules is probably a very rare phenomenon, typical of lattices with low packing densities. Such a structure is characteristic, for example, of SiO_2 . Its lattice contains channels along which the oxygen molecules can readily travel [17, 191-194]. K. Motzfeldt [191] found good agreement between the permeability of the SiO_2 layer to oxygen molecules and its growth rate. Calculations of the lattice-diffusion coefficient, D_{O} , of oxygen atoms using Arrhenius-type equations, obtained by different authors and compiled in a review by M.A. Lamkin *et al.* [194], produce values of the order of 10^{-18} - $10^{-23} \text{ m}^2 \text{ s}^{-1}$ at 1000°C , which are evidently insufficient to account for the observed rate of growth of the SiO_2 layer [17].

S.S. Kristy and J.B. Condon [192] found a value of D_{O} of the order of $10^{-23} \text{ m}^2 \text{ s}^{-1}$ at 700°C and arrived at the conclusion that this value could not have any noticeable effect on the kinetics of reaction of silicon with oxygen. This is undoubtedly the case in view of much greater values of the diffusional constant, k_1 , listed in Table 1.2. From the work of J.A. Costello and R.E. Tressler [193], it can be concluded that the diffusion coefficient of oxygen atoms found by radiotracers becomes comparable with the growth-rate constant of the SiO_2 layer at temperatures above 1300°C .

The difference in values of the diffusion coefficient of a constituent in the growing and non-growing layers of a chemical compound is often explained by the influence of grain-boundary diffusion. Such an explanation seems too “universal” in order to be valid in all cases.

Firstly, the “width” of any grain boundary is small in comparison with the sizes of adjacent grains except, perhaps, for very fine ones. Therefore, in spite of high values of grain-boundary diffusion coefficients of reacting atoms, their fluxes along grain boundaries across a growing chemical compound layer can hardly be large, at least in coarse-grained structures like Fe_2Al_5 (see Fig. 1.6).

Secondly, if grain-boundary diffusion predominates, a growing compound layer should be thicker in the vicinity of the boundaries of any grain in comparison with the central part of that grain. This is quite opposite to what has been observed experimentally in the case of growing Fe_2Al_5 layers [195].

The main reason for the difference in reaction- and self-diffusion coefficients appears to lie in the peculiarities of the reaction-diffusion mechanism itself. Indeed, the description of diffusion processes in both growing and non-growing compound layers conventionally based upon Fick’s laws that are too fundamental for their validity and applicability to be doubted in such simple cases. Of all quantities entering into Fick’s equations, only the concentration, c , of a diffusing species can be treated ambiguously. Diffusion coefficient, D , of any component, being a characteristic of the squared atomic displacement per unit time, can

hardly be expected to be dependent on whether this compound is growing or non-growing, if the diffusion mechanism is the same in both cases.

Most chemical compounds are characterised by diffusion of the components across the bulks of their growing layers in the form of atoms or ions and not in the form of molecules or radicals, just because the former are of smaller size than the latter. The process of bulk diffusion is described by Fick's laws. The first Fick law relates the flux of atoms of a given component to its diffusion coefficient and concentration gradient in the direction of diffusion at constant surface area of contacting phases:

$$j_A = -D_A \frac{\partial c_A}{\partial x} \quad (1.109)$$

where j_A is the flux of A atoms across the bulk of a growing layer ($\text{mol m}^{-2} \text{s}^{-1}$ or $\text{kg m}^{-2} \text{s}^{-1}$), D_A is the diffusion coefficient of the A atoms in the lattice of a compound ($\text{m}^2 \text{s}^{-1}$), c_A is the concentration (content) of component A in a compound (mol m^{-3} or kg m^{-3}).

The second Fick law describes a change in concentration of diffusing particles at a given point of space with passing time:

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} \quad (1.110)$$

Note that the use in Fick's equations of concentration units other than the number of particles or their mass per unit volume (molar, mass or volume fraction, percent, *etc.*) must be substantiated in each particular case. Otherwise, the numerical values of the diffusion coefficients obtained will be incorrect. Though widespread, employment of these other units in theoretical treatments does not appear reasonable.

In the case of chemical compounds of constant composition, application of Fick's equations is, on the one hand, facilitated by the obvious fact that it is not necessary to take into account the concentration dependence of the diffusion coefficient. On the other hand, however, there arise serious, if not insurmountable, difficulties with the direct use of those equations because no concentration gradient can evidently exist in any growing layer, if a compound has no homogeneity range. It is therefore not surprising that most authors give preference to analysing the process of formation of the layers of chemical compounds having a narrow range of homogeneity (in comparison with the average content of a given component). This is one of ideal cases for theoreticians to treat.

Firstly, the concentration dependence of the diffusion coefficient can be neglected. Secondly, the concentration of components at the interfaces of any growing layer can be assumed to be equal to the limits of the homogeneity range of a compound according to the equilibrium phase diagram of the A - B binary system. Thirdly, the concentration distribution

of the components across a compound layer at any instant can reasonably be assumed to be close to linear (Fig. 1.26a), so that

$$\frac{\partial c_A}{\partial t} \approx 0. \quad (1.111)$$

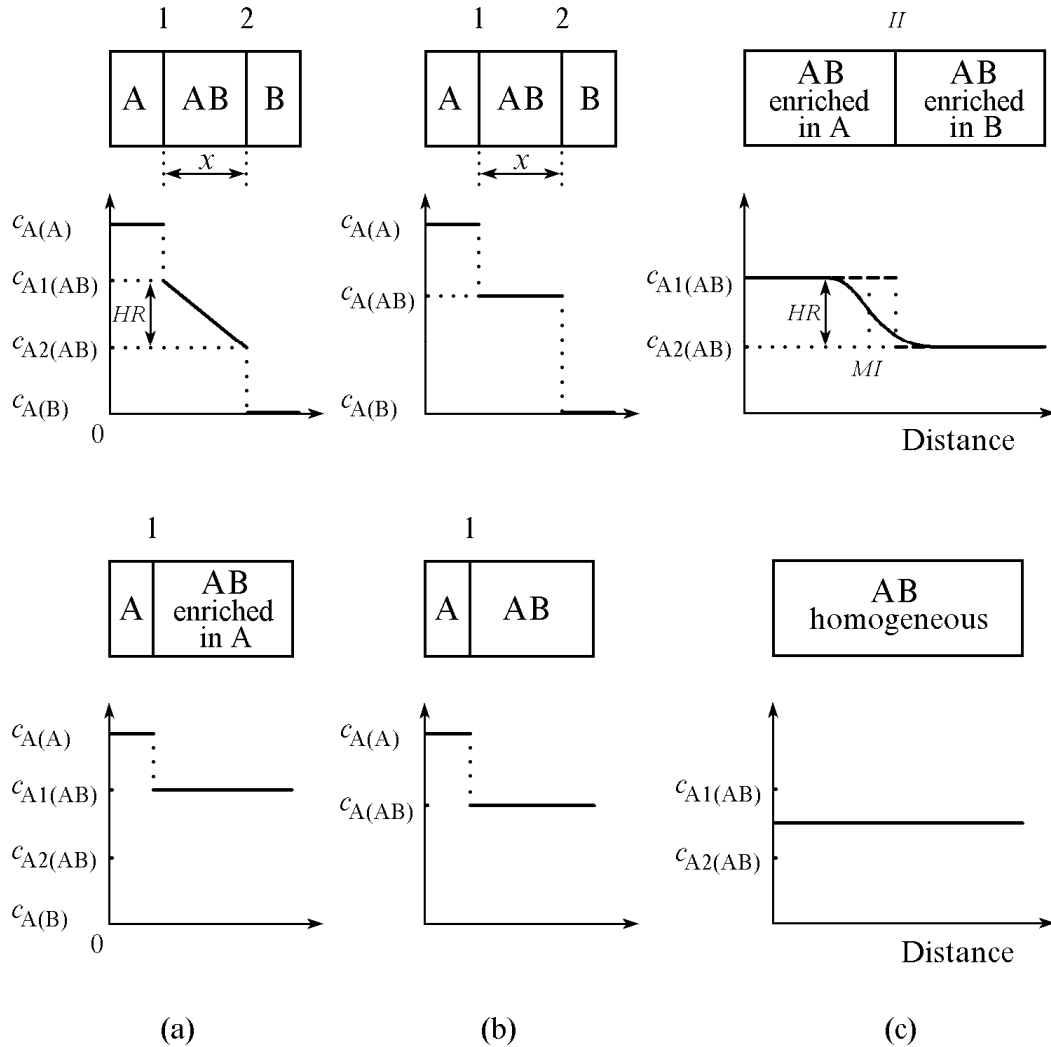


Fig. 1.26. Evolution of reaction couples up to the establishment of equilibrium. (a) Growth process of a layer of the compound AB having a (narrow) range of homogeneity. Phase A and the compound AB with the content of component A equal to the upper limit of the range of homogeneity remain under equilibrium. (b) Growth process of a layer of the compound AB without any range of homogeneity. (c) Homogenising a diffusion couple consisting of the compound AB with different contents of component A. HR is the range of homogeneity of the compound AB , II is the initial interface, MI is Matano's plane.

Equation (1.111) expresses the condition of the quasi-stationary concentration distribution when the concentrations of components *A* and *B* in the growing layer *AB* or *A_pB_q* are functions of only coordinate, *x*, and do not depend on time, *t*. Simply speaking, on a time scale of the diffusion of atoms across the layer, the redistribution of concentration of the components along the layer takes place at a relatively high rate. For compounds of constant composition, this condition is clearly always satisfied. The distribution of concentration of the components in each particular case can readily be established, for example, by means of electron probe microanalysis.

Indeed, if for the layers of a given compound of different thickness obtained on the same *A–B* specimen by interrupting the chemical reaction at certain moments of time, the distribution of contents of the components across the width of the layer proves close to linear as shown in Fig. 1.26a, then the quasi-stationary condition is fulfilled quite satisfactorily. Of course, one may object that, firstly, the accuracy of measurements is not always sufficiently high and, secondly, the content of the components in any compound layer can be measured only at some distance from the interfaces.

The latter difficulty is easily overcome by extrapolation. Furthermore, it is clear that if the mean content of a component in a compound is equal to 40-60%, while the range of homogeneity is 1-2% or less, then possible deviations from the quasi-stationary concentration distribution can hardly be expected to have any noticeable effect on the results of analytical description of layer-growth kinetics. This is especially so in the case of the reaction-diffusion process. The layer of any chemical compound grows at the expense of *stoichiometry* of that compound and not at the expense of its range of homogeneity. Therefore, from the point of view of formal kinetics, it does not matter whether the compound has any range of homogeneity or not. To explain why this conclusion (quite opposite to the views of most, if not all, investigators in the field) was drawn, consider a conventional treatment of diffusional processes.

If the concentration distribution of component *A* in the *AB* layer is linear (see Fig. 1.26a), then its concentration gradient can be expressed through the boundary values, *c_{A1}* and *c_{A2}*, and the thickness, *x*, of the growing layer:

$$-\frac{\partial c_A}{\partial x} = \frac{c_{A1} - c_{A2}}{x} . \quad (1.112)$$

Hence, the flux of component *A* across the bulk of the *AB* layer from interface 1 to interface 2 is

$$j_A = D_A \frac{(c_{A1} - c_{A2})}{x} . \quad (1.113)$$

This flux is entirely consumed in the formation of the AB chemical compound at interface 2. Therefore, assuming that the chemical transformations with participation of the diffusing A atoms and the surface B atoms take place instantaneously, its value can also be expressed as follows

$$j_A = \frac{c_{A1} + c_{A2}}{2} \left(\frac{dx}{dt} \right)_{\text{diffusional regime}}. \quad (1.114)$$

Equating the right-hand sides of equations (1.113) and (1.114) yields

$$\left(\frac{dx}{dt} \right)_{\text{diffusional regime}} = \frac{2D_A(c_{A1} - c_{A2})}{(c_{A1} + c_{A2})x}. \quad (1.115)$$

As, on the other hand (see equation (1.58)),

$$\left(\frac{dx}{dt} \right)_{\text{diffusional regime}} = \frac{k_{1A2}}{x}, \quad (1.116)$$

a relation between the diffusion coefficient of the A atoms across the bulk of any growing compound layer and the diffusional constant is

$$D_A = \frac{(c_{A1} + c_{A2})}{2(c_{A1} - c_{A2})} k_{1A2}. \quad (1.117)$$

Note that this equation holds for chemical compounds of any composition A_pB_q , not only for AB . Equations similar to (1.116) and (1.117) were proposed by T. Heumann to treat the experimental data on the growth kinetics of intermetallic compounds [52, 170].

The quantity $(c_{A1} + c_{A2})/2 = c_{\text{average}}$ is the average content of component A in a chemical compound. The difference of its contents at the layer interfaces $\Delta c_A = c_{A1} - c_{A2} = HR$ represents the range of homogeneity of the compound under given temperature-pressure conditions.

It is usually assumed that Δc_A is the driving force for the process of formation of a chemical compound layer, *i.e.* $j_A \sim \Delta c_A$. However, if it were the case, the layers of chemical compounds without any homogeneity ranges like Al_2O_3 or $NiBi_3$ would not grow at all that contradicts experimental observations. This is the first inconsistency of the conventional diffusional approach. Again, at any finite value of k_{1A2} equation (1.117) produces unrealistically high values of the diffusion coefficient because $D_A \rightarrow \infty$, as $\Delta c_A \rightarrow 0$ (second inconsistency). In the limit, it actually means dividing by zero. From a physical viewpoint, such values are hardly possible.

Generally, wide ranges of homogeneity are not characteristic of chemical compounds. Therefore, equation (1.117) either yields too high values of diffusion coefficients of the components in growing layers of chemical compounds having narrow ranges of homogeneity (Fe_2Al_5 , CoSn_2 , $\text{Fe}_{3-\delta}\text{O}_4$) or cannot be employed at all in the case of compounds without any homogeneity range (NiBi_3 , FeB , Al_2O_3). The introduction of the so-called integrated diffusion coefficient [50] can hardly be regarded as a satisfactory solution to this problem. It is solved in a more reasonable way by assuming that the driving force for the reaction-diffusion process of the A atoms across the bulk of the growing AB layer is the difference in *concentration of vacancies* of component A in this layer at the A – AB and AB – B interfaces [196]. Then, both inconsistencies of the diffusional approach are readily eliminated.

It is necessary, however, to distinguish between the newly-formed and native (equilibrium) vacancies. The newly-formed vacancies arise in the course of partial chemical reactions proceeding at the layer interfaces. These are thus reaction-induced vacancies which do not normally exist in a given equilibrated compound. The native (inherent), mainly thermal, vacancies are present in the compound initially (in the equilibrium state), their number being quite negligible by comparison, except perhaps at temperatures close to its melting point. Both the newly-formed and native vacancies are clearly supposed to be of the same character.

Equation (1.117) can be re-written as

$$k_{1A2} = \frac{2D_A(c_{A1} - c_{A2})}{(c_{A1} + c_{A2})} = \frac{D_A(c_{A1} - c_{A2})}{c_{\text{average}}}, \quad (1.118)$$

where $(c_{A1} + c_{A2})/2$ is the average content of component A in the compound layer, c_{average} .

If the concentration of newly-formed vacancies of component A in the AB layer at the reacting interface 2 (see Fig. 1.26a) where these vacancies are continuously created as a result of partial chemical reaction $A_{\text{dif}} + B_{\text{surf}} = AB$, like (1.49), is assumed to be *numerically* equal to the content of this component in the AB compound with the opposite sign

$$-C_{\text{vacancies } A} = c_A,$$

while that at another (non-reacting) interface 1 zero (ideal case in which no native vacancies are available in the compound), then from equation (1.118) it follows

$$k_{1A2} = \frac{D_A(0 + c_{A2})}{c_{\text{average}}}. \quad (1.119)$$

If $HR = 0$ (see Fig. 1.26b), then $c_{A1} = c_{A2} = c_{\text{average}}$. Hence, $k_{1A2} = D_A(0 + c_{A2})/c_{\text{average}} = D_A$. Thus, the physical (diffusional) constant k_{1A2} is identified with the reaction-diffusion coefficient, D_A , of component A in the lattice of any chemical compound.

If $HR \neq 0$,

$$k_{1A2} = \frac{D_A(0 + c_{A2})}{c_{\text{average}}} \approx D_A, \quad (1.120)$$

with the difference between k_{1A2} and D_A decreasing as HR tends to zero. In other words, the closer the compound to its stoichiometric composition, the more nearly k_{1A2} approaches D_A .

From equations (1.118)-(1.120), it must be clear that the role of native point defects such as vacancies of component A in the reaction-diffusion process of formation of any chemical compound is *quite opposite* to their role in the process of self-diffusion of that component in the compound taken as a separate phase.

In the absence of complicating factors, the *higher* the amount of native A vacancies in AB , the *higher* is the rate of self-diffusion of component A in the separate AB phase. Contrary to this, the *higher* the amount of native A vacancies in AB , the *less* is the rate of growth of the AB layer in the A – B couple at the expense of diffusion of component A , i.e. the *less* is a value of the physical (diffusional) constant k_{1A2} .

From a chemical viewpoint, this conclusion appears to be quite understandable because unoccupied (empty) sites (vacancies) can hardly take part in chemical reactions yielding material products. It is just available atoms, ions, molecules or radicals and not native vacancies that are responsible for the progress of any interfacial chemical reaction. The formation of a reaction product is a result of their joint efforts. In the case of the reaction-diffusion process, it does not seem substantiated to make a relatively small amount of missing atoms, say one atom in every hundred atoms, responsible for its course and to consider a much greater amount of available atoms (99) as an inert mass. The actual role of this single missing atom can roughly be estimated as 100% with the plus sign in the self-diffusion process and as 1% with the minus sign in the reaction-diffusion one.

The influence of deviations from the stoichiometry of any chemical compound on the growth rate of its solid layer can be illustrated by the following numerical example. If at some fixed temperature the AB homogeneity range is 5% (35 to 40% A), then a relation between the physical (diffusional) constant, k_{1A2} , of the AB layer and the reaction-diffusion coefficient, D_A , of component A in the AB lattice is (see equations (1.118)-(1.120))

$$k_{1A2} = \frac{D_A(0 + 35)}{(40 + 35)/2} = 0.93D_A.$$

If at the same temperature the AB homogeneity range is reduced (by change of pressure or any other means) to 2% (38 to 40% A), then this relation is

$$k_{1A2} = \frac{D_A(0 + 38)}{(40 + 38)/2} = 0.97D_A.$$

The effect is seen to be rather perceptible. Its magnitude is in general agreement with the values observed for oxides of deficient structure [13, 14, 197-199]. Similar effect must also be observed, though not so easily experimentally, with intermetallics and other chemical compounds.

Clearly, similar consideration also applies to component *B*. A row (a plane in two dimensions) of *B* vacancies is formed in the *AB* layer at interface 1 as a result of chemical interaction between the diffusing *B* atoms and the surface *A* atoms (Fig. 1.27, $t_1 > t_0$). From Fig. 1.27, it can easily be understood that, on the one hand, the concentration of newly-formed *B* vacancies, continuously created at the *A*–*AB* interface (interface 1) in the course of partial chemical reaction $B_{\text{dif}} + A_{\text{surf}} = AB$, is *numerically* equal to the content of component *B* in the *AB* compound. On the other hand, there are almost no *B* vacancies at the *AB*–*B* interface (interface 2) since those are mainly thermal, their amount at not too high temperatures being negligibly small by comparison. Therefore, due to this difference in vacancy concentrations, during $t_2 > t_1$ the row of *B* vacancies moves as a whole across the bulk of the *AB* layer until it reaches interface 2 at $t_3 > t_2$. At $t_4 > t_3$, this basic act of the reaction-diffusion process is completed by the formation of an additional row of “molecules” *AB* and then is repeated with the *AB* layer thicker by one “molecule” *AB*, and so on. Its driving force is the difference in values of the chemical potential of component *B* in initial phases *A* and *B*. This constant difference exists until at least one of initial substances *A* or *B* is entirely exhausted.

In the general case where both components *A* and *B* are sufficiently mobile in the *AB* lattice, two rows (planes) of vacancies are formed, namely, one row of *A* vacancies and one row of *B* vacancies, as shown in Fig. 1.28. Measurement of partial increases in thickness of the layer at its interfaces makes it possible to calculate

$$k_{1A2} = D_A \text{ and } k_{1B1} = D_B$$

for the compound without any homogeneity range, $HR = 0$, or

$$k_{1A2} \approx D_A \text{ and } k_{1B1} \approx D_B$$

for the compound with a homogeneity range, $HR > 0$.

Generally, during growth of any chemical compound layer, the rows of *A* and *B* vacancies move across its bulk in opposite directions. These vacancies appear as a result of the occurrence of chemical reactions at the interfaces of this layer with initial phases. It should be stressed that the vacancies formed cannot be distributed uniformly within the bulk of a chemical compound layer. Their amount exceeds all permissible equilibrium limits under given temperature-pressure conditions. Existence of such vacancies is only possible in growing compound layers.

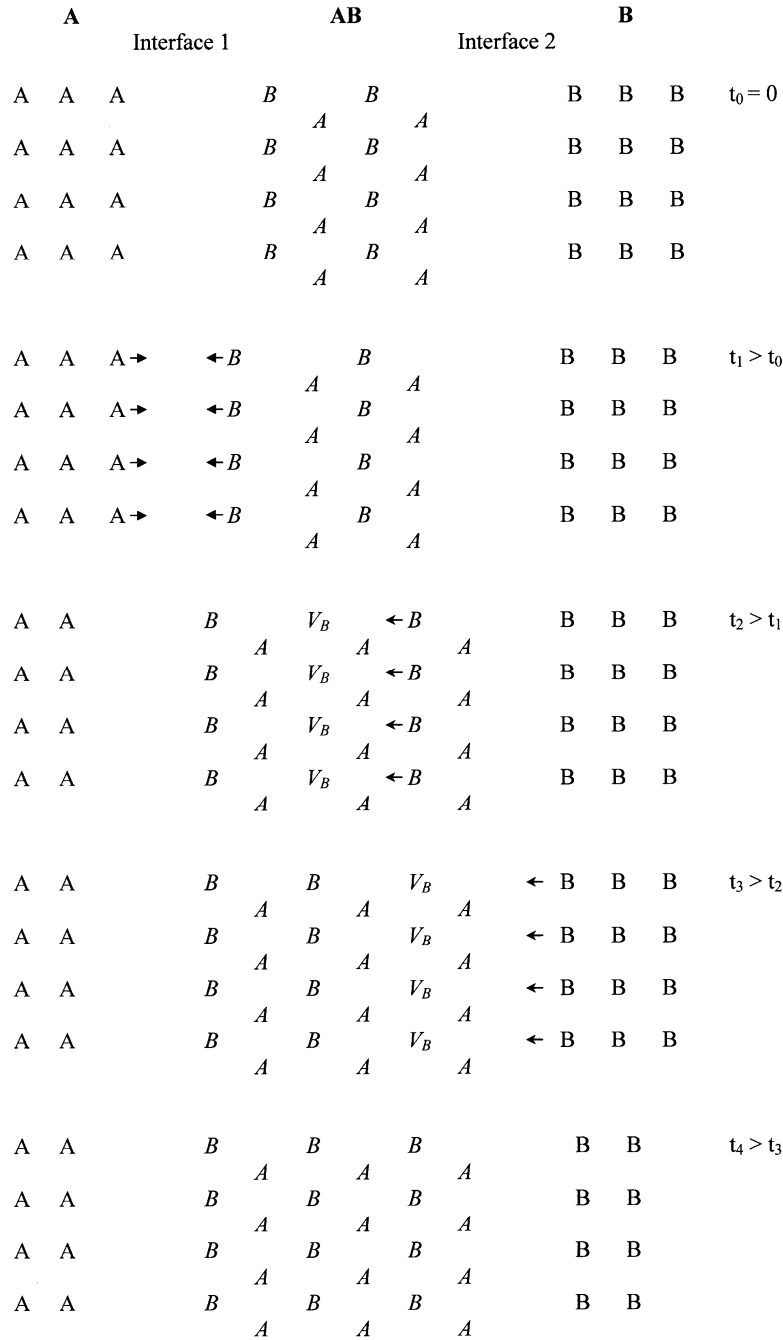


Fig. 1.27. Formation and displacement of a row (a plane in two dimensions) of vacancies of component *B* in the bulk of the growing *AB* layer in the course of the reaction-diffusion process. Component *A* is considered to be immobile in the *AB* lattice. At t_1 , the diffusing *B* atoms start to interact chemically with the surface *A* atoms to form the *AB* “molecules” at interface 1. As a result, a row (a plane) of *B* vacancies occurs in the *AB* layer at t_2 . These vacancies are filled with neighbouring *B* atoms, so that a row (a plane) of *B* vacancies moves as a whole towards interface 2. At t_3 , this row (plane) of *B* vacancies is filled with *B* atoms from phase *B*. At t_4 , the system returns to a new initial state and all the processes described are repeated again and again with the increasingly thicker *AB* layer.

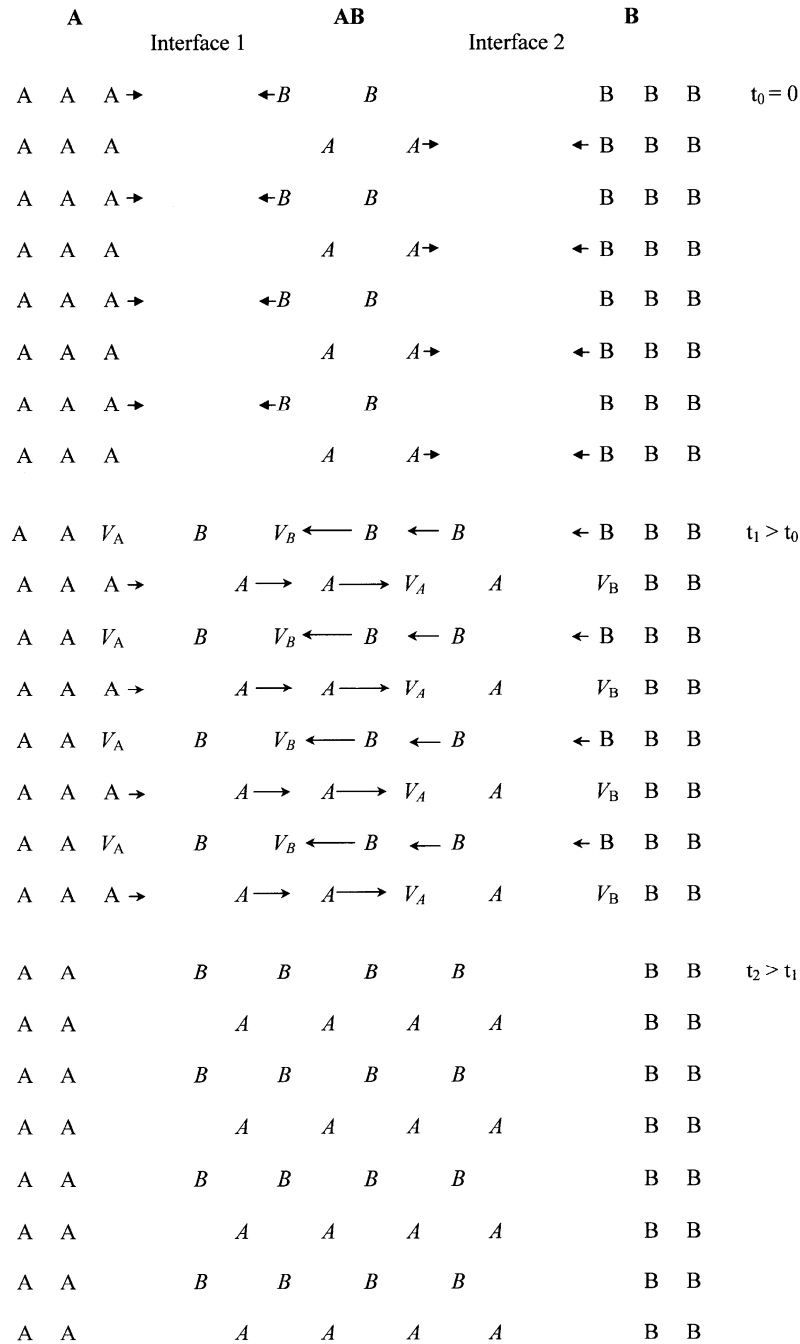


Fig. 1.28. Formation and displacement of rows (planes) of A and B vacancies across the bulk of the AB layer in the course of reaction diffusion of both components. At t_0 , chemical reactions start to proceed simultaneously at both interfaces of the AB layer with initial phases. As a result of those reactions, a row (a plane) of A vacancies and a row (a plane) of B vacancies occur in the AB layer. Between t_1 and t_2 , these move across the AB layer in opposite directions towards its interfaces and then are filled with appropriate atoms from A or B phases. Arrows of different length indicate the sequence of movement of diffusing atoms. At t_2 , the system returns to a new initial state, and all the processes are repeated again and again.

If the reaction is arrested at some moment of time when a moving row of vacancies is far away from the interfaces, component *A* or *B* must form a separate phase within the bulk of a grown layer of the compound *AB* or A_pB_q . In thin films, the amount of this phase is relatively large. It must therefore be detectable by sufficiently sensitive experimental methods.

In real reaction couples the interaction rarely starts simultaneously over the whole interface between initial substances *A* and *B*. The reasons may be different, from local contaminations of the surface of reacting phases to inherent structure imperfections. In such cases, a few shorter rows of vacancies are formed and move with some shift in space across the layer of any chemical compound.

The formation of vacancy rows in the layers of ionic compounds must result in the occurrence of strong electrical fields, especially at low temperatures when their electrical conductivity is insufficiently high. These fields will undoubtedly affect the process of layer growth and may even lead to its arrest. The value of this effect may be estimated following N.F. Mott and R.W. Gurney [200].

Note that the concentration gradient of components *A* and *B* in the growing layer of any chemical compound is established only in the case of existence of a considerable homogeneity range of that compound (see Fig. 1.26b). Establishment of this gradient is in fact a *consequence* of the *reaction-diffusion process* and not the *reason* for this process to proceed, as is conventionally assumed.

The quantity $\Delta c_A = HR$ is the driving force for the *diffusion* process when two specimens of substance *AB* with contents of *A* equal to c_{A1} and c_{A2} are brought into close contact with each other and then annealed for some period of time at a constant temperature. This is in fact the process of formation of a solid solution resulting in complete homogenising the examined diffusion couple (Fig. 1.26c). Such experiments can readily be carried out with chemical compounds having considerable ranges of homogeneity (a few per cent).

Figure 1.29 shows the concentration profile of Co in a $\text{Co}_{54}\text{Ti}_{46}$ – $\text{Co}_{50}\text{Ti}_{50}$ diffusion couple (for the CoTi intermetallic compound $HR = 4$ at.%), obtained by W. Sprengel *et al.* [201]. It is like that shown in Fig. 1.26c. Similar plots were obtained, for example, by M. Salamon *et al.* [202] for Al in FeAl ($HR = 20$ at.%) at 1000 °C and by Y. Nose *et al.* [203] for Fe in Pt_3Fe ($HR = 3$ at.%) at 1060 °C. These concentration profiles are quite different from the straight-line (horizontal if $HR = 0$ or inclined if $HR > 0$) ones that are typical of growing compound layers (compare Figs 1.26a and b with Fig. 1.26c).

Any reaction couple tends with passing time to its equilibrium state. According to the Gibbs phase rule [128-133], in any binary system at most two phases can coexist under equilibrium, if temperature and pressure are maintained constant. These are either the compound layer of constant composition and one of initial substances (see Fig. 1.26b), or the compound layer itself, if the amounts of initial substances correspond to its composition.

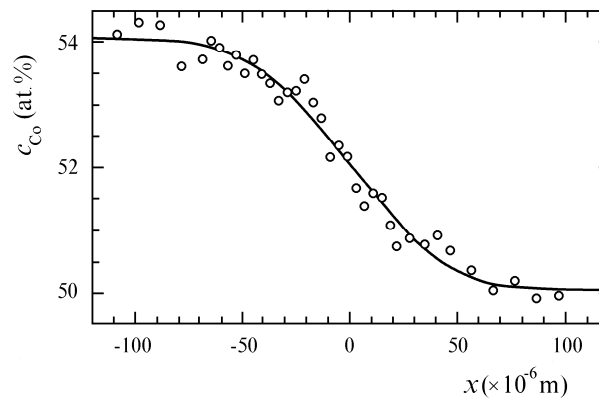


Fig. 1.29. Concentration profile of cobalt in a $\text{Co}_{54}\text{Ti}_{46}$ – $\text{Co}_{50}\text{Ti}_{50}$ diffusion couple annealed at $1300\text{ }^{\circ}\text{C}$ for $11.4 \times 10^3\text{ s}$. According to the work of W. Sprengel *et al.* [202].

This is one of two modes of attaining equilibrium, namely, by consumption of an initial phase. It is typical of systems with no solid-state solubility. Another is a smooth homogenisation, as shown in Fig. 1.26c. Figure 1.26a represents a combination of the two extremes. First, phase *B* is completely consumed and subsequently the *AB* layer attains the concentration c_{A1} (the upper limit of the range of homogeneity in regard to component *A*).

1.9.2: Kirkendall effect

The difference in diffusivities of the components in a growing chemical compound layer is often connected, especially in the literature on physics and metallurgy and especially in relation to intermetallics, with the Kirkendall effect. From historical and scientific viewpoints, this does not always appear to be sufficiently substantiated.

The Kirkendall effect was established in 1939–1947. Its final formulation was presented in a paper published by E. Kirkendall in collaboration with his student Alice Smigelskas in 1947 [204] (see also Refs [5, 8]). After this, E. Kirkendall stopped his research career and gave preference to administrative work. Those wishing to know more historical details are advised to read an article by H. Nakajima [205] and a historical overview in the book of H. Mehrer [188].

The Kirkendall effect arises from the different values of the self-diffusion (intrinsic) coefficients of the components of a *substitutional solid solution*, determined by Matano's method. Matano's interface is defined by the condition that as much of the diffusing atoms have migrated away from its one side as have entered the other. To understand the essence of the Kirkendall effect, it suffices to consider a schematic representation of the diffusion processes taking place during annealing of any couple *A–B*, the components of which are capable of forming an extended or terminal solid solution under given temperature-pressure conditions. Its initial state is shown in Fig. 1.30a.

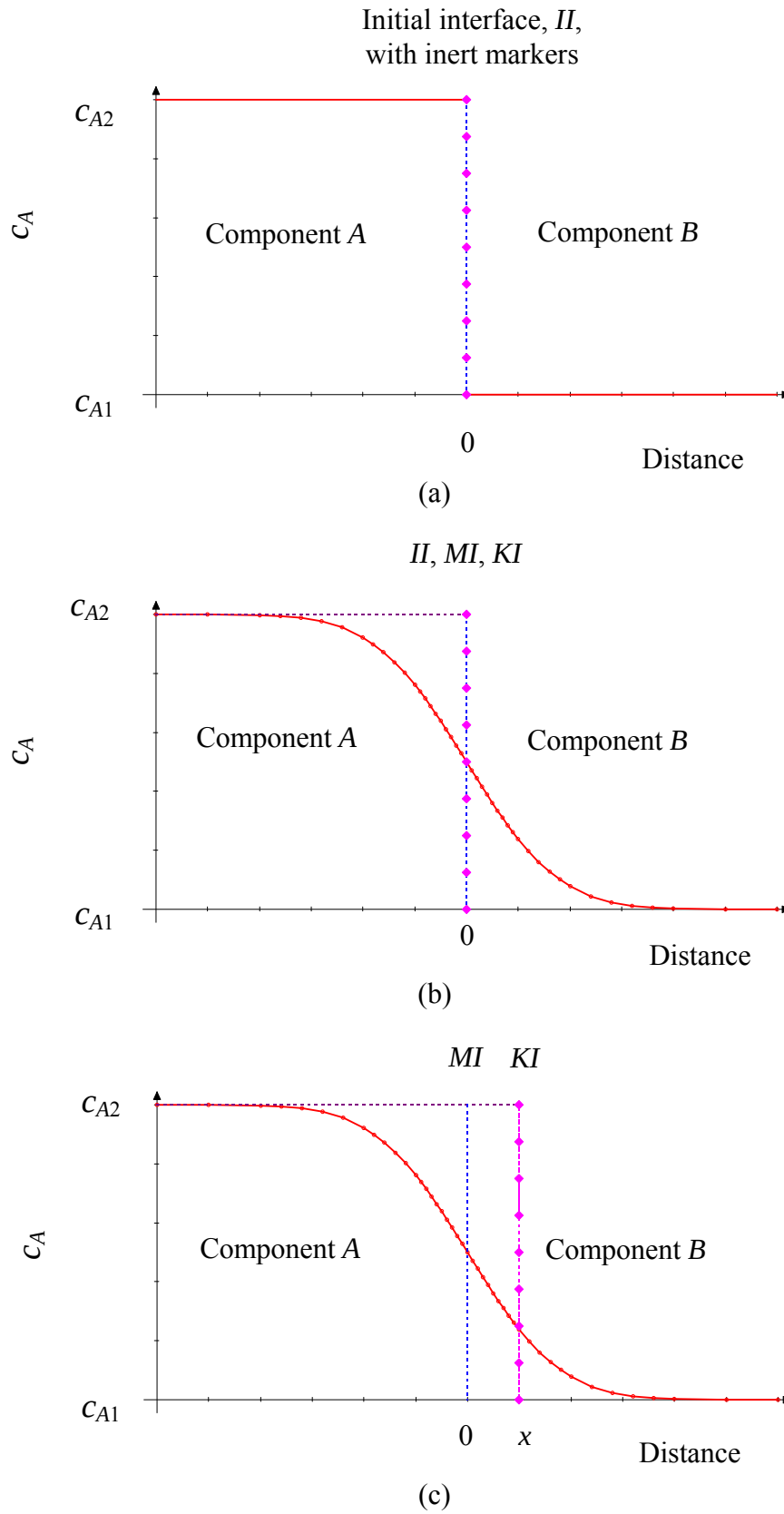


Fig. 1.30. Concentration profile of component A in the A–B diffusion couple in the case of formation of a solid solution. (a) Initial condition, (b) Kirkendall effect is missing, (c) Kirkendall effect is available.

If $D_A = D_B$ (Kirkendall effect is missing), the area confined between Matano's interface (MI), the experimental concentration curve and the horizontal line $c_{A2} = \text{const}$, representing the amount of component B that has diffused in time $t_{\text{equilibrium}} > t > 0$, is at any instant equal to the area confined between MI , the concentration curve and the horizontal line $c_{A1} = \text{const}$, representing the amount of component A that has diffused during the same time, as shown in Fig. 1.30b. With increasing time, the concentration curve gradually flattens but the marked initial interface (Kirkendall interface) always coincides with Matano's interface.

In diffusion couples $A-B$ of finite dimensions, a homogeneous solid solution AB is eventually formed, if the components were taken in the proper amount following from the phase diagram of a given binary system. In the process of its formation, both parts of the concentration curve approach the equilibrium composition of this solution at equal rates. If the initial amounts of the components were improper, the excess component will co-exist with the solid solution at equilibrium.

If $D_A \neq D_B$ (Kirkendall effect is present), the final result is the same (formation of a homogeneous solid solution) but with increasing time the diffusion zone not only flattens but also simultaneously displaces as a whole relative to the marked initial interface or Kirkendall interface, KI . In this case, a certain Kirkendall shift, 0 to x in Fig. 1.30c, arises between the Kirkendall interface, KI , and Matano's interface, MI , so that at any instant, excepting $t = 0$, these do not coincide.

This shift may be considered as a result of either the lattice plastic flow or the movement of excess vacancies arising from the side of a faster diffusing component. In the absence of complicating factors, both approaches produce identical results, enabling to treat the process of diffusion in a two-component solid solution in terms of a single *interdiffusion coefficient*, $D_{\text{interdiffusion}}$ (see, for example, Refs [5, 8, 21, 183-190].

Note that *interdiffusion* is often called *chemical diffusion*. The former term appears to be more suitable because the *interdiffusion* coefficient characterises the rate of *intermixing* of components A and B to form a solid solution in the diffusion zone, whereas the latter may even be misleading since the formation of a solid solution is not a chemical process.

The theoretical treatment of interdiffusion in a two-component binary system appears to have been given for the first time by L.S. Darken in 1948 [206] and since is and probably will be cited or reproduced, because of its fundamental nature, in numerous subsequent papers, handbooks, textbooks and monographs where diffusion processes are considered. In this, it is briefly reproduced, just to show the limits of applicability of Darken's approach to chemical compounds.

According to the second Fick law,

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x} \left(D_A \frac{\partial c_A}{\partial x} - c_A v_K \right), \quad (1.121)$$

$$\frac{\partial c_B}{\partial t} = \frac{\partial}{\partial x} \left(D_B \frac{\partial c_B}{\partial x} - c_B v_K \right), \quad (1.122)$$

where v_K is the velocity of movement of the Kirkendall interface; the concentration, c , of the components A and B is expressed in number (or moles) of particles per cubic metre and the volume of the diffusion couple is assumed to be constant.

Since the total number of the A and B atoms in unit volume, $c = c_A + c_B$, in the course of formation of any substitutional solid solution remains unchanged, the sum of these equations must be zero. Hence,

$$\frac{\partial}{\partial t} (c_A + c_B) = \frac{\partial}{\partial x} \left(D_A \frac{\partial c_A}{\partial x} + D_B \frac{\partial c_B}{\partial x} - c v_K \right) = 0. \quad (1.123)$$

From this equation, it follows

$$D_A \frac{\partial c_A}{\partial x} + D_B \frac{\partial c_B}{\partial x} - c v_K = \text{const.} \quad (1.124)$$

At $x = \pm \infty$, the integration constant is equal to zero. Beyond the diffusion zone, the concentration gradients and the Kirkendall velocity are also assumed to be zero. Then, taking into account that for any solid solution $\partial c_A / \partial x = -(\partial c_B / \partial x)$, one obtains

$$v_K = (D_A - D_B) \frac{\partial c_A}{\partial x} \frac{1}{c} = (D_A - D_B) \frac{\partial N_A}{\partial x}, \quad (1.125)$$

where $N_A = c_A / c$ is the mole fraction of component A in the solid solution.

By substituting this expression for v_K into equation (1.121), the following equation is obtained

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x} \left[(D_A N_B + D_B N_A) \frac{\partial c_A}{\partial x} \right] = \frac{\partial}{\partial x} \left(D_{\text{interdiffusion}} \frac{\partial c_A}{\partial x} \right), \quad (1.126)$$

where

$$D_{\text{interdiffusion}} = D_A N_B + D_B N_A \quad (1.127)$$

is the *interdiffusion* coefficient.

Written in terms of $D_{\text{interdiffusion}}$, equation (1.126) is seen to be similar to equation (1.110), thus permitting to treat the diffusional formation of any binary solid solution in a mathematically consistent manner by a single interdiffusion coefficient.

Note that, from this derivation, it must be clear that Darken's equations are not applicable at all to chemical compounds without any range of homogeneity because for these the total number of the A and B atoms in unit volume, $c = c_A + c_B$, is not simply constant at any instant, as for solid solutions, but in addition is unable, unlike solid solutions, to vary under any circumstances. Any change of their composition is not allowed by the laws of definite and multiple proportions. In such a case, there are merely no theoretical grounds to apply Darken's equations. With chemical compounds, Darken's approach is only applicable to diffusion couples formed by two (terminal) solid solutions of different composition, based on one and the same chemical compound of the type A_pB_q having some range of homogeneity, but this case does not differ essentially from that where a couple is formed by two pure components A and B .

To distinguish between different diffusion coefficients, it appears relevant to introduce more detailed designations, namely, $D_A = D_{A \text{ in } AB}$ and $D_B = D_{B \text{ in } AB}$. Variation of $D_{\text{interdiffusion}}$, $D_{A \text{ in } AB}$ and $D_{B \text{ in } AB}$ with concentration for an extended solid solution is shown schematically in Fig. 1.31. Generally, these dependences are clearly more complicated than simple straight lines.

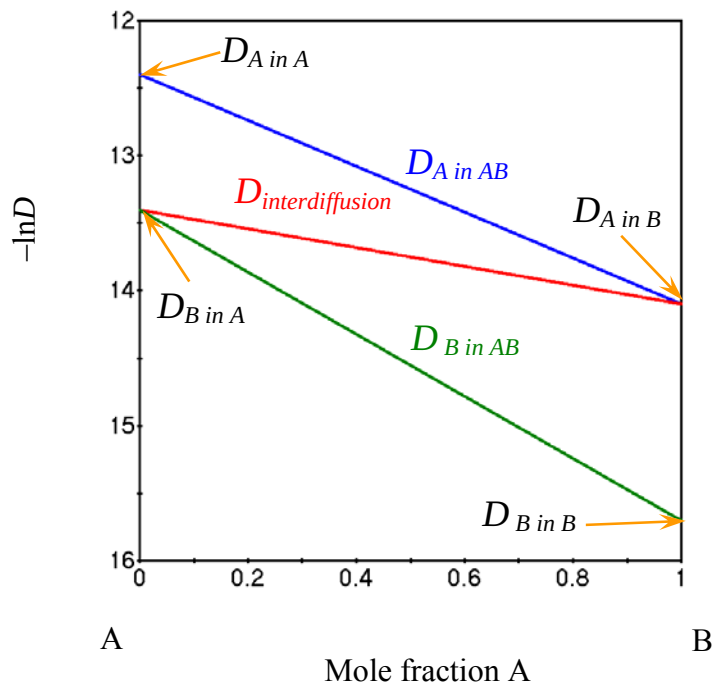


Fig. 1.31. Interconnection among various diffusion coefficients in the case of formation of an extended solid solution between components A and B .

For dilute solutions of A in B ($N_A \rightarrow 0$, $N_B \rightarrow 1$), $D_{\text{interdiffusion}} \approx D_{A \text{ in } AB}$. In the limit $N_A = 0$, $D_{\text{interdiffusion}} = D_{A \text{ in } AB} = D_{A \text{ in } B}$, $D_{A \text{ in } B}$ being the tracer-diffusion coefficient of A in B. Similarly, for dilute solutions of B in A ($N_B \rightarrow 0$, $N_A \rightarrow 1$), $D_{\text{interdiffusion}} \approx D_{B \text{ in } AB}$. In the limit $N_B = 0$, $D_{\text{interdiffusion}} = D_{B \text{ in } AB} = D_{B \text{ in } A}$, $D_{B \text{ in } A}$ being the tracer-diffusion coefficient of B in A. $D_{A \text{ in } A}$ and $D_{B \text{ in } B}$ are tracer-diffusion coefficients of A in A and B in B, respectively.

It should be emphasised that Kirkendall's discovery was probably indeed a discovery since at that time most researchers in the field of diffusion considered the relation $D_A = D_B$ to hold for *any* solid solution of the substitutional type. Kirkendall's experiments showed that in fact this is not always the case.

At the time of E. Kirkendall, his interpretation of the experimental results obtained was severely criticised. Then, as often happens, the situation changed to the contrary. Now, the Kirkendall effect is found even in those cases to which it has no attitude. In particular, it is so in the case of formation of chemical compound layers at the interface of initial substances A and B. However, it does not appear to be justified not only from a scientific viewpoint, as stressed above, but also from a historical one.

That the components of a *chemical compound* generally diffuse in its growing layer at *different* speeds became known far before the appearance of the works of E. Kirkendall [5, 6, 8, 200, 207]. It suffices to remind marker experiments in tarnishing reactions carried out by L.B. Pfeil in 1929-1931 or the investigation of interaction of silver with liquid sulphur performed by C. Wagner in the early 1930s (see Refs [1, 5, 6, 8]). Using inert markers, L.B. Pfeil found cations to be the main diffusing species in the oxidation of many metals. C. Wagner showed silver cations to be the only diffusing species in growing layers of α -Ag₂S. In view of these and numerous other well-known experiments carried out with chemical compounds, there are no historical grounds to attribute revealing the difference in the diffusion coefficients of the components in growing compound layers to E. Kirkendall.

Moreover, it was probably commonplace, at least to chemists, to regard diffusional contributions of the components to the growth process of a *chemical compound layer* as different and not equal. The reasons for this are obvious. Firstly, formation of chemical compounds is typical of the elements strongly differing by their physical and chemical properties including atomic radii and melting points. In view of these differences, equal diffusivities of the components in a growing compound layer could hardly be expected. Secondly, chemical compounds are ordered phases. Though nature often allows some degree of disorder, each of the components of any chemical compound is free to move on its own sublattice. There are therefore no reasonable grounds to assume that the speeds of such a movement are equal for both components of any compound including intermetallics. Note that in this respect solid solutions of the interstitial type are more similar to chemical compounds than to substitutional solid solutions.

In the light of this short consideration, it appears obvious that different diffusional contributions, for example, of nickel and bismuth to the growth process of the NiBi₃ layer (see Section 1.8.3) can by no means be regarded as a manifestation of the Kirkendall effect.

Moreover, in this and similar systems the Kirkendall effect is in principle unobservable since the intermetallic compounds have no range of homogeneity. To reveal this effect, an intermetallic phase must be taken in the form of its two pieces differing by their composition, as shown in Fig. 1.22c. With intermetallics like CoTi, NiAl, ReAl₄, MoIr₃, *etc.*, having relatively wide ranges of homogeneity, such experiments are quite feasible.

1.9.3: Ratio of reaction- and self-diffusion coefficients

Let us now continue an analysis of the interrelation between the reaction- and self-diffusion coefficients. It is obvious that a mere recalculation using equation (1.117) and substituting into its denominator the total content, c_A , of component A in the chemical compound instead of the concentration difference Δc_A , can hardly produce close values, for example, of the diffusion coefficient of aluminium in the growing Fe₂Al₅ layer on the one hand and in the non-growing one on the other because in this case $c_A/\Delta c_A \approx 20$.

Therefore, the primary contribution to the difference observed in practice appears to arise from the relatively small number of vacancies in non-growing compounds. Note that in non-growing stoichiometric compounds these are mainly thermal. Their relative amount is known to be 10^{-1} - 10^{-3} at temperatures close to the melting point of a compound and 10^{-6} - 10^{-11} at room temperature (see, for example, Refs [5, 207]).

Seeing at these very small figures on the one hand and at very large values of the ratio of the reaction- to self-diffusion coefficient, like those presented in Table 1.6, on the other, it only remains to assume that the relation [196]

$$\frac{D}{c_v} = \text{const} \quad (1.128)$$

must hold for the components of a given compound, at least to the first approximation.

Table 1.6. Ratios between the reaction- and self-diffusion coefficients for some oxides with the predominant oxygen diffusion at a temperature of 1000 °C, calculated using the experimental data from the book by P. Kofstad [14]

Oxide	SiO ₂	ZrO ₂	UO ₂
$D_O^{(rd)} = k_1 \text{ (m}^2 \text{ s}^{-1}\text{)}$	1.3×10^{-16}	1.7×10^{-13}	1.6×10^{-12}
$D_O^{(sd)} \text{ (m}^2 \text{ s}^{-1}\text{)}$	1.3×10^{-22}	2.2×10^{-16}	1.6×10^{-15}
$D_O^{(rd)} : D_O^{(sd)}$	1.0×10^6	0.8×10^3	1.0×10^3

When normalised per unit vacancy concentration using the equation

$$\left(\frac{D}{c_v}\right)_{\text{growing compound}} = \left(\frac{D}{c_v}\right)_{\text{non-growing compound}} \quad (1.129)$$

the reaction- and self-diffusion coefficient of any component of a chemical compound may therefore be expected to become close, if not identical, under similar experimental conditions, as it should be from a physical viewpoint.

When applying this relationship, one must be aware of (i) all diffusion mechanisms operative in a non-growing compound, (ii) the concentration of vacancies of a given component in the solid layer of this compound and (iii) the value of its self-diffusion coefficient associated with the vacancy mechanism. In view of the lack of specially planned experiments aimed at obtaining all necessary data for the same compound, including reaction- and self-diffusion coefficients of its components, only evaluations based on the results compiled from several works are at present possible.

The accuracy of such calculations is not too high due mainly to the poor reproducibility of experimental data, especially of values of the self-diffusion coefficients. As the vacancy concentration in a non-growing compound is strongly dependent upon preparation conditions, presence of impurities and thermal pre-treatment of its sample, the data of different authors, though self-consistent and almost always claimed to be accurate to within $\pm 10\%$ or so, are hardly comparable, with the difference in self-diffusion coefficients reaching a few orders of magnitude. In this respect, the situation with reaction-diffusion coefficients (diffusional constants) is much more favourable. Against the background of the huge amount of reaction-produced vacancies, the amount of thermal ones as well as those connected with the non-stoichiometry, if not too large, of a compound is negligibly small and has practically no influence on the layer-growth kinetics. Therefore, for any compound, experimental values of the reaction-diffusion coefficients are in general much more accurate than those of the self-diffusion coefficients.

In the case of non-stoichiometric compounds, the vacancy concentration is mainly associated with their degree of deficiency [14, 197]. When comparing the reaction- and self-diffusion coefficients of iron cations in $\text{Fe}_{3-\delta}\text{O}_4$, satisfactory results can be obtained simply by setting $c_v \approx 3/4$ for the growing $\text{Fe}_{3-\delta}\text{O}_4$ phase and $c_v \approx \delta$ for the non-growing one. The value of δ characterizing the cation deficiency of the crystal structure of this phase is known to be around 1.0×10^{-2} [14, 174, 197], considerably higher than the concentration of thermal vacancies. The $\text{Fe}_{3-\delta}\text{O}_4$ layer grows mainly at the expense of diffusion of iron cations. The value of their reaction-diffusion coefficient determined from the $\text{Fe}_{3-\delta}\text{O}_4$ parabolic-growth kinetics is just two orders of magnitude greater than the value of the self-diffusion coefficient of iron cations in the non-growing compound [174]. It means that equation (1.129) may be expected to produce a fair agreement between the values of reaction- and self-diffusion coefficients.

To accurately verify the proposed relations, further experimental work is badly needed. It must include

- (i) choice of a chemical compound with a sufficiently wide range of homogeneity. If a binary system is multiphase, the compound should be the first to occur and grow at the A–B interface, while the other compounds should be missing (see Chapters 2 and 3). It is desirable that the stoichiometric composition be located near the middle of the range of homogeneity of the compound.
- (ii) separate determination of the reaction-diffusion coefficients (diffusional constants) for both components of the compound from the parabolic layer-growth kinetic relationships, as discussed in Section 1.4.3. Comparable values of these constants are clearly desired.
- (iii) measurement of self-diffusion coefficients of both components in a sample of that compound taken alone using radioactive tracers, with the simultaneous determination of the concentration of the vacancies. Numerous examples of determination of self-diffusion coefficients by the tracer technique can readily be found, for example, in the book of H. Mehrer [188] or in the papers of Y. Nose *et al.* [203], Chs. Herzig *et al.* [208], S.V. Divinski *et al.* [209], I. Stloukal and J. Čermak [210], V. Rothová *et al.* [211] and many other investigators.

The tracer technique is based on the measurement of concentration or activity of a radioactive element, deposited initially onto the surface of a solid sample, in different sections of the sample after its diffusion treatment at a chosen temperature for a given period of time. In the case of an infinitely thin sufficiently powerful (not changing essentially its intensity during the time of the experiment) tracer layer of concentration c_{surface} on a semi-infinite sample, the concentration varies with the depth of penetration, x , and the time, t , as (see, for example, [8, 183, 186, 188, 189])

$$c(x, t) = \frac{c_{\text{surface}}}{2(\pi Dt)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right). \quad (1.130)$$

A typical plot of $c(x, t)$ against x at a fixed time is shown in Fig. 1.32a. If $\ln c(x, t)$ is plotted against x^2 , a straight line is obtained (Fig. 1.32b), from the slope of which the tracer diffusion coefficient D can readily be evaluated. Examples of such plots based on the experimental results of S.V. Divinski *et al.* [209] (diffusion of ^{63}Ni and ^{64}Ni in NiAl) and I. Stloukal and J. Čermak [210] (diffusion of ^{65}Zn in Mg–Al eutectic alloy) for different values of temperature and time of observations are provided in Fig. 1.32c and d.

- (iv) investigation of homogenising the diffusion couple consisting of two samples of the compound with the content of the components equal respectively to the upper and lower limit of its range of homogeneity, as shown in Fig 1.26c. This enables revealing the Kirkendall effect, if sufficiently pronounced, calculation of the integrated diffusion coefficient and establishment of its concentration dependence.

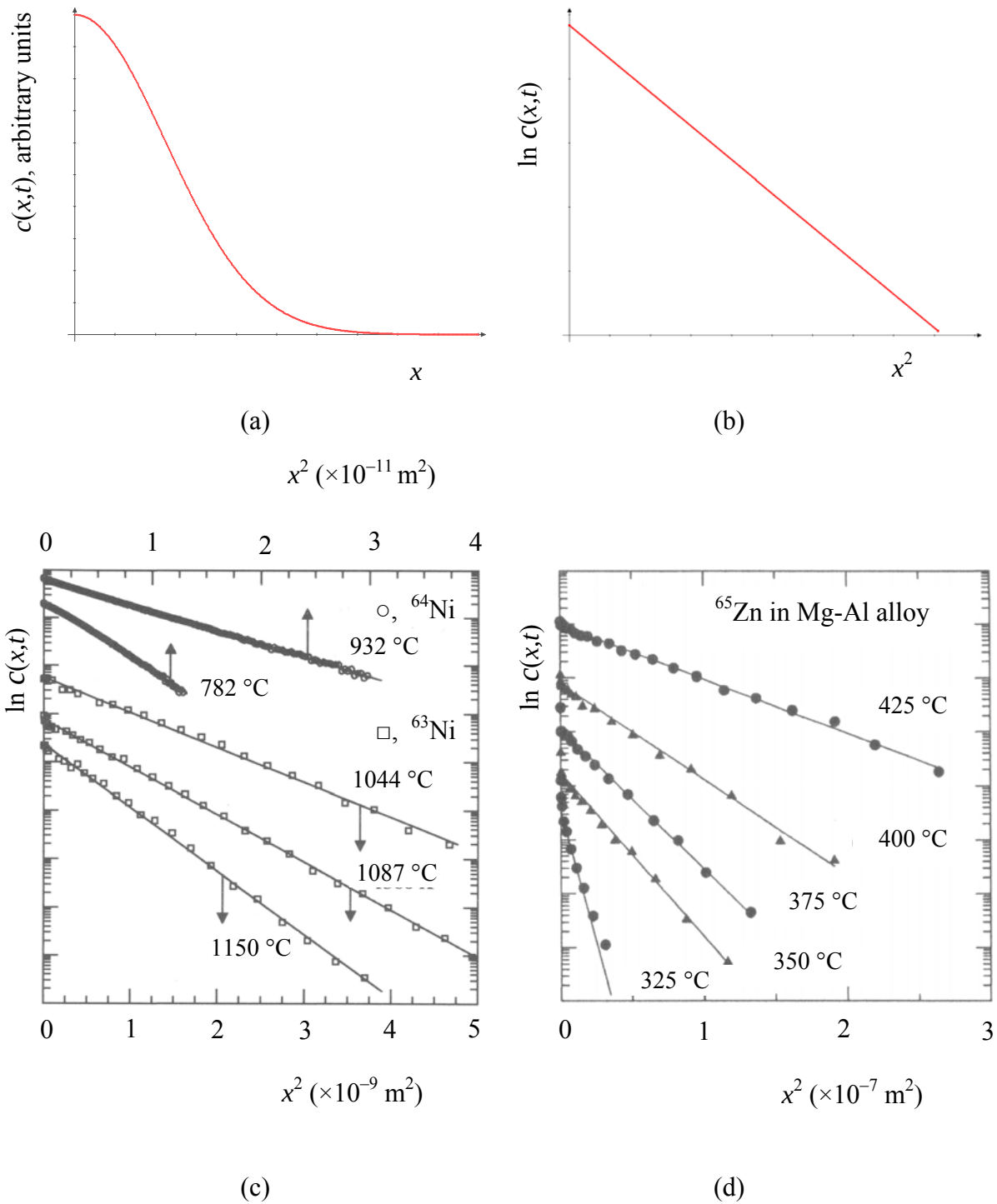


Fig. 1.32. Typical plots of (a) $c(x,t)$ against x and (b) $\ln c(x,t)$ against x^2 , and examples of experimental penetration profiles according to the works of (c) S.V. Divinski *et al.* [209] (diffusion of ^{63}Ni and ^{64}Ni in NiAl) and (d) I. Stloukal and J. Čermak [210] (diffusion of ^{65}Zn in Mg-Al eutectic alloy).

Such data would give an impact to further development of the theory of reaction-diffusion kinetics. This should by no means be considered in isolation from the general theory of diffusion. It is essential to remember, however, that any consideration has certain limitations. Therefore, for example, application of Wagner's concept of the integrated diffusion coefficient and Darken's equations to growing compound layers does not seem substantiated. In the case of compounds without any range of homogeneity, it is physically meaningless and produces *fictitious* diffusion coefficients of little scientific and practical value.

Also, a simple dependence like equation (1.129) can hardly be expected to hold for all chemical compounds without any exceptions under a variety of experimental conditions. The value of the self-diffusion coefficient of any component in the non-growing layer of a chemical compound is known to be strongly affected not only by the amount of vacancies but also by the mode of their formation and interaction with each other, the value of their charge, and other factors (see, for example, Refs [198-200, 212-214]). Perhaps, better results might in some cases be obtained using the equation

$$D(c) = D(c_i) \left(\frac{c}{c_i} \right)^{q_v} \quad (1.131)$$

proposed in the work by T.Y. Tan and U. Gösele [213] (see also a review paper by I. Harrison [214]), where $D(c)$ and $D(c_i)$ are the values of the diffusion coefficient at the vacancy concentrations c and c_i , respectively, while the exponent q_v is equal to the charge of a vacancy or is its function.

It is worth noting that physico-chemical considerations predict the opposite influence of the degree of deficiency of a chemical compound on the values of the reaction- and self-diffusion coefficients. The former is predicted to decrease, while the latter to increase with increasing compound deficiency. This appears to be the case, for example, with oxides like FeO, Fe₃O₄, MnO, CoO, *etc.*, though complicating factors often mask these effects.

Note that certain care must be taken when using the literature data on the diffusion coefficients for estimating the parameters of technological processes which include the reaction-diffusion process as one of the stages (solid-state synthesis of inorganic compounds, making the composite materials or very-large-scale-integrated circuits for microelectronics, joining the dissimilar metals including welding and brazing, protective coating, corrosion, *etc.*). In view of a wide variety of available (self-diffusion, reaction-diffusion, interdiffusion, intrinsic diffusion, tracer diffusion, chemical diffusion and integrated diffusion) coefficients, not always the choice of a relevant value can be made unambiguously.

It should be emphasised that the main kinetic equations presented in this chapter hold for any mechanism of transfer of the atoms across the bulk of a growing compound layer since the basic assumption "the longer the diffusion path, the greater the time to overcome it" is clearly always fulfilled. Knowledge of the details of this mechanism is only important when

establishing a relationship between the transport properties of the layer of a given phase and the diffusion characteristics of its components.

1.10: Single compound layer: comparison of diffusional and physico-chemical approaches

Most essential distinctions between the conventional diffusional approach and the proposed physico-chemical one in the case of solid-state formation of one compound layer are briefly summarised in Table 1.7. A thorough analysis of available experimental and theoretical data provides evidence that the latter is generally more adequate.

For the sake of further visual comparison of the layer-growth mechanism in the case of one, two and multiple compound layers, it would be helpful to remember a schematic diagram of Fig. 1.33.

1.11: Single compound layer: short conclusions

1. Solid-state growth of the layer of any chemical compound A_pB_q between two mutually insoluble elementary substances A and B is due to two parallel partial chemical reactions proceeding at its interfaces, each of which takes place in two consecutive, alternate steps:

- (i) diffusion of atoms of a given component across the bulk of the layer,
- (ii) chemical transformations with the participation of these atoms and the surface atoms of another component.

2. Both reactions as well as the diffusion fluxes of the components across the bulk of a growing compound layer are assumed to be independent of each other.

3. The layer thickness-time kinetic dependence is in general described by a linear-parabolic equation. Its initial region is close to a straight line, while then there is a gradual transition to a parabola. The higher the temperature, the narrower is the region of linear growth.

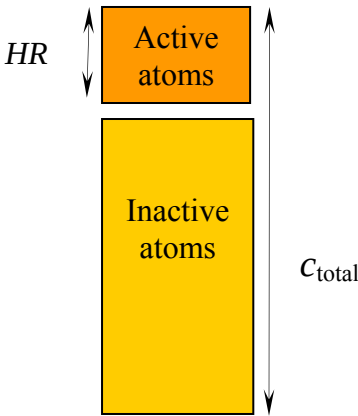
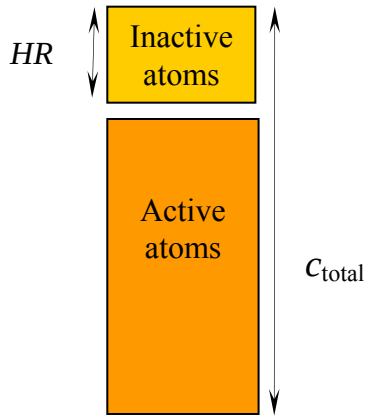
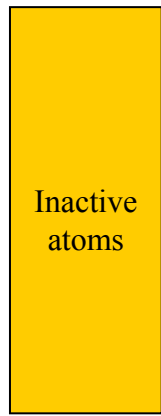
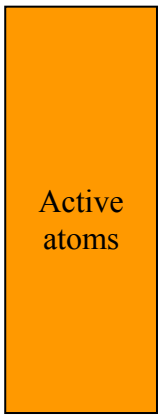
4. There are two critical values, $x_{1/2}^{(A)}$ and $x_{1/2}^{(B)}$, of the layer thickness, which divide this dependence into the reaction controlled and diffusion controlled regions with regard to components A and B , respectively.

5. For any chemical compound A_pB_q , the reaction-diffusion coefficient and the self-diffusion coefficient of a given component (A or B) are in general different, the former being much greater than the latter. The difference in their values may reach several orders of magnitude. After normalising to the same vacancy concentration, these become at least close, if not identical, provided that the mechanism of diffusion is of the vacancy type in both the growing and non-growing layer of that compound.

6. Different diffusional contributions of the components of a chemical compound to the growth process of its layer at the interface between phases A and B should not generally be

regarded as a manifestation or result of the Kirkendall effect, the essence of which consists in different diffusivities of the components of a substitutional solid solution.

Table 1.7. Comparison of diffusional and physico-chemical approaches to compound layer-growth kinetics

Diffusional approach	Physico-chemical approach
1. One step: diffusion. 2. Layer-growth kinetics are parabolic. 3. Layer-growth rate is proportional to the width of the range of homogeneity, HR, of a given chemical compound. 4. Only a small portion of atoms ($HR \ll c_{\text{total}}$) of a compound is active in the layer-growth process.	1. Two alternate steps: diffusion and reaction. 2. Layer-growth kinetics are linear-parabolic. 3. Layer-growth rate depends very slightly upon the width of the range of homogeneity of a given chemical compound. 4. All available atoms of a compound are active in the layer-growth process.
 $HR \neq 0$, D is too high	 $HR \neq 0$, $D \approx k_1$
 $HR = 0$, D is infinity	 $HR = 0$, $D = k_1$
5. The <i>greater</i> the amount of native structure defects (vacancies) of a compound, the <i>greater</i> will be the rate of growth of its layer at the interface of initial substances.	5. The <i>greater</i> the amount of native structure defects (vacancies) of a compound, the <i>less</i> will be the rate of growth of its layer at the interface of initial substances.

One compound layer: reaction or diffusion control

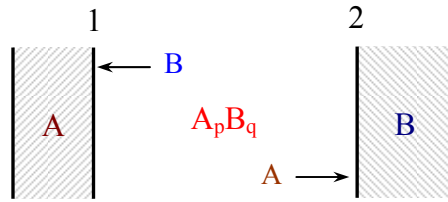


Fig. 1.33. Schematic diagram to illustrate the mechanism of growth of one compound layer.

2: Growth kinetics of two compound layers between elementary substances A and B

Growth kinetics of two chemical compound layers in a binary heterogeneous system have been treated theoretically, from a diffusional viewpoint, by V.I. Arkharov [1, 48], K.P. Gurov *et al.* [22], B. Schröder and V. Leute [54], A.T. Fromhold and N. Sato [55], G.-X. Li and G.W. Powell [57], A.M. Gusak *et al.* [26] and other investigators. Purely diffusional considerations predict that (i) both layers must occur simultaneously and (ii) the thickness of each of them as well as their total thickness should increase parabolically with passing time.

However, available experimental data provide evidence that this is not always the case. In fact, in many binary systems the layer growth is neither simultaneous, nor parabolic. Instead, a variety of kinetic laws (linear, asymptotic, parabolic, *etc.*) are observed experimentally. Only a certain portion of the layer thickness-time kinetic dependence in the region of long reaction times and hence large layer thicknesses is close to a parabola.

Moreover, one of the layers is often missing from the $A-B$ reaction couple over a long period of time, while the other grows from the very beginning of interaction of initial substances. This is the case, for example, with the NiSi and PdAl₃ intermetallic compound layers in the Ni–Si and Pd–Al reaction couples, respectively, the first occurred layers being those of Ni₂Si and Pd₂Al₃ [27, 103]. At 20 °C, a single layer of the Cu₆Sn₅ intermetallic compound is known to grow between copper and tin [66], while above 150 °C both Cu₃Sn and Cu₆Sn₅ were observed by M. Oh and M.R. Notis [215] and S. Däbritz *et al.* [216] to occur simultaneously in the same time range, with growth kinetics of the Cu₆Sn₅ layer not always obeying a parabolic law.

There are two compounds of the type $MeAg$ and Me_2Ag ($Me = Zr$ or Hf) on appropriate equilibrium phase diagrams of the Zr–Ag and Hf–Ag binary systems [217]. However, according to O. Taguchi and Y. Iijima, the Zr₂Ag and ZrAg layers grow between zirconium and silver simultaneously [218], whereas the Hf₂Ag layer occurs in the Hf–Ag couple after an incubation period reaching 432 ks at 900 °C [219]. Below about 880 °C, it does not form at all. Quite different behavior of chemical compounds can thus be expected even in very similar binary systems like these.

Y. Fujiwara *et al.* [78] found that the thickness of the NiSb layer in the Ni–Sb reaction couple reaches a maximum value within about 15 minutes and then remains almost unchanged, whereas the Ni₅Sb₂ layer continues to grow (annealing times were up to 960 min). The maximum thickness of the NiSb layer was 2 μm at 460 °C and 6 μm at 600 °C. The same applies to intermetallic layers based on the Fe₂Al₅ and FeAl₃ compounds, which

are formed at the interface between a commercial 18Cr–10Ni stainless steel and aluminium saturated with its components at 700 °C [220, 221]. When studying the process of simultaneous formation of the Mo_5Si_3 and MoSi_2 layers between molybdenum and silicon at 1200–1350 °C, V.I. Zmiy and A.S. Seryugina [222] found growth kinetics of the Mo_5Si_3 layer to be linear, whereas the thickness of the MoSi_2 layer increased linearly during the first 40 minutes and then parabolically in the 1–20 h time range.

Any unambiguous interpretation of these well-known experimental observations in the framework of the diffusional theory is hardly possible. To overcome considerable difficulties arisen, use is usually made of different additional (not very convincing) assumptions and suggestions. In contrast, from a physico-chemical viewpoint, the phenomena and dependences observed in practice seem to be quite natural and easily explainable [146, 148, 151, 153, 223]. These can therefore readily be expected to hold in binary systems of whatever chemical nature.

It should be noted that a theoretical approach close to, but not identical with, the physico-chemical one was proposed by U. Gösele and K.N. Tu [27] (see also Ref. [32]). It is worth mentioning, just as a curious fact, that both approaches were described in the papers published in the same year 1982 (see Refs [27] and [146]). Analysis of various stages of the growth process of two compound layers can be found in works by F.M. d'Heurle and P. Gas [29], W.C. Johnson and G. Martin [31], J. Philibert [35, 36], A.M. Gusak *et al.* [26] and other investigators.

To derive a system of two differential equations describing the rate of formation of two compound layers at the A – B interface, it is necessary:

(i) to write down equations of partial chemical reactions taking place at layer interfaces with adjacent phases (there are four such reactions, two for each layer);

(ii) to find out relations between the changes in thicknesses of the layers due to those reactions;

(iii) to establish mathematical equations relating the differential time, dt , to the differential changes, dx and dy , of the layer thicknesses, using the postulate about the summation of the time of diffusion and the time of chemical transformations;

(iv) to write down the required general system of differential equations, taking into account the principle of independency of the elementary acts of chemical reactions.

2.1: Partial chemical reactions at layer interfaces

A schematic diagram illustrating the growth process of the layers of two chemical compounds A_pB_q and A_rB_s , with p , q , r and s being positive numbers, at the A – B interface is shown in Fig. 2.1. Note that the lines showing the concentration profiles of components A and B in the phases involved into the interaction are parallel to the distance axis since (i) formation of the layers of chemical compounds which have no range of homogeneity is considered and (ii) initial substances are assumed to be mutually insoluble.

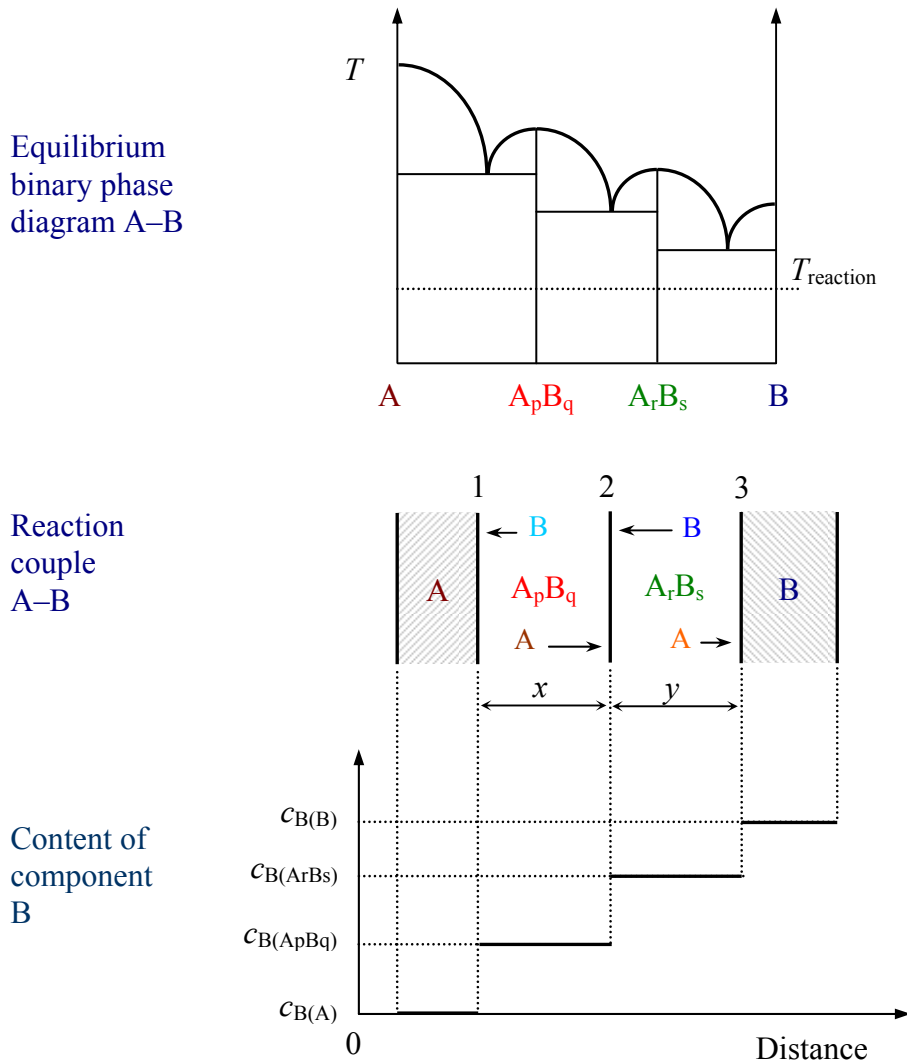


Fig. 2.1. Schematic diagram to illustrate the growth process of the layers of two chemical compounds A_pB_q and A_rB_s at the interface between mutually insoluble elementary substances A and B .

In such a case, immediate application of Fick's laws is clearly impossible. Therefore, it is not surprising that the smooth concentration distributions characteristic of solid solutions are usually drawn by most theoreticians, while the results obtained are then applied to chemical compounds. Many of them, especially physicists and metallurgists, even do not employ the term *chemical compound*, giving preference to analysing the formation of a *new phase*. No difference is thus made between solid solutions and chemical compounds.

Although in many binary systems there is no clear-cut distinction between a chemical compound and a solid solution, it is nonetheless necessary, as already pointed in Chapter 1, to distinguish between them on the basis of (i) constancy or variability of their composition and (ii) degree of ordering their crystal lattices. Also, usually the chemical compound has a

crystal lattice different from crystal lattices of parent phases A and B , while the solid solution has either a similar one or the same. It would be a rough mistake to ignore these differences. Otherwise, as will be seen later, far-reaching misleading conclusions are likely to be drawn.

Whether a particular phase is a chemical compound or a solid solution can hardly be subject to any doubt in obvious cases such as in the Ni–Bi binary system with the intermetallics NiBi (homogeneity range $HR \leq 0.3$ at.%) and NiBi₃ (stoichiometric phase) [148] or in the Ti–Al binary system with the intermetallics Ti₃Al ($HR \approx 12$ at.% at 600 °C), TiAl ($HR \approx 7$ at.%), TiAl₂ ($HR \leq 1$ at.%) and TiAl₃ (stoichiometric phase) [142, 145, 193].

Definitely, NiBi, NiBi₃, TiAl₂ and TiAl₃ are chemical compounds, not differing, for example, from Bi₂O₃ or TiO₂. Phases like Ti₃Al or TiAl can, of course, be treated ambiguously. This point will be analysed once again in the next chapter.

Also, formation of a solid solution is often considered to be a pre-requisite for the occurrence of a chemical compound layer, with the latter being a result of supersaturation of the former. In fact, however, these are two concurrent, competing processes, if both solid solutions and chemical compounds are present on the phase diagram of a binary system. In any reaction couple A – B given to itself under conditions of constant temperature and pressure or tending to its equilibrium state from below (from lower to higher temperatures and pressures), no supersaturation is possible.

Clearly, any direct chemical reaction between elementary substances A and B ceases after the formation of compound layers A_pB_q and A_rB_s a few crystal-lattice units thick, which separate the reacting phases from each other. Subsequently, four partial chemical reactions take place at the layer interfaces. These are as follows:

Layer	Interface	Partial chemical reaction	
A_pB_q	1	$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q,$	(2.1 ₁)
	2	$(sp - qr)A_{\text{dif}} + qA_rB_s = sA_pB_q,$	(2.1 ₂)
A_rB_s	2	$(sp - qr)B_{\text{dif}} + rA_pB_q = pA_rB_s,$	(2.2 ₁)
	3	$rA_{\text{dif}} + sB_{\text{surf}} = A_rB_s.$	(2.2 ₂)

The A_pB_q compound layer grows at the expense of diffusion of the B atoms to interface 1 where these atoms then enter into reaction (2.1₁) with the surface A atoms. It is seen that the same partial chemical reaction takes place at the A – A_pB_q interface in the A – A_pB_q – B (see Section 1.2) and A – A_pB_q – A_rB_s – B heterogeneous systems. The difference between these two systems is that in the former the B atoms which have crossed only the bulk of the A_pB_q layer enter into the chemical reaction at interface 1, while in the latter the B atoms have to diffuse across the bulks of both layers A_rB_s and A_pB_q before entering into this reaction because the only source of the B atoms in both systems is in fact substance B .

The thickness of the A_pB_q layer also increases at the expense of diffusion of the A atoms to interface 2 and their subsequent partial chemical reaction with the A_rB_s compound in accordance with equation (2.1₂). Thus, another difference between the $A-A_pB_q-B$ and $A-A_pB_q-A_rB_s-B$ systems is that in the former an increase in thickness of the A_pB_q layer at interface 2 is a result of reaction of the A atoms diffusing across its bulk with phase B , while in the latter with the A_rB_s compound.

Growth of the A_rB_s compound layer is due to both partial chemical reaction (2.2₁) taking place at interface 2 between the diffusing B atoms and the A_pB_q compound and partial chemical reaction (2.2₂) at interface 3 between the diffusing A atoms and the surface B atoms. It must be clear that only the diffusing A atoms which have not entered earlier into reaction (2.1₂) at interface 2 can then enter into reaction (2.2₂) at interface 3.

Note that no reactions proceed within the bulks of both compound layers. Layer bulks only serve as a transport medium for diffusing atoms. Chemical transformations take place exclusively at the phase interfaces that are regarded as transition regions between the interacting phases, whose widths are not very different from the lattice spacing of those phases.

The A_pB_q chemical compound is seen to be a product of reactions (2.1₁) and (2.1₂). At the same time, it is also a reactant of reaction (2.2₁). The A_rB_s chemical compound is a product of reactions (2.2₁) and (2.2₂) and a reactant of reaction (2.1₂). Thus, each of the two compound layers grows not only at the expense of the A and B atoms diffusing from initial phases A and B , but also partly at the expense of an adjacent compound layer [1, 48]. Hence, the change in thickness of the A_pB_q layer is a result of (i) growth due to reactions (2.1₁) and (2.1₂) and (ii) consumption during the formation of the A_rB_s chemical compound by reaction (2.2₁). Similarly, the A_rB_s layer grows in the course of reactions (2.2₁) and (2.2₂) and is consumed by reaction (2.1₂).

2.2: A system of differential equations describing the rates of formation of two compound layers

During an infinitesimal period of time, dt , the thickness of the A_pB_q layer increases by dx_{B1} at interface 1 as a result of reaction (2.1₁) and by dx_{A2} at interface 2 as a result of reaction (2.1₂), as shown in Fig. 2.2. At the same time, the thickness of the A_rB_s layer increases by dy_{B2} at interface 2 and by dy_{A3} at interface 3 due to reactions (2.2₁) and (2.2₂), respectively.

To establish differential equations relating dt to the increases, dx_{B1} , dx_{A2} , dy_{B2} and dy_{A3} , in thicknesses of the A_pB_q and A_rB_s layers, use is again made of the postulate about the summation of the time of diffusion of the A or B atoms and the time of subsequent chemical transformations for each of four partial chemical reactions taking place at phase interfaces 1, 2 and 3. It yields

$$dt = dt_{\text{dif}}^{(B \rightarrow A_pB_q)} + dt_{\text{chem}}^{(B \rightarrow A_pB_q)}, \quad (2.3_1)$$

$$dt = dt_{\text{dif}}^{(A \rightarrow A_p B_q)} + dt_{\text{chem}}^{(A \rightarrow A_p B_q)}, \quad (2.3_2)$$

$$dt = dt_{\text{dif}}^{(B \rightarrow A_r B_s)} + dt_{\text{chem}}^{(B \rightarrow A_r B_s)}, \quad (2.4_1)$$

$$dt = dt_{\text{dif}}^{(A \rightarrow A_r B_s)} + dt_{\text{chem}}^{(A \rightarrow A_r B_s)}, \quad (2.4_2)$$

where the superscripts of the type $(B \rightarrow A_p B_q)$ in equation (2.3₁) indicate that such a time is required for the diffusion of the B atoms across the bulk of the $A_p B_q$ layer (first term) or for subsequent chemical transformations with their participation (second term).

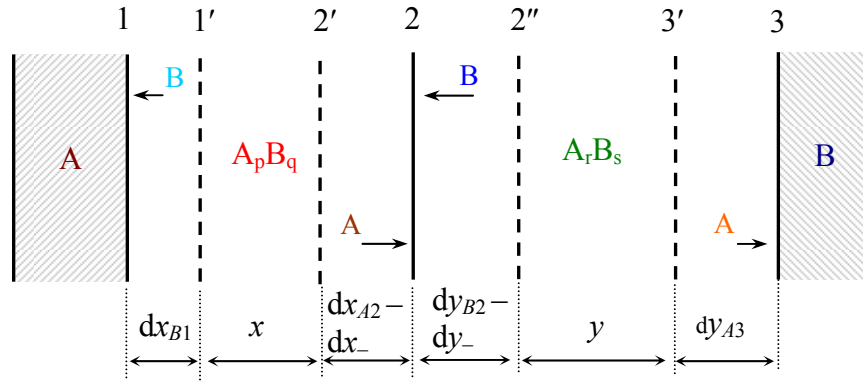


Fig. 2.2. Schematic diagram to illustrate the changes, dx_{B1} , dx_{A2} , dy_{B2} , dy_{A3} , dx_{-} and dy_{-} , in thicknesses of the $A_p B_q$ and $A_r B_s$ compound layers during the time dt in the general case where both layers grow at the expense of diffusion of both components across their bulks.

Like the case of formation of the layer of a single chemical compound, it is assumed that the time of diffusion is directly proportional to both the increase of the thickness of a given compound layer and its total thickness, whereas the time of chemical transformations is directly proportional to the increase of the thickness of the layer and is quite independent of its total thickness (see Section 1.3). Hence,

$$dt = \left(\frac{x}{k_{1B1}} + \frac{1}{k_{0B1}} \right) dx_{B1}, \quad (2.5_1)$$

$$dt = \left(\frac{x}{k'_{1A2}} + \frac{1}{k'_{0A2}} \right) dx_{A2}, \quad (2.5_2)$$

$$dt = \left(\frac{y}{k'_{1B2}} + \frac{1}{k'_{0B2}} \right) dy_{B2}, \quad (2.6_1)$$

$$dt = \left(\frac{y}{k_{1A3}} + \frac{1}{k_{0A3}} \right) dy_{A3}, \quad (2.6_2)$$

where all k_0 are chemical constants, while all k_1 are physical (diffusional) constants.

The designations with strokes were only introduced to avoid confusion with the results of Chapter 1. Partial chemical reactions at interface 1 are the same in the $A-A_pB_q-B$ and $A-A_pB_q-A_rB_s-B$ systems, whereas at interface 2 these are different. Therefore, equations (1.53) and (2.5₁) are identical, while equations (1.68) and (2.5₂) are different.

Note that not only k'_{0A2} is not equal to k_{0A2} , but also k'_{1A2} is not equal to k_{1A2} , although the diffusion coefficient of the A atoms across the bulk of the A_pB_q layer does not depend on whether this layer borders phase B or A_rB_s . However, different amounts of the diffusing A atoms are necessary to form one molecule of the A_pB_q chemical compound by reactions (1.49) and (2.1₂). In Section 1.4 k_{1A2} was used to denote the physical (diffusional) constant relating to reaction (1.2). From equations (1.49) and (2.1₂), it follows

$$k'_{1A2} = \frac{sp}{sp - qr} k_{1A2}. \quad (2.7)$$

Relations between different constants will be considered in greater detail, when comparing the growth rates of the same chemical compound layer in various reaction couples of a multiphase binary system (Chapter 4).

On the basis of the principle of independency of the rates of elementary acts of chemical reactions, equations (2.5₁)-(2.6₂) are assumed to be independent of each other. Therefore, the increases of layer thicknesses can explicitly be expressed from these equations as follows:

$$dx_{B1} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} dt, \quad (2.8_1)$$

$$dx_{A2} = \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}} dt, \quad (2.8_2)$$

$$dy_{B2} = \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}} dt, \quad (2.9_1)$$

$$dy_{A3} = \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}} dt. \quad (2.9_2)$$

The increase in thickness of the A_pB_q layer during the time dt is

$$dx_+ = dx_{B1} + dx_{A2}, \quad (2.10)$$

while that of the A_rB_s layer is

$$dy_+ = dy_{B2} + dy_{A3}. \quad (2.11)$$

During the same period of time, dt , the thickness of the A_pB_q layer decreases by dx_- due to partial chemical reaction (2.2₁). The value of this decrease can easily be found using equation (2.2₁). Calculations are like conventional ones generally accepted for chemical reactions. The only difference is that the diffusing component must be written in equations (1.1), (1.2), (2.1₁)-(2.2₂) in that form (atom, ion, *etc.*) in which it diffuses across the bulks of growing compound layers and then reacts at an appropriate phase interface and not in the form in which it exists in an initial substance. Consider a few examples.

The process of growth of the Cu_3Sn and Cu_6Sn_5 intermetallic layers in the $\text{Cu-Cu}_3\text{Sn-Cu}_6\text{Sn}_5\text{-Sn}$ system can be represented as follows:

Layer	Interface	Partial chemical reaction	
Cu_3Sn	$\text{Cu-Cu}_3\text{Sn}$	$\text{Sn}_{\text{dif}} + 3\text{Cu}_{\text{surf}} = \text{Cu}_3\text{Sn},$	(2.12 ₁)
	$\text{Cu}_3\text{Sn-Cu}_6\text{Sn}_5$	$9\text{Cu}_{\text{dif}} + \text{Cu}_6\text{Sn}_5 = 5\text{Cu}_3\text{Sn},$	(2.12 ₂)
Cu_6Sn_5	$\text{Cu}_6\text{Sn}_5\text{-Cu}_3\text{Sn}$	$3\text{Sn}_{\text{dif}} + 2\text{Cu}_3\text{Sn} = \text{Cu}_6\text{Sn}_5,$	(2.13 ₁)
	$\text{Cu}_6\text{Sn}_5\text{-Sn}$	$6\text{Cu}_{\text{dif}} + 5\text{Sn}_{\text{surf}} = \text{Cu}_6\text{Sn}_5.$	(2.13 ₂)

In this obvious case, there is no ambiguity in writing partial chemical reactions. It can only be noted that the copper and tin ions, not atoms, are most likely to diffuse across the growing Cu_3Sn and Cu_6Sn_5 intermetallic layers, whereas electrons simply accompany them, so that the final result is such, as if the atoms were the diffusing species. For formal kinetic considerations, such details of the mechanism of atomic transfer are clearly of no importance.

A somewhat different situation arises in the case of formation of the TiO and TiO_2 layers in the $\text{Ti-TiO-TiO}_2\text{-O}_2$ reaction system. Most probably, oxygen and titanium diffuse across layer bulks in the form of ions or atoms, whereas in the initial gaseous phase oxygen exists in the form of molecules O_2 . Therefore, the partial chemical reactions taking place at phase interfaces must be written as follows:

Layer	Interface	Partial chemical reaction	
TiO	Ti–TiO	$O_{\text{dif}} + Ti_{\text{surf}} = TiO,$	(2.14 ₁)
	TiO–TiO ₂	$Ti_{\text{dif}} + TiO_2 = 2TiO,$	(2.14 ₂)
TiO ₂	TiO ₂ –TiO	$O_{\text{dif}} + TiO = TiO_2,$	(2.15 ₁)
	TiO ₂ –O ₂ (gas)	$Ti_{\text{dif}} + 2O_{\text{surf}} = TiO_2,$	(2.15 ₂)

but not as



and



The last two reactions may proceed if very porous layers are formed, not preventing the Ti and TiO surfaces from the direct oxygen attack. However, if the oxide layers are compact and have no macroscopic defects, oxygen can only diffuse across their bulks after its molecules have dissociated into atoms or ions onto the surface of the TiO₂ layer bordering the gaseous phase. Clearly, the time of dissociation of the O₂ molecules into atoms is independent of the thickness of the TiO₂ layer. Therefore, it must be included into the value of the chemical constant corresponding to partial chemical reaction (2.15₂).

If initial phases are chemical compounds, not elementary substances, the growth of the layers of two new chemical compounds in a quasi-binary system takes place as a result of counter diffusion of the same-type ions or atoms of smaller size. The common ion usually does not take active part in the layer-growth process. This does not mean, however, that its presence exerts no influence on the mechanism of formation of the layers. The Rb₂AgI₃ and RbAg₄J₅ layers are known to form in the RbI–AgI system [54, 224, 225]. Their formation is due to the following partial chemical reactions:

Layer	Interface	Partial chemical reaction	
Rb ₂ AgI ₃	RbI–Rb ₂ AgI ₃	$Ag^+ + 3RbI = Rb_2AgI_3 + Rb^+,$	(2.18 ₁)
	Rb ₂ AgI ₃ –RbAg ₄ J ₅	$7Rb^+ + 3RbAg_4J_5 = 5Rb_2AgI_3 + 7Ag^+,$	(2.18 ₂)
RbAg ₄ J ₅	RbAg ₄ J ₅ –Rb ₂ AgI ₃	$7Ag^+ + 5Rb_2AgI_3 = 3RbAg_4J_5 + 7Rb^+,$	(2.19 ₁)
	RbAg ₄ J ₅ –AgJ	$Rb^+ + 5AgJ = RbAg_4J_5 + Ag^+.$	(2.19 ₂)

It can easily be seen that the total yield of partial chemical reactions (2.18₂) and (2.19₁) is zero. This is caused by the presence of the third, low-mobile component (iodine anions I[–]). Because of their presence, rubidium and silver cations are unable to move in the lattices of the growing Rb₂AgI₃ and RbAg₄J₅ compounds independently of each other. The fluxes of

these cations should necessarily be balanced since partial chemical reactions (2.18₁) and (2.19₂) are mutually dependent. In this respect, the system under consideration and other similar systems differ from binary ones in which all four partial chemical reactions taking place at layer interfaces are independent of each other unless any diffusional constraints arise (see the next chapter).

Thus, the increase in thickness of the Rb₂AgI₃ layer is due to partial chemical reaction (2.18₁), while that of the RbAg₄J₅ layer to partial chemical reaction (2.19₂). The overall reaction is the sum of these two partial chemical reactions:



Formally, the final result is such, as if the initial phases RbI and AgI reacted immediately, although they have no direct contact. Similar reactions are likely to take place during the interaction of metal oxides and other chemical compounds [10, 15, 16, 226].

Let us now return to analysing the process of growth of the A_pB_q and A_rB_s compound layers at the interface between elementary substances A and B . From equation (2.2₁), it follows that the ratio of the mass of the A_pB_q compound entering into partial chemical reaction (2.2₁) to the mass of the A_rB_s compound formed as a result of this reaction is equal to the ratio of the molecular masses of the compounds A_pB_q and A_rB_s with the factors r and p , respectively:

$$\frac{m_{A_pB_q}}{m_{A_rB_s}} = \frac{rM_{A_pB_q}}{pM_{A_rB_s}}, \quad (2.21)$$

where m is the mass and M is the molecular mass of an appropriate compound. This is a conventional chemical relation.

The mass is equal to the product of the density, ρ , and the volume which in turn is the product of the surface area of the phase interface and the thickness of the growing layer. Since the surface area of the interfaces between all the reacting phases is assumed to be the same and constant during the whole course of layer growth, then

$$\frac{\rho_{A_pB_q} dx_-}{\rho_{A_rB_s} dy_{B2}} = \frac{rM_{A_pB_q}}{pM_{A_rB_s}}. \quad (2.22)$$

Taking into account that the quotient of dividing the molecular mass by the density of a given compound is its molar volume, V , one obtains

$$dx_- = \frac{rg}{p} dy_{B2}, \quad (2.23)$$

where g stands for the ratio of the molar volumes of chemical compounds A_pB_q and A_rB_s :
 $g = V_{A_pB_q} / V_{A_rB_s}$.

Similarly, from equation (2.12), one finds

$$dy_- = \frac{q}{sg} dx_{A2}. \quad (2.24)$$

Equations (2.23) and (2.24) take account of the mutual consumption of the A_pB_q and A_rB_s layers during their simultaneous formation.

The total change in thickness of the A_pB_q layer during the time dt is equal to the difference between the right-hand parts of equations (2.10) and (2.23):

$$dx = dx_{B1} + dx_{A2} - dx_-. \quad (2.25)$$

For the A_rB_s layer, this value is (see equations (2.11) and (2.24))

$$dy = dy_{B2} + dy_{A3} - dy_-. \quad (2.26)$$

Substituting the expressions (2.8₁)-(2.9₂) for the increases in thicknesses of the A_pB_q and A_rB_s compound layers into these equations yields the required general system of two differential equations describing their growth rates at the A - B interface:

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}} - \frac{rg}{p} \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}}, \quad (2.27_1)$$

$$\frac{dy}{dt} = \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}} + \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}} - \frac{q}{sg} \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}}. \quad (2.27_2)$$

The system of equations (2.27) belongs to the so-called autonomous systems that have been analysed in detail, for example, in Refs 227 and 228. Note, however, that, to avoid misleading conclusions concerning layer-growth kinetics, an approach to its solution should by no means be purely mathematical. Namely, besides the initial conditions $x = 0$ and $y = 0$ at $t = 0$, the existence of the critical values of the thicknesses of the A_pB_q and A_rB_s compound layers must necessarily be taken into account. These are as follows (see equations (1.17) and (1.22) in Chapter 1):

$$x_{1/2}^{(B)} = \frac{k_{1B1}}{k_{0B1}}, \quad (2.28_1)$$

$$x_{1/2}^{(A)} = \frac{k'_{1A2}}{k'_{0A2}}, \quad (2.28_2)$$

$$y_{1/2}^{(B)} = \frac{k'_{1B2}}{k'_{0B2}}, \quad (2.29_1)$$

$$y_{1/2}^{(A)} = \frac{k_{1A3}}{k_{0A3}}. \quad (2.29_2)$$

They divide the $x - t$ and $y - t$ kinetic dependences into the reaction controlled and diffusion controlled regions with regard to components A and B (in the theoretical definition given in Section 1.3.2 of Chapter 1).

It should be emphasised that, according to the designations accepted throughout the book, the plus sign only indicates an increase of the thickness of an appropriate compound layer, while the minus sign indicates its decrease and not the direction of movement of the interfaces of this layer with adjacent phases relative to some (laboratory) frame of reference. Therefore, the quantities, for example, dx_{B1} and dx_{A2} were taken with the plus sign, although interfaces 1 and 2 (see Fig. 2.1) move in the opposite direction during the course of reactions (2.1₁) and (2.1₂).

Clearly, in such a case x and y correspond to the experimentally measured values in thicknesses of the A_pB_q and A_rB_s compound layers. This form of writing mathematical equations also makes it possible to easily take account of a change in volume of the system resulting from the formation of chemical compounds, which in many cases is too considerable to be neglected without a noticeable error.

The system of equations (2.27) is seen to be rather complicated. Its solution, if obtainable at all in quadratures, must probably be even more complicated. However, in experiments certain conditions which enable the initial equations to be simplified are usually fulfilled. Consider limiting cases of particular interest from both theoretical and practical view-points [146, 148, 151-155]. The process of growth of the A_pB_q and A_rB_s layers will be analysed following its development with increasing time from the start of interaction of initial substances A and B up to the establishment of equilibrium at which, according to the Gibbs phase rule (see, for example, Refs 128, 130-132, 138), not more than two phases should remain in any two-component system at constant temperature and pressure.

2.3: Initial linear growth of the A_pB_q and A_rB_s layers

Evidently, in an initial period of interaction of substances A and B when the thicknesses of the A_pB_q and A_rB_s layers are relatively small, the conditions $k_{0B1} \ll k_{1B1}/x$,

$k'_{0A2} \ll k'_{1A2}/x$, $k'_{0B2} \ll k'_{1B2}/y$ and $k_{0A3} \ll k_{1A3}/y$ are satisfied. Hence, at low t the terms of the type k_0x/k_1 and k_0y/k_1 can be neglected in comparison with unity. Therefore, the system of equations (2.27) is simplified to

$$\frac{dx}{dt} = k_{0B1} + k'_{0A2} - \frac{rg}{p} k'_{0B2}, \quad (2.30_1)$$

$$\frac{dy}{dt} = k'_{0B2} + k_{0A3} - \frac{q}{sg} k'_{0A2}. \quad (2.30_2)$$

Integration with initial conditions $x = 0$ and $y = 0$ at $t = 0$ yields

$$x = \left(k_{0B1} + k'_{0A2} - \frac{rg}{p} k'_{0B2} \right) t, \quad (2.31_1)$$

$$y = \left(k'_{0B2} + k_{0A3} - \frac{q}{sg} k'_{0A2} \right) t. \quad (2.31_2)$$

The systems of equations (2.30) and (2.31) describe the reaction controlled stage of growth of the A_pB_q and A_rB_s compound layers, where the rates of diffusion of the atoms across layer bulks are so high that their effect on the overall rates of formation of the layers is negligible in comparison with that of the rates of chemical transformations taking place at phase interfaces. This is that case in which the purely chemical processes are rate-determining (chemical control), for there is a great excess of diffusing atoms of both kinds for both layers to grow.

It does not mean, however, that under such circumstances the A_pB_q and A_rB_s compound layers must necessarily occur at the $A-B$ interface simultaneously. Clearly, their simultaneous occurrence is only possible if the derivatives dx/dt and dy/dt in equations (2.30) are positive ($dx/dt > 0$ and $dy/dt > 0$), and consequently the inequalities $k_{0B1} + k'_{0A2} > (rg/p)k'_{0B2}$ and $k'_{0B2} + k_{0A3} > (q/sg)k'_{0A2}$ are satisfied. In such a case, both layers can grow simultaneously from the very start of interaction of phases A and B according to the linear law (2.31), as illustrated in Fig. 2.3a. Note that they will grow at the highest rates possible under given (constant) temperature-pressure conditions.

If $k_{0B1} + k'_{0A2} = (rg/p)k'_{0B2}$, then $dx/dt = 0$. This corresponds to the stationary state where the rate of growth of the A_pB_q layer due to partial chemical reactions (2.1₁) and (2.1₂) is equal to the rate of its consumption in the course of formation of the A_rB_s layer by reaction (2.2₁). If the A_pB_q layer were in the initial specimen $A-B$, then its thickness would remain constant (Fig. 2.3b). At the same time, the A_rB_s layer continues to grow linearly.

If the condition

$$k_{0B1} + k'_{0A2} < \frac{rg}{p} k'_{0B2} \quad (2.32)$$

is satisfied, the A_pB_q layer cannot form at all ($dx/dt < 0$). Therefore, only the A_rB_s layer will be observed to grow at the A – B interface (Fig. 2.3c). If the A_pB_q layer were in the initial specimen A – B , then its thickness would decrease, and it might eventually disappear completely (Fig. 2.3d). In this case, the A_pB_q compound layer is kinetically unstable since the decrease in its thickness due to the consumption during growth of the A_rB_s layer exceeds the increase due to reactions (2.1₁) and (2.1₂).

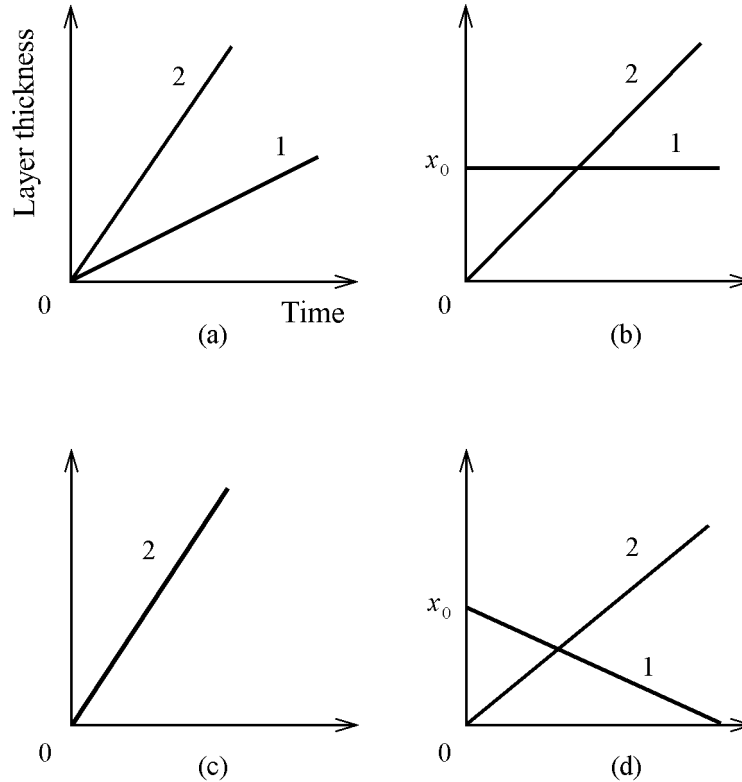


Fig. 2.3. Initial stage of formation of the A_pB_q (line 1) and A_rB_s (line 2) compound layers in the course of interaction of elementary substances A and B . (a) Both layers grow simultaneously in accordance with the linear law; (b) thickness of the A_pB_q layer remains constant, while the A_rB_s layer grows linearly; (c) the A_pB_q layer is missing, and only the A_rB_s layer is formed; (d) thickness of the A_pB_q layer decreases until it disappears completely, while the A_rB_s layer grows linearly.

From the system of equations (2.30), it follows that the thickness of the A_rB_s layer remains constant or equal to zero if $k'_{0B2} + k_{0A3} = (q/sg)k'_{0A2}$. If the inequality

$$k'_{0B2} + k_{0A3} < \frac{q}{sg} k'_{0A2} \quad (2.33)$$

is satisfied, the A_rB_s layer is missing at the A_pB_q - B interface as kinetically unstable. If present initially, it would be prone to full degradation with passing time.

In cases where the manufacturing technology includes the deposition of the layers of chemical compounds (intermetallics, silicides, oxides, *etc.*) onto a solid substrate and their subsequent annealing as, for example, in fabricating very-large-scale-integrated circuits for microelectronics, their probable kinetic instability in contact with parent and other phases should necessarily be taken into account. Otherwise, during service compound layers will gradually degrade, and this may lead to undesirable consequences, especially in the case of thicknesses of several tens of nanometers. Their long-term stability may prove to be insufficient even at room temperature.

Unfortunately, in the framework of the proposed physico-chemical approach, it is impossible to predict theoretically the values of chemical constants k_0 for each particular reaction couple A - B . This limitation is known to be characteristic of any phenomenological consideration. Therefore, the inverse task is exercised in practice, namely, the experimentally established kinetic dependences $x - t$ and $y - t$ are employed to calculate appropriate constants.

Note that the kinetic data must necessarily be supplemented by measurements of the displacement of phase interfaces relative to inert markers located within the bulks of growing A_pB_q and A_rB_s layers (Fig. 2.4). Otherwise, it is impossible to find out all four chemical constants, k_{0B1} , k'_{0A2} , k'_{0B2} and k_{0A3} , from the system (2.30) containing only two equations.

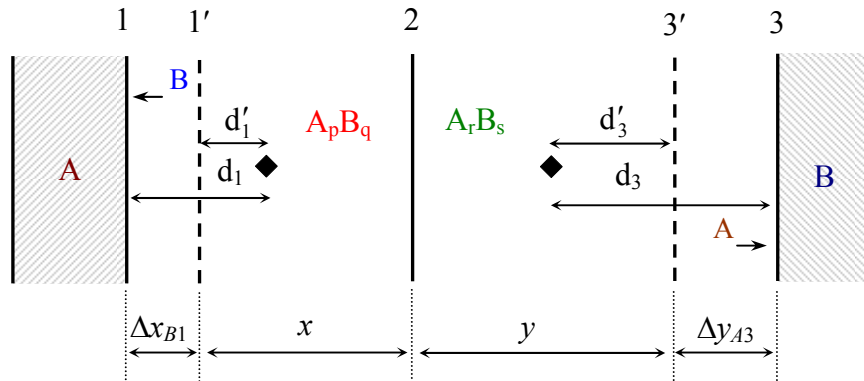


Fig. 2.4. Schematic diagram to explain one of the methods of determining the values of the chemical constants k_0 in the system A - A_pB_q - A_rB_s - B . $\Delta x_{B1} = d_1 - d'_1$, $\Delta y_{A3} = d_3 - d'_3$. To simplify the figure, displacement of interface 2 during layer formation is not shown.

To determine the values of the chemical constants, initial linear portions of the plots of layer thicknesses against time, where $x \ll x_{1/2}^{(B)}$, $x \ll x_{1/2}^{(A)}$, $y \ll y_{1/2}^{(B)}$ and $y \ll y_{1/2}^{(A)}$, must be investigated. By measuring the distance from a marker located inside the

A_pB_q layer to the former $A-A_pB_q$ interface 1' prior to annealing the $A-A_pB_q-A_rB_s-B$ reaction couple and then to its new position 1 after its isothermal annealing during a certain time Δt , one can calculate a value of the chemical constant k_{0B1} from the equation $k_{0B1} = \Delta x_{B1} / \Delta t$. Similarly, by measuring the distance from a marker located inside the A_rB_s layer to the former position of the A_rB_s-B interface 3' and to its new position 3, a value of the chemical constant k_{0A3} is determined from the equation $k_{0A3} = \Delta y_{A3} / \Delta t$. Having obtained the constants k_{0B1} and k_{0A3} , the values of the constants k'_{0B2} and k'_{0A2} can readily be found. In doing so, it is preferable to employ the system of equations (2.31) instead of (2.30) since the total thickness of any compound layer at a certain time t is always measured at a higher accuracy than its increase during Δt .

After measuring the thicknesses of the A_pB_q and A_rB_s layers grown in time t_i , the values of k'_{0B2} and k'_{0A2} are calculated from the system of two algebraic equations with two unknown quantities:

$$k'_{0A2} - \frac{rg}{p} k'_{0B2} = \left(\frac{x}{t} \right)_{t=t_i} - k_{0B1}, \quad (2.34_1)$$

$$k'_{0B2} - \frac{q}{sg} k'_{0A2} = \left(\frac{y}{t} \right)_{t=t_i} - k_{0A3}. \quad (2.34_2)$$

The required quantities p , q , r , s and g become known if the phase identity and chemical compositions of growing compound layers as well as the pyknometric and X-ray density of the compounds were determined experimentally.

It should be noted that the separate determination of the chemical constants is yet *terra incognita* because of experimental difficulties associated with putting inert markers and measuring layer thicknesses in very thin films (some tens to some hundreds of nanometers thick). Much work is still to be done in this field.

It must be quite clear that in the vast majority of binary systems with two chemical compounds on equilibrium phase diagrams both layers can hardly be expected to occur at the $A-B$ interface simultaneously. Rather, their formation will be sequential. This immediately follows even from a formal probability consideration.

Indeed, of three possible combinations of the signs (+, +; +, -; -, +) of the derivatives dx/dt and dy/dt in equations (2.30), there are two cases of different signs, in which one of the layers is lacking, and only one case of the same sign, in which both layers occur and grow simultaneously from the very beginning of interaction of initial substances A and B . Hence, if a number of binary systems are considered, the probability of simultaneous formation of two compound layers in any particular reaction couple $A-B$ is one-third.

In fact, it is far less in view of too many physico-chemical conditions to be satisfied to make their simultaneous occurrence possible. Therefore, one of the layers almost always occurs at the $A-B$ interface somewhat earlier than the other. The absence of one of the layers

is thus a physical reality. To explain this phenomenon, there is no need to invoke additional causes like difficulties with nucleating new phases or too slow growth rates yielding invisible compound layers.

It must be clear, however, that on a time scale of their further growth the difference in the times of layer occurrence (incubation or retardation period) can in many cases be very small. If insufficiently thin compound layers are investigated, this difference may remain unnoticed, thereby producing an impression of simultaneous formation of both layers.

2.4: Minimal thickness of the A_rB_s layer necessary for the A_pB_q layer to occur

The absence of the A_pB_q compound layer from the $A-B$ reaction couple during some period of time in the initial stage of interaction of substances A and B does not mean that this compound cannot then occur and grow between A and A_rB_s . Indeed, equation (2.27₁) shows that the rate of consumption of the A_pB_q layer gradually decreases with increasing thickness of the A_rB_s layer.

Hence, a certain *minimal* value, $y_{\min}$, of the thickness of the A_rB_s layer is always reached at which the condition

$$k_{0B1} + k'_{0A2} = \frac{rg}{p} \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y_{\min}}{k'_{0B2}}} \quad (2.35)$$

is satisfied. Therefore, the derivative dx/dt in equation (2.27₁) becomes first equal to zero and then positive. Hence, the A_pB_q layer will occur at the $A-A_rB_s$ interface after some delay, as shown schematically in Fig. 2.5.

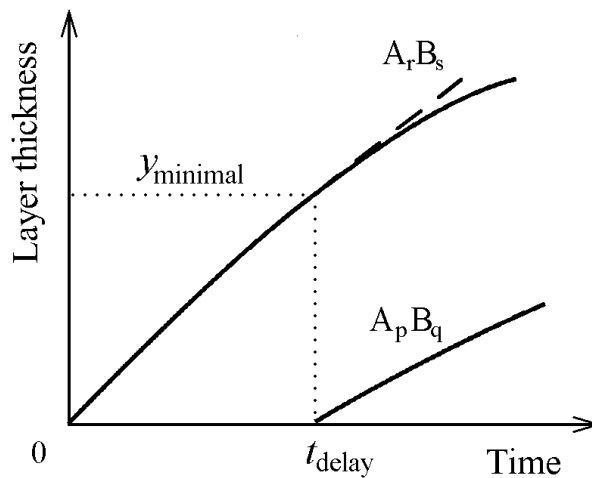


Fig. 2.5. Schematic illustration of the concept of a minimal thickness of the A_rB_s layer necessary for the A_pB_q layer to occur and grow in the $A-B$ reaction couple.

As long as both derivatives dx/dt and dy/dt prove to be positive, the A_pB_q and A_rB_s layers will grow simultaneously until at least one of initial substances *A* or *B* is consumed completely. The delay with the formation of the A_pB_q layer is thus due to purely kinetic reasons and is not associated with either the thermodynamic stability of the A_pB_q compound or its nucleation rate. It should be noted that after the appearance of the A_pB_q layer the rate of growth of the A_rB_s layer appreciably decreases because it is partially consumed in the process of formation of the A_pB_q compound.

If the A_rB_s layer was initially missing from the *A*–*B* reaction couple, it occurs between A_pB_q and *B* after the A_pB_q layer has reached a necessary minimal value

$$k'_{0B2} + k'_{0A3} = \frac{q}{sg} \frac{k'_{0A2}}{1 + \frac{k'_{0A2} x_{\min}}{k'_{1A2}}} \quad (2.36)$$

With transition metal silicides, the necessary minimal thickness may reach a few micrometres. For example, the NiSi layer starts to grow at 300–430 °C only after the Ni_2Si layer between nickel and silicon has reached a thickness of about 2 μm [27, 32]. B. Blanpain *et al.* [102] found that the first layer to grow in the palladium–aluminium reaction couple at 343–431 °C is that of the Pd_2Al_3 intermetallic compound. After the Pd_2Al_3 layer has reached a thickness of 3.9–6.5 μm (depending on annealing temperature), the PdAl_3 intermetallic compound layer starts to grow. Figure 2.6 shows a plot of the thicknesses of the Pd_2Al_3 and PdAl_3 layers against the annealing time of palladium–aluminium specimens at 386 °C [102]. The PdAl_3 layer is seen to be missing from the Pd–Al reaction couple over a time period of approximately 500 seconds.

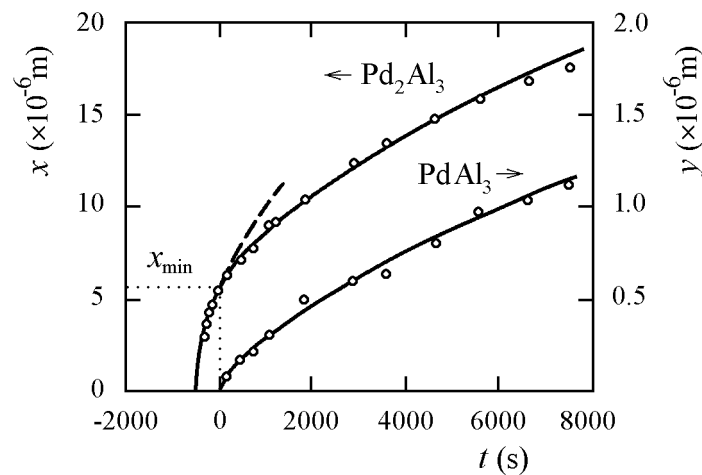


Fig. 2.6. Kinetics of sequential growth of the Pd_2Al_3 and PdAl_3 layers in the Pd–Al reaction couple at 386 °C according to the data of B. Blanpain *et al.* [102]. The PdAl_3 layer starts to grow after the Pd_2Al_3 layer has reached a thickness of 5.7 μm . The rate of growth of the Pd_2Al_3 layer is seen to decrease from the point $x_{\min}$ on compared to its initial value.

Sequential layer formation is often considered to be a consequence of the existence of an interfacial barrier preventing the reaction of formation of a given compound. Such an interpretation of this phenomenon is misleading. Indeed, it may seem that after removing this barrier, for example, by artificial depositing the Pd_2Al_3 and PdAl_3 layers, both will grow simultaneously in $\text{Pd-Pd}_2\text{Al}_3\text{-PdAl}_3\text{-Al}$ specimens. However, this is not the case. Even the existing PdAl_3 layer of whatever thickness will not grow unless the thickness of the Pd_2Al_3 layer exceeds the minimal necessary value $x_{\min}$, because the consuming reaction is more rapid than the two forming ones.

2.5: Non-linear growth of the A_pB_q layer

Thickening the A_pB_q and A_rB_s layers with increasing time of interaction of initial substances A and B leads to a change in the regimes of their growth (see Sections 1.3.2 and 1.4.1). Let us assume that the regime of growth of the A_pB_q layer with regard to component B became diffusion controlled in the theoretical definition ($x > x_{1/2}^{(B)}$), and consider the case where $x \gg x_{1/2}^{(B)}$.

As before in Section 2.3, the regime of growth of the A_pB_q layer with regard to component A and also that of the A_rB_s layer with regard to both components are assumed to be reaction controlled, so that $x \ll x_{1/2}^{(A)}$, $y \ll y_{1/2}^{(B)}$ and $y \ll y_{1/2}^{(A)}$. These conditions can also be written as $k_{0B1} \gg k_{1B1}/x$, $k'_{0A2} \ll k'_{1A2}/x$, $k'_{0B2} \ll k'_{1B2}/y$ and $k_{0A3} \ll k_{1A3}/y$. Therefore, the system of equations (2.27) takes the form

$$\frac{dx}{dt} = \frac{k_{1B1}}{x} + k'_{0A2} - \frac{rg}{p} k'_{0B2}, \quad (2.37_1)$$

$$\frac{dy}{dt} = k'_{0B2} + k_{0A3} - \frac{q}{sg} k'_{0A2}. \quad (2.37_2)$$

The latter equation of this system indicates that the A_rB_s layer will grow linearly with passing time. The $x - t$ dependence is more complicated. Let us briefly analyse its possible variants.

(1) If the condition $k'_{0A2} = (rg/p)k'_{0B2}$ happens to be satisfied for a particular $A-B$ reaction couple under certain experimental conditions, then equation (2.37₁) becomes $dx/dt = k_{1B1}/x$. Hence, the A_pB_q layer will grow parabolically, as shown schematically in Fig. 2.7a.

(2) If $k'_{0A2} < (rg/p)k'_{0B2}$, then

$$\frac{dx}{dt} = \frac{k_{1B1}}{x} - R, \quad (2.38)$$

where $R = (rg/p)k'_{0B2} - k'_{0A2}$. From equation (2.38), it is easy to conclude that the thickness of the A_pB_q layer will asymptotically tend with passing time to some limiting value $x_{\max}$ (Fig. 2.7b). To find this value, it suffices to put $dx/dt = 0$ in equation (2.38), giving

$$x_{\max} = \frac{k_{1B1}}{R}. \quad (2.39)$$

Note that a certain portion of the $x - t$ curve, where the condition $k_{1B1}/x \gg R$ is satisfied, is close to the parabola $x^2 = 2 k_{1B1}t$.

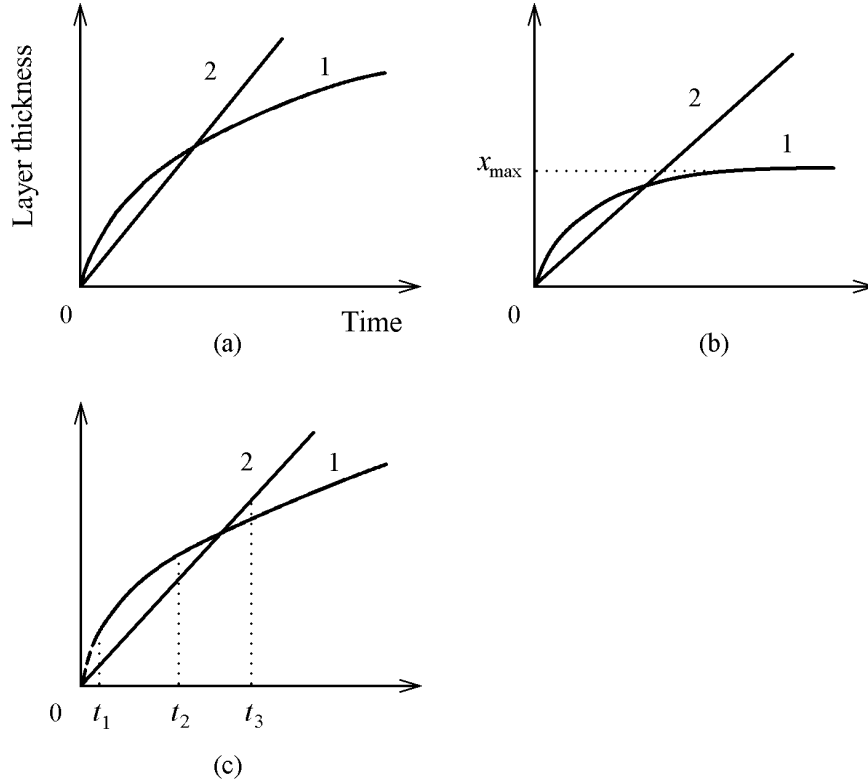


Fig. 2.7. The non-linear–linear stage of simultaneous growth of the A_pB_q (line 1) and A_rB_s (line 2) layers between substances *A* and A_rB_s . Growth of the A_rB_s layer is linear. Growth of the A_pB_q layer is (a) parabolic, (b) asymptotic or (c) close to parabolic in the $t_1 - t_2$ range and almost linear at $t > t_3$.

(3) If $k'_{0A2} > (rg/p)k'_{0B2}$, then the derivative dx/dt is positive, and therefore the A_pB_q layer continuously grows with passing time. That portion of the $x - t$ dependence between t_1 and t_2 , where the condition $k_{1B1}/x \gg k'_{0A2} - (rg/p)k'_{0B2}$ is fulfilled, is close to a parabola, whereas the region of long times $t > t_3$, where $k_{1B1}/x \ll k'_{0A2} - (rg/p)k'_{0B2}$, is almost linear (Fig. 2.7c).

Similar considerations clearly apply to the A_rB_s layer if the regime of its growth is diffusion controlled with regard to component *A*, so that $y \gg y_{1/2}^{(A)}$, and reaction controlled

with regard to component B ($y \ll y_{1/2}^{(B)}$), while that of the A_pB_q layer is reaction controlled with regard to both components, so that $x \ll x_{1/2}^{(A)}$ and $x \ll x_{1/2}^{(B)}$. Then, the A_rB_s layer will grow non-linearly, while the A_pB_q layer linearly.

2.6: Effect of the critical thickness of the A_pB_q layer with regard to component A on the process of growth of the A_rB_s layer

Due to further thickening the A_pB_q layer, its growth regime becomes diffusion controlled (in the theoretical definition) not only with regard to component B but also with regard to component A ($x > x_{1/2}^{(B)}$ and $x > x_{1/2}^{(A)}$). This case differs essentially from that considered in the previous section. Indeed, if the growth regime of the A_pB_q layer is diffusion controlled with regard to component A , then the A_rB_s layer cannot grow at the expense of diffusion of component A because at $x > x_{1/2}^{(A)}$ all the A atoms crossing the bulk of the A_pB_q layer per unit time are combined into the A_pB_q compound at interface 2 according to partial chemical reaction (2.1₂).

Subsequent increasing the thickness of the A_pB_q layer makes a deficit of the diffusing A atoms progressively large in comparison with the reactivity of the surface of the A_rB_s layer towards these atoms. Therefore, no atom A is able to enter into partial chemical reaction (2.2₂). Interface 2 or, rather, the surface of the A_rB_s layer thus becomes an insurmountable barrier for the A atoms. Hence, at $x > x_{1/2}^{(A)}$ simply there are no diffusing A atoms for the A_rB_s layer to grow. All of them are consumed during formation of the A_pB_q layer.

It is surprising why this obvious conclusion remained overlooked until the 1980's [145-149], although in examining the process of layer growth the equations of mass balance at phase interfaces are always written. The answer is that, firstly, the constancy of the composition of any chemical compound is usually not taken into account and, secondly, each interface is examined separately from others, whereas it is necessary to analyse the mutual effect on each other of the physical and chemical processes taking place at the interfaces between all the phases involved in the interaction.

It must be clear that at $x > x_{1/2}^{(A)}$ the term

$$\frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}}$$

of the system of equations (2.27), though quite sound from a mathematical viewpoint, nonetheless has no physical meaning and therefore should be omitted whatever y . Hence, the rate of growth of the A_rB_s layer will appreciably decrease after the thickness of the A_pB_q layer has reached its critical value of $x_{1/2}^{(A)}$, as shown schematically in Fig. 2.8.

Indeed, at $x < x_{1/2}^{(A)}$ the A_rB_s layer grows at the expense of diffusion of both components A and B followed by partial chemical reactions (2.2₁) and (2.2₂), while at $x > x_{1/2}^{(A)}$ it only grows at the expense of diffusion of component B and subsequent partial chemical reaction (2.2₁). Therefore, the $y - t$ curve will exhibit a deviation from its former course reflecting a decrease of the growth rate of the A_rB_s layer. This deviation is due to the existence of the

critical thickness, $x_{1/2}^{(A)}$, of the A_pB_q layer, which divides the $x - t$ dependence into the reaction controlled and diffusion controlled regions with regard to component *A*.

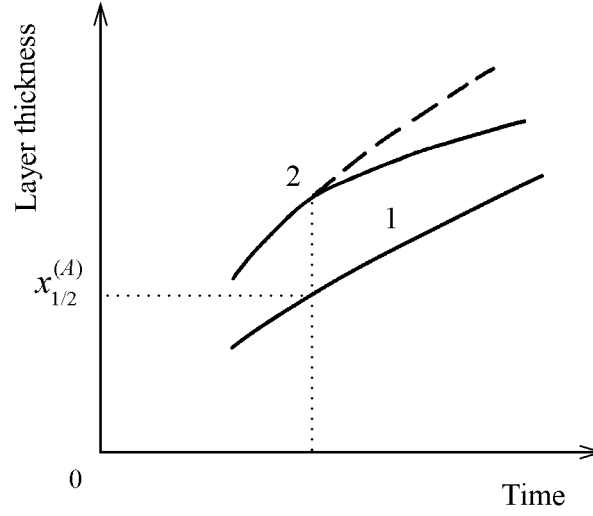


Fig. 2.8. Decreasing the growth rate of the A_rB_s layer after the A_pB_q layer has reached its critical thickness, $x_{1/2}^{(A)}$, with regard to component *A*. 1, thickness of the A_pB_q layer; 2, thickness of the A_rB_s layer.

Decreasing the growth rate of the A_rB_s layer is clearly smooth and not abrupt, since a relative deficit of the diffusing *A* atoms in comparison with the reactivity of the surface of substance *B* towards these atoms becomes perceptible somewhat earlier than the thickness of the A_pB_q layer reaches $x_{1/2}^{(A)}$. However, if sufficiently wide portions of the layer thickness-time dependences in the vicinity of the point $x_{1/2}^{(A)}$ of the $x - t$ curve and the corresponding point of the $y - t$ curve are investigated, then a decrease in the growth rate of the A_rB_s layer may readily be noticed.

2.7: Paralinear growth kinetics of two compound layers

If the A_pB_q layer grows in the diffusion controlled regime with regard to components *A* and *B*, while the A_rB_s layer grows in the reaction controlled regime with regard to component *B*, so that $x \gg x_{1/2}^{(B)}$, $x \gg x_{1/2}^{(A)}$ and $y \ll y_{1/2}^{(B)}$, then the system of equations (2.27) is simplified to

$$\frac{dx}{dt} = \frac{k_{1B1} + k'_{1A2}}{x} - \frac{rg}{p} k'_{0B2}, \quad (2.40_1)$$

$$\frac{dy}{dt} = k'_{0B2} - \frac{q}{sg} \frac{k'_{1A2}}{x}. \quad (2.40_2)$$

Since equation (2.40₁), similar to equation (2.38), does not contain y , it can be solved separately from equation (2.40₂). It is clear that under constant temperature and pressure conditions the thickness of the A_pB_q layer asymptotically tends with passing time to the maximal possible value (see Section 2.5, equation (2.39))

$$x_{\max} = \frac{(k_{1B1} + k'_{1A2})p}{rgk'_{0B2}}, \quad (2.41)$$

theoretically never reaching it, whereas the growth of the A_rB_s layer is almost linear if $k'_{0B2} \gg (q/sg)k'_{1A2}/x$. If the latter condition is satisfied, then the system of equations (2.40) takes a simpler form

$$\frac{dx}{dt} = \frac{k_{1B1} + k'_{1A2}}{x} - \frac{rg}{p}k'_{0B2}, \quad (2.42_1)$$

$$\frac{dy}{dt} = k'_{0B2}. \quad (2.42_2)$$

A system of differential equations of this type appears to have been first proposed by J. Loriers in 1949 (see Ref. [13]) to describe *paralinear* growth kinetics of two oxide layers. The term *paralinear* growth, being a combination of the words *parabolic* and *linear*, means that some initial portion of the time dependence of the total thickness or mass of two compound layers is almost parabolic and then there is a gradual transition to linear kinetics.

Indeed, from the system of equations (2.42), it is easily seen that at low values of t and consequently x $(k_{1B1} + k'_{1A2})/x \gg (rg/p)k'_{0B2}$ and therefore this dependence is close to the parabola $x^2 = 2(k_{1B1} + k'_{1A2})t$ in view of small contribution from the straight line $y = k'_{0B2}t$ to the total thickness of both layers. Its long-time portion, being the sum of two straight lines $x = x_{\max}$ (see equation (2.41)) and $y = k'_{0B2}t$, is linear.

Paralinear kinetics are especially often observed if one of the layers is compact, while the other porous. It should be noted, however, that the presence of pores, cracks or other macroscopic defects in one of the layers is not a necessary condition for employing the system of equations (2.42) to treat the experimental data. Only a large difference in the diffusivities of the components in compound layers, ensuring different regimes of their growth, is important. Also, the duration of experimental observations must be sufficiently long because the final stage of asymptotic growth of one of the layers is extremely slow.

In the oxidation of metals, paralinear growth kinetics of oxide layers are known to be a quite usual phenomenon [11, 13, 122-124]. Such a dependence is observed much less frequently with metallic systems due to three reasons. Firstly, the duration of investigation of the process of oxidation of metals is far longer than that in examining the solid-state interaction of two metals. Secondly, the minimal measurable thickness (or mass) of compound layers which can be detected using available techniques is much less in the

former case than in the latter. Thirdly, since this “anomalous” dependence has no satisfactory explanation from a diffusional viewpoint, experimentalists investigating metallic systems probably prefer not to accentuate on it.

In fact, however, paralinear growth can readily be observed not only with metal-gas systems. Kinetics of formation of the intermetallic layers based on the Fe_2Al_5 and FeAl_3 compounds between an 18Cr–10Ni stainless steel and aluminium saturated with its components at 700 °C are also paralinear [220, 221], even though this system does not belong to binary systems. Investigations were carried out using a commercial 18Cr–10Ni stainless steel containing 70 ± 1 % Fe, 18.0 ± 0.5 % Cr, 10.5 ± 0.2 % Ni and 0.08 ± 0.01 % C and high-purity aluminium (99.995 % Al) as starting materials. First, an aluminium alloy containing 2.5 % Fe and corresponding amounts of other steel constituents was prepared by arc melting the appropriate amounts of aluminium and steel shavings under argon. Pieces of this alloy were then used as the melt material. Since the melt had thus been saturated with respect to the steel constituents, no dissolution of the steel specimens could clearly occur during the experiments at a temperature of 700 °C.

The rapid-quenching device employed will be described in Chapter 5. A polished cylindrical steel specimen, 11.28 mm diameter (1 cm^2 area) and 5 mm high, was held in a liquid aluminium alloy (10 cm^3 volume) protected by a flux for 100 to 3600 s, and then the solid specimen together with the melt were rapidly cooled by quenching in water to arrest the reactions at the steel-aluminium interface. The time of cooling from 700 °C down to room temperature did not exceed 2 s. The bimetallic specimen thus obtained was cut along the cylindrical axis, ground flat and polished electrolytically [129]. The cross-sections prepared in such a way were examined metallographically. Microhardness measurements were also made. Concentration profiles of aluminium, iron, chromium and nickel in the reaction zone between steel and aluminium were recorded using a JEOL Superprobe 733 microanalyser. In addition, the values of concentration of those elements near the middle part of the intermetallic layers and in the bulk of both steel and aluminium were determined by point-to-point electron probe measurements. To identify the phases formed, use was made of X-ray diffraction techniques.

Two intermetallic layers were found to occur at the interface between the stainless steel and the saturated aluminium melt. A typical optical micrograph of the steel- aluminium transition zone is shown in Fig. 2.9. The layer (layer I) adjacent to the steel base was compact, while that (layer II) adjacent to the melt material porous. The thickness of layer II was a few times greater than that of layer I.

The bimetallic steel- aluminium specimens in which the intermetallic layers were thick enough (30 to 40 μm) could easily be fractured along the interface between layers I and II. After slight mechanical polishing, the surfaces of both parts of the specimen proved to be suitable for X-ray examination, and the first two X-ray patterns were obtained. The cross-sections were then again ground and polished to remove additional portions of the material from their surfaces, and new X-ray patterns were taken.

In total, one X-ray pattern of the aluminium matrix, two X-ray patterns of layer II in its different sections (about 5 and 15 μm away from the interface between layers I and II), one X-ray pattern of layer I and one X-ray pattern of the steel base were obtained using one and the same bimetallic steel-aluminium specimen. From these, the values of interplanar spacing were calculated for all the phases investigated, employing the Bragg equation. Their comparison with the available literature data [229, 230] showed layer I to be based on the Fe_2Al_5 intermetallic compound, while layer II on the FeAl_3 intermetallic compound.

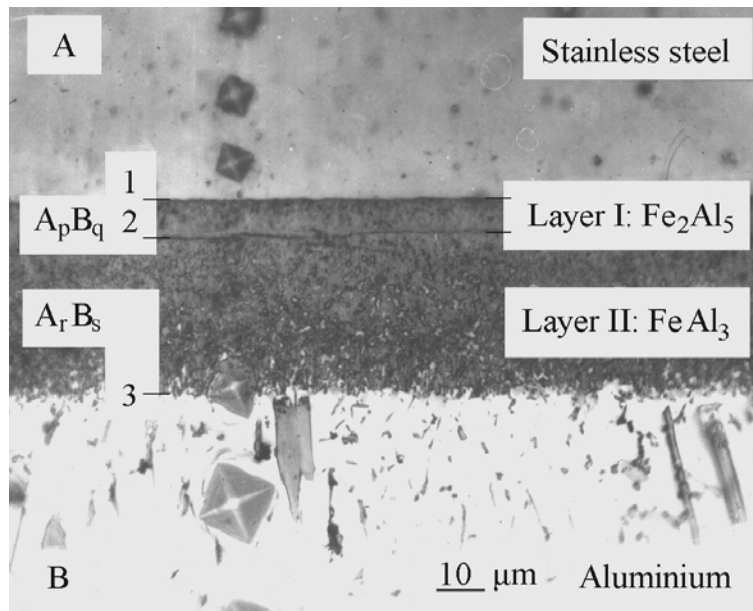


Fig. 2.9. Microstructure of the stainless steel- aluminium transition zone [221]. Temperature 700 °C, dipping time 3000 s, melt: Al + 2.5 % Fe and corresponding amounts of other elements from the steel. Microhardness indentations were made at a load of 0.196 N (20 g).

As evidenced from Fig. 2.10, both layers also contained considerable amounts of chromium and nickel. Electron probe microanalysis showed layer I to contain 48.0-55.5 % Al, 31.5-39.8 % Fe, 5.0-9.2 % Cr and 2.5-6.9 % Ni. Thus, its composition can be expressed by the chemical formula $(\text{Fe,Cr,Ni})_2\text{Al}_5$. Layer II consisted of 60.2-68.1 % Al, 27.2-31.9 % Fe, 2.9-4.3 % Cr and 1.2-2.0 % Ni. This composition can be represented by the chemical formula $(\text{Fe,Cr,Ni})\text{Al}_3$.

It should be noted that the FeAl_3 intermetallic compound has a rather wide range of homogeneity and therefore its composition varies from FeAl_3 to Fe_2Al_7 depending on

formation conditions [157, 159, 231]. For simplicity, the chemical formulae Fe_2Al_5 and FeAl_3 will be used throughout.

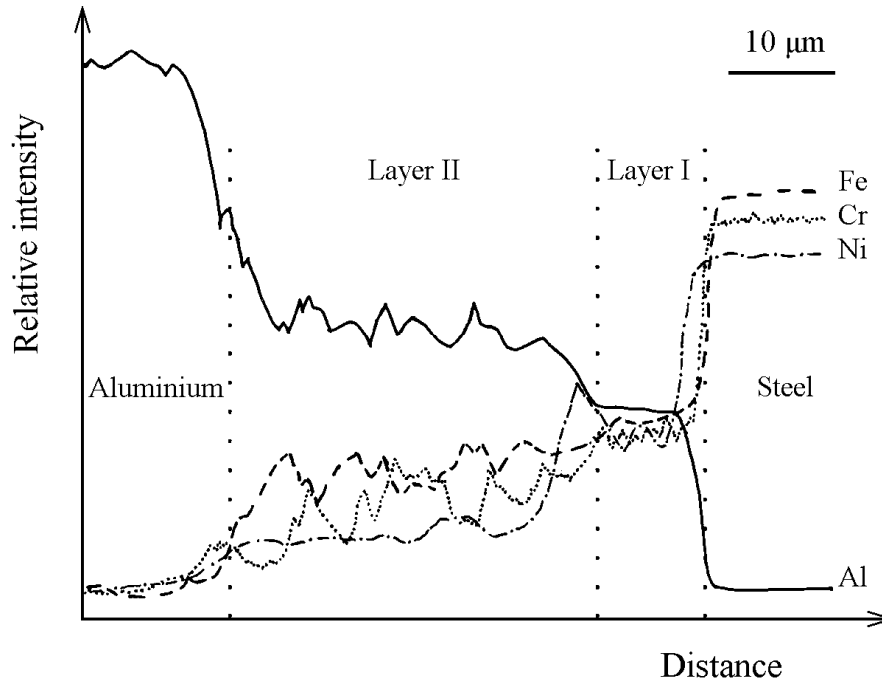


Fig. 2.10. Concentration profiles of aluminium, iron, chromium and nickel in the transition zone between stainless steel and aluminium [221]. For experimental conditions, see Fig. 2.9.

As seen in Fig. 2.9, microhardness of the phases involved in the interaction differs considerably. Values of microhardness of the steel base were the same, $\text{HV}_{20} = 1.8 \pm 0.2$ GPa, at any point up to its interface with layer I. Of all the phases investigated, layer I had the highest microhardness, $\text{HV}_{20} = 8.9 \pm 0.9$ GPa. Values of microhardness gradually decreased within layer II from $\text{HV}_{20} = 4.5$ GPa to $\text{HV}_{20} = 3.06$ GPa with increasing distance away from its interface with layer I. The microhardness of the aluminium matrix was 0.6 ± 0.1 GPa.

The time dependence of the thickness of the intermetallic layers formed at the interface between steel and saturated aluminium melt is shown in Fig. 2.11. It is seen that the thickness, x , of layer I gradually increases in the 100-2000 s time range and then remains unchanged, $x_{\text{max}} = 10$ μm. Meanwhile, the thickness, y , of layer II continuously increases with increasing dipping time of steel in aluminium. The kinetic curve for layer II can be divided into two distinct regions. In the first region (from 0 to about 200 s), its growth rate is almost twice that in the second region ($t > 200$ s). It is difficult to establish a kinetic layer-growth law in the first region, whereas in the second region it is close to linear. Accordingly, the time dependence of the total thickness of both layers also consists of two regions with different growth rates.

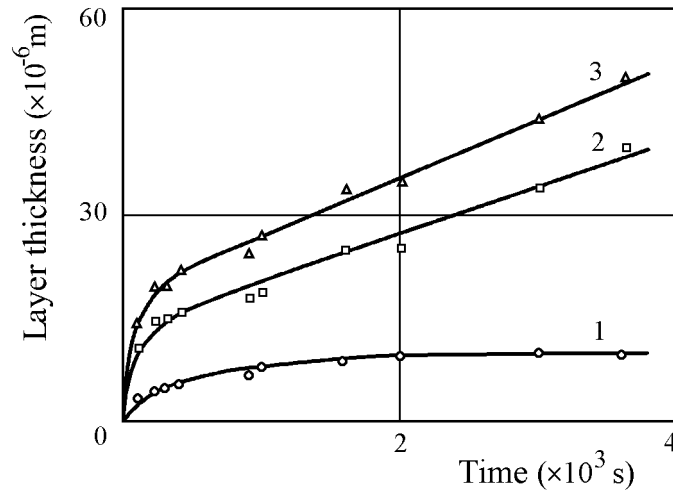


Fig.2.11. Plots of layer thickness against dipping time [221]. 1, thickness of layer I; 2, thickness of layer II; 3, total thickness of both layers. Temperature 700 °C, melt: Al + 2.5 % Fe and corresponding amounts of other elements from the steel.

Although a few elements (Fe, Cr, Ni, *etc.*) diffuse from the bulk of the steel specimen across layer I, the diffusion of iron appears to be dominant. The other main element diffusing in the growing layers is aluminium. Formation of the intermetallic layers can therefore be represented by the following scheme (see Fig. 2.9 and equations (2.1₁)-(2.2₂)):

Layer	Interface	Partial chemical reaction	
Fe_2Al_5	1	$5\text{Al}_{\text{dif}} + 2\text{Fe}_{\text{surf}} = \text{Fe}_2\text{Al}_5,$	(2.43 ₁)
	2	$\text{Fe}_{\text{dif}} + 5\text{FeAl}_3 = 3\text{Fe}_2\text{Al}_5,$	(2.43 ₂)
FeAl_3	2	$\text{Al}_{\text{dif}} + \text{Fe}_2\text{Al}_5 = 2\text{FeAl}_3,$	(2.44 ₁)
	3	$\text{Fe}_{\text{dif}} + 3\text{Al}_{\text{surf}} = \text{FeAl}_3.$	(2.44 ₂)

First, both layers grow at the expense of diffusion of iron and aluminium. Then, the regime of growth of the Fe_2Al_5 layer with regard to the iron atoms becomes diffusion controlled in the theoretical definition given in Chapter 1, and consequently the FeAl_3 layer loses a source of these atoms. As a result, the growth rate of the FeAl_3 layer must decrease almost twice, in accord with the experiment.

In the case under consideration, reaction (2.44₂) does not take place at all. Thus, the Fe_2Al_5 layer grows at the expense of diffusion of the aluminium and iron atoms across its bulk and subsequent partial chemical reactions (2.43₁) and (2.43₂), while the FeAl_3 layer grows only at the expense of diffusion of the aluminium atoms and subsequent partial

chemical reaction (2.44₁). In view of the data by T. Heumann and S. Dittrich [170] about the predominant diffusion of aluminium in the lattice of the Fe₂Al₅ intermetallic compound, the contribution of partial chemical reaction (2.43₂) to the process of formation of the Fe₂Al₅ layer is probably small in comparison with that of partial chemical reaction (2.43₁). Hence, the system of equations (2.42) assumes the form ($p = 2, r = 1$)

$$\frac{dx}{dt} = \frac{k_{1AlI} + k'_{1Fe2}}{x} - \frac{g}{2} k'_{0Al2}, \quad (2.45_1)$$

$$\frac{dy}{dt} = k'_{0Al2}. \quad (2.45_2)$$

Growth kinetics of the FeAl₃ layer in the 900-3600 s time range was found to obey the linear relationship $y = 1 \times 10^{-8} t + 6 \times 10^{-6}$, m. Hence, $k'_{0Al2} = 1 \times 10^{-8} \text{ m s}^{-1}$. Using the experimental value $x_{\max} = 10 \text{ } \mu\text{m}$, the sum $(k_{1AlI} + k'_{1Fe2})$ can be evaluated assuming the molar volume of (Fe,Cr,Ni)₂Al₅ and (Fe,Cr,Ni)Al₃ to be equal to that of Fe₂Al₅ and FeAl₃, respectively. The latter quantities can be calculated from the values of the density of the intermetallic compounds:

$$\rho_{A_p B_q} = 4.1 \times 10^3 \text{ kg m}^{-3} \text{ [170] and } \rho_{A_r B_s} = 3.8 \times 10^3 \text{ kg m}^{-3} \text{ [159].}$$

Thus, $V_{A_p B_q} = 6.0 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ and $V_{A_r B_s} = 3.6 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. Consequently, $g = 1.7$. Then, equation (2.41) yields

$$k_{1AlI} + k'_{1Fe2} = \frac{r g k'_{0Al2} x_{\max}}{p} = 0.8 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}.$$

Since $k_{1AlI} \gg k'_{1Fe2}$, the value obtained must in all probability be close to the reaction-diffusion coefficient of the aluminium atoms across the (Fe,Cr,Ni)₂Al₅ layer in the course of its formation (see Ref. [196]).

It should be emphasised that in general initial portions of the $x - t$ and $y - t$ dependences are not strictly parabolic. Nonetheless, in the case under consideration some initial portion of the time dependence of the total thickness of both layers is close to a parabola. This portion (from 0 to about 400 s) can be described with fairly good accuracy by the parabolic equation $x^2 = 2k_1 t$, where $k_1 = (8 \pm 2) \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. From a formal viewpoint, it can therefore be concluded (especially if only the dependence of the total thickness or mass of both compound layers upon time is analysed) that the parabolic growth law gradually transforms into the linear growth law, whereas the layer-growth kinetics are in fact somewhat more complicated.

Note that the transition from the parabolic to linear kinetics with passing time can take place only in the case of simultaneous growth of the layers of two or more chemical compounds. Therefore, if a thermogravimetric curve is well described by paralinear

equations (2.42), it provides evidence for the presence of at least two growing compound layers at the interface of reacting substances. If a single compound layer is formed, only the reverse transition where a straight line gradually transforms into a parabola is possible. This must be kept in mind to avoid misleading conclusions regarding the rate-determining step in layer formation.

Often, the parabolic-to-linear transition is interpreted in such a way, as if initially the diffusion is the rate-controlling step, while then (with increasing time) the reaction becomes the rate-controlling step. Firstly, during the parabolic growth no change of the rate-controlling steps ever occurs. Secondly, if the diffusion is already dominant at smaller layer thicknesses, the reaction can never become dominant at larger layer thicknesses.

2.8: Diffusion controlled growth of the A_pB_q and A_rB_s layers

Increasing the thickness of the A_rB_s layer will inevitably result in a change of its growth regime from reaction to diffusion controlled with regard to component B (at $y > y_{1/2}^{(B)}$). This change immediately affects the growth rate of the A_pB_q layer. Namely, at $y > y_{1/2}^{(B)}$ the A_pB_q layer loses a source of B atoms and consequently its further growth proceeds at the expense of diffusion of only component A .

Thus, at $x > x_{1/2}^{(A)}$ and $y > y_{1/2}^{(B)}$ the A_pB_q layer grows at the expense of diffusing A atoms and subsequent partial chemical reaction (2.1₂), while the A_rB_s layer grows at the expense of diffusing B atoms and subsequent partial chemical reaction (2.2₁). Both reactions take place at their common interface 2 (Fig. 2.12).

Partial chemical reactions (2.1₁) and (2.2₂) cannot proceed at all in view of the lack of excessive diffusing B and A atoms. These are completely consumed at the A_pB_q – A_rB_s interface. Hence, the terms

$$\frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} \quad \text{and} \quad \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}}$$

of the system of equations (2.27) lose their physical meaning and should be omitted whatever x and y . The time dependence of the total thickness or mass of two compound layers must therefore exhibit two more or less pronounced deviations from their former course, as shown schematically in Fig. 2.13.

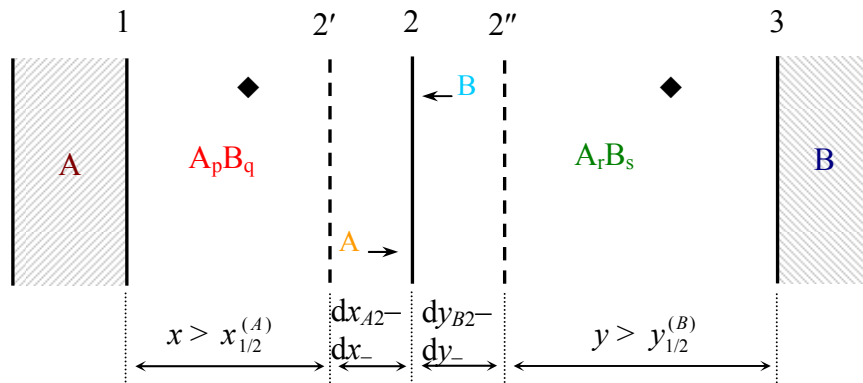


Fig. 2.12. Schematic diagram to illustrate the growth process of two chemical compound layers under conditions of diffusion control ($x > x_{1/2}^{(A)}$ and $y > y_{1/2}^{(B)}$). Only component A is diffusing across the A_pB_q layer, while only component B is diffusing across the A_rB_s layer. Both layers thicken at their common interface 2. No partial chemical reactions take place at interfaces 1 and 3 in view of the lack of appropriate diffusing atoms. The symbol $\blacklozenge$ designates an inert marker.

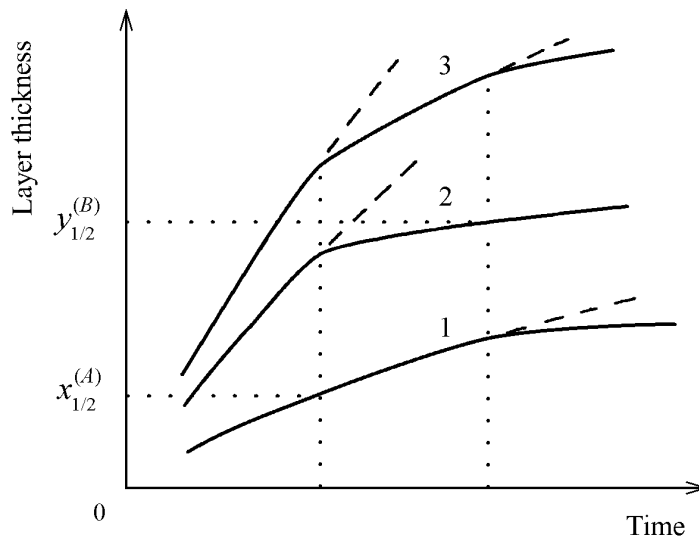


Fig. 2.13. Deviations of the kinetic dependences due to the existence of the critical thicknesses of growing A_pB_q and A_rB_s layers. 1, thickness of the A_pB_q layer; 2, thickness of the A_rB_s layer; 3, total thickness of both layers.

One of these deviations is due to a change of the regime of growth of the A_pB_q layer from reaction (at $x < x_{1/2}^{(A)}$) to diffusion (at $x > x_{1/2}^{(A)}$) controlled with regard to component A . After the A_pB_q layer has reached the thickness $x_{1/2}^{(A)}$, a deviation occurs on the $y - t$ curve describing the time dependence of the thickness of the A_rB_s layer. Another deviation is due to a change of the regime of growth of the A_rB_s layer from reaction (at $y < y_{1/2}^{(B)}$) to diffusion (at $y > y_{1/2}^{(B)}$) controlled with regard to component B . When the A_rB_s layer reaches the thickness $y_{1/2}^{(B)}$, a deviation occurs on the dependence, $x - t$, of the thickness of the A_pB_q layer upon time. Note that in the case under consideration the deviations observed on the kinetic dependences are caused solely by quantitative changes in thickness of growing compound layers. Neither their number, nor phase identity, nor structure are changed. This is an instructive example of the transformation of quantity into quality.

2.8.1: Late diffusional stage of growth of two compound layers: system of differential equations

The late diffusional stage of growth of the A_pB_q and A_rB_s layers is the one where the conditions $x \gg x_{1/2}^{(A)}$ and $y \gg y_{1/2}^{(B)}$ are satisfied. This means that $k'_{0A2} \gg k'_{1A2}/x$ and $k'_{0B2} \gg k'_{1B2}/y$. Therefore, by omitting, as physically meaningless, both the first term of the right-hand side of equation (2.27₁) and the second term of the right-hand side of equation (2.27₂) and neglecting unity in the denominators of the other terms, one obtains

$$\frac{dx}{dt} = \frac{k'_{1A2}}{x} - \frac{rg}{p} \frac{k'_{1B2}}{y}, \quad (2.46_1)$$

$$\frac{dy}{dt} = \frac{k'_{1B2}}{y} - \frac{q}{sg} \frac{k'_{1A2}}{x}. \quad (2.46_2)$$

Similar systems of differential equations, differing only by their coefficients, were obtained in the framework of diffusional considerations by V.I. Arkharov [4], B. Schröder and V. Leute [54], A.T. Fromhold and N. Sato [55] and other researchers. Actually, they have examined one of a few limiting cases following from the general system of equations (2.27) under certain constraints.

For the late diffusional stage of growth of two compound layers, most frequently observed in practice, the physico-chemical and diffusional approaches give almost identical kinetic equations because in this stage the rates of their formation are restricted almost entirely by the rate of diffusion of the A and B atoms across layer bulks, with the rate of chemical transformations at the interfaces being practically instantaneous by comparison. In other words, the time of chemical transformations (chemical reaction as such) is negligible compared to the time of diffusional transport of reacting species to the reaction site.

2.8.2: Late diffusional stage of growth of two compound layers: ratio of their thicknesses

When solving any system of differential equations like (2.46), it is usually assumed that either

$$x \sim t^{1/2} \text{ and } y \sim t^{1/2} \text{ or } \frac{dx}{dt} : \frac{dy}{dt} = \text{const.}$$

Therefore, the (parabolic) type of the $x - t$ and $y - t$ dependences becomes predetermined beforehand. Also, the ratio of the growth rates (and thicknesses) of the layers is considered to be unchanged during their formation. It is supposed to follow from the available experimental data. However, this is not the case.

In fact, the ratio of the thicknesses of growing compound layers changes with passing time, but relatively slowly, and not always this change can be noticed in view of the limited duration of experimental observations. To determine the range in which the ratio of the thickness of the A_pB_q and A_rB_s layers can vary during their growth in the late diffusional stage, let us analyse the system of equations (2.46) in more detail.

Positive values of the derivatives dx/dt and dy/dt are clearly a necessary condition for the simultaneous growth of the A_pB_q and A_rB_s layers. Therefore, instead of the system of equations (2.46), the following system of inequalities is obtained

$$\frac{k'_{1A2}}{x} - \frac{rg}{p} \frac{k'_{1B2}}{y} > 0, \quad (2.47_1)$$

$$\frac{k'_{1B2}}{y} - \frac{q}{sg} \frac{k'_{1A2}}{x} > 0. \quad (2.47_2)$$

These inequalities must be satisfied simultaneously. Hence, the limits within which the ratio of the thickness of the A_pB_q and A_rB_s layers can vary are as follows

$$\frac{q}{sg} \frac{k'_{1A2}}{k'_{1B2}} < \frac{x}{y} < \frac{p}{rg} \frac{k'_{1A2}}{k'_{1B2}}. \quad (2.48)$$

It is seen, firstly, that the ratio of the thicknesses of the A_pB_q and A_rB_s layers depends upon:

- (i) values of the physical (diffusional) constants,
- (ii) ratio of the molar volumes of the A_pB_q and A_rB_s compounds,
- (iii) stoichiometry of these compounds.

Secondly, the closer the compositions of the compounds A_pB_q and A_rB_s to each other, the narrower is the range of variation of the ratio x/y . For example, for chemical compounds of the type AB and AB_2 ,

$$\frac{1}{2g} \frac{k'_{1A2}}{k'_{1B2}} < \frac{x}{y} < \frac{1}{g} \frac{k'_{1A2}}{k'_{1B2}}. \quad (2.49)$$

Therefore, in prolonged experiments the x/y ratio can change by as much as 50%. This range (50%) is rather wide in comparison with the experimental error of measuring the thickness of the layers, which is known to be 5 to 25% of the average value. Therefore, in this case a gradual change in the ratio of the thicknesses of the AB and AB_2 layers during their diffusional growth can readily be noticed, if the time of observation is not too short.

For the AB_4 and AB_5 compounds,

$$\frac{4}{5g} \frac{k'_{1A2}}{k'_{1B2}} < \frac{x}{y} < \frac{1}{g} \frac{k'_{1A2}}{k'_{1B2}}. \quad (2.50)$$

Thus, in the course of diffusional growth of the AB_4 and AB_5 layers the x/y ratio varies only by 20%. Taking into account the limited duration of any experiment, it must be clear that in practice the change of the x/y ratio is much less and therefore can hardly be noticed, especially if the researcher is not aware of its probable existence. This explains why it is often assumed that $x/y = \text{const}$. In fact, the latter is nothing more than an approximation, though sufficiently substantiated in some particular cases.

From the system of equations (2.46), it follows that the layers of the A_pB_q and A_rB_s compounds already present in an $A-A_pB_q-A_rB_s-B$ specimen should not necessarily simultaneously grow during its further isothermal annealing. If their initial thicknesses, x_0 and y_0 , are such that, for example, the derivative $(dx/dt)_{t=t_0}$ is negative and the derivative $(dy/dt)_{t=t_0}$ is positive, then the thickness of the A_pB_q layer will decrease, while the thickness of the A_rB_s layer will increase until the x/y ratio falls into the range defined by inequality (2.48). Subsequently, both layers will grow simultaneously.

Thus, the $y - x$ phase plane [31, 227, 228] is divided into three regions, as shown schematically in Fig. 2.14. In regions I and III the thickness of one of the layers increases and that of the other decreases. In region II the thickness of both layers increases.

Region I is separated from region II by the nodal line

$$y = \frac{sgk'_{1B2}}{qk'_{1A2}} x. \quad (2.51)$$

To obtain this equation, it suffices to put $dx/dt = 0$ in equation (2.46₁).

The nodal line between regions II and III is the straight line

$$y = \frac{rgk'_{1B2}}{pk'_{1A2}}x, \quad (2.52)$$

which is obtained from equation (2.46₂) by putting $dy/dt = 0$.

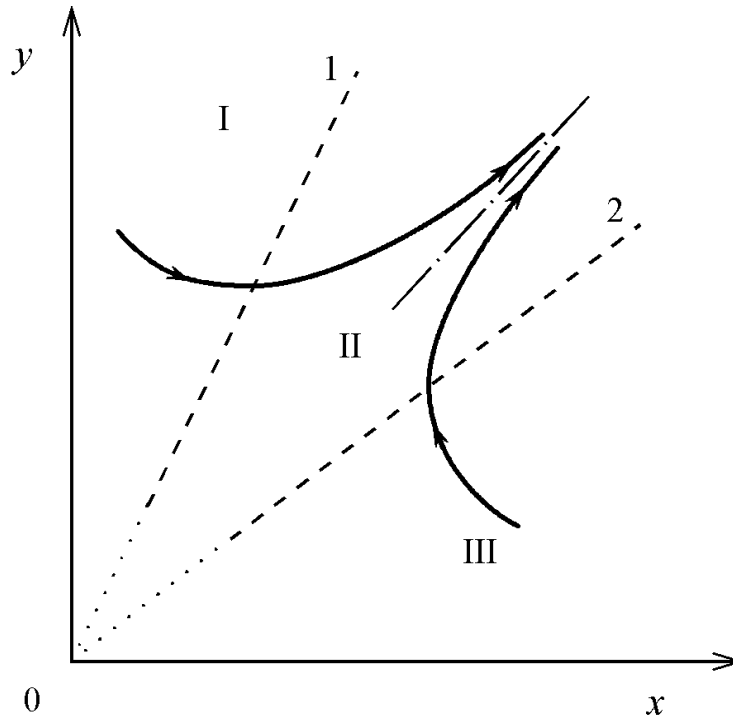


Fig. 2.14. The $y - x$ phase plane in the late diffusional stage of formation of two compound layers. The nodal lines 1 and 2 separate the phase plane into three regions. In regions I and III the thickness of one of the layers increases, while that of the other decreases. In region II both layers grow simultaneously. The arrows at phase trajectories indicate the direction of variation of the layer thicknesses with increasing time.

If the initial thicknesses of the A_pB_q and A_rB_s layers correspond to any point in region I, then with passing time the A_pB_q layer will grow, whereas the A_rB_s layer will shrink until the phase trajectory indicating the direction of growth enters region II in which both layers will grow. If these thicknesses correspond to any point in region III, then the A_rB_s layer will grow, whereas the A_pB_q layer will shrink until again the phase trajectory enters region II where both layers will grow. If the initial thicknesses of the A_pB_q and A_rB_s layers correspond

to any point in region II, then the A_pB_q and A_rB_s layers will grow simultaneously from the very beginning of isothermal annealing of an $A-A_pB_q-A_rB_s-B$ specimen.

Both trajectories are seen in Fig. 2.14 to tend asymptotically with increasing time to a straight line corresponding to a constant ratio of the layer thicknesses. Whenever these are sufficiently close to this line, the parabolic growth law becomes a good approximation for both layers and therefore can be employed to treat the experimental kinetic data.

During the natural course of the process of formation of the A_pB_q and A_rB_s layers between elementary substances A and B when an $A-B$ specimen is given to itself at constant temperature and pressure, a correct ratio of their thicknesses is established automatically. However, if an $A-A_pB_q-A_rB_s-B$ specimen was prepared artificially, this ratio can hardly be expected to be correct. Therefore, during subsequent isothermal annealing of the specimen, one of the layers will shrink and can even disappear as occurred before its turn if, of course, by that time the other layer has not reached a minimal thickness required for the former to occur. Such a phenomenon was observed, for example, by G. Ottaviani and M. Costato [76] with the PtSi layer in Pt-Pt₂Si-PtSi-Si specimens and by K.N. Tu *et al.* [82] with the CoSi layer in Co-Co₂Si-CoSi-Si specimens.

G. Ottaviani and M. Costato [76] have investigated the process of compound formation at the platinum-silicon interface. Platinum films, 115, 205, 268 and 357 nm thick, were sputtered on Si(111) single crystals under hard vacuum. The interaction of the Pt and Si phases during isothermal annealing was followed using Rutherford backscattering spectroscopy of helium ions.

It seems relevant to remind that this technique is based on recording the backscattered light (usually helium) ions occurred as a result of their interaction with the matter of a solid layered specimen (for more detail, see Ref. [126]). Experimental data are presented as plots of intensity, I , against energy, E , of the beam of backscattered ions (Fig. 2.15).

For sufficiently thin films, the loss, ΔE , in energy of helium ions is directly proportional to the thickness, x , of the layer of a given substance: $\Delta E = N\varepsilon x$, where N is the number of atoms of an element in question per unit volume of the substance and ε characterises its stopping power for helium ions. As the scattering processes in solids have been studied rather well, it is possible to determine fairly accurately the thickness of the layer of a given phase from the loss in energy of the ions. Note that in order to establish the layer-growth law, there is no need to carry out the energy to thickness conversion. It is sufficient to represent the experimental data as plots of either ΔE against t in the linear region or $(\Delta E)^2$ against t in the parabolic region.

After annealing at 325 °C for 5 min, the Pt₂Si layer, about 98 nm thick, was formed in all four initial specimens. During its growth for 10 min, the platinum layer, 115 nm thick, was consumed. Therefore, the first specimen transformed into the Pt₂Si-Si(111) one. The layer of the PtSi compound started to grow in this specimen. The same sequence of the growth processes was also observed in other Pt-Si (111) specimens but after longer annealing times

because the thickness of the platinum layers in those specimens was greater. Simultaneous growth of the layers of the Pt_2Si and PtSi compounds was not observed.

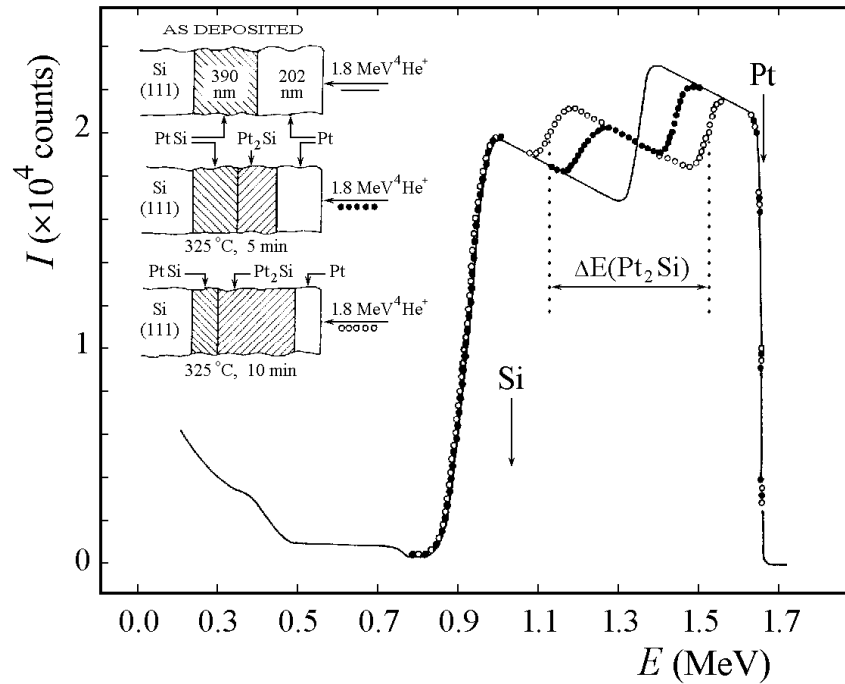


Fig. 2.15. Scheme of formation of silicide layers and a spectrogram of Rutherford backscattering of helium ions with an initial energy of 1.8 MeV in a Pt–Pt₂Si–PtSi–Si(111) specimen. The figure from the work by G. Ottaviani and M. Costato [76]. Reprinted with permission from Elsevier Science.

In the case under consideration, the most instructive results were obtained by G. Ottaviani and M. Costato on Pt–PtSi–Si(111) specimens. To prepare these, a platinum layer, 202 nm thick, was additionally deposited on the top of the PtSi layer with a thickness of 390 nm in the PtSi–Si(111) specimens. During annealing at the same temperature 325 °C, the Pt_2Si layer grew, whereas the PtSi and Pt layers shrunk, with the silicon atoms from the single-crystal Si(111) substrate taking no part in the phase interaction. Similar results were obtained by K.N. Tu *et al.* [82] on Co–Co₂Si–CoSi–Si specimens in which the growing phase was Co₂Si, with CoSi disappearing.

It should be noted that the indifference of the silicon layer and the disappearance of the CoSi layer in the Co–Co₂Si–CoSi–Si system and also of the PtSi layer in the Pt–Pt₂Si–PtSi–Si system cannot be explained from a diffusional viewpoint. Indeed, according to the diffusional theory, the existing CoSi and PtSi layers should have grown parabolically. Evidently, their growth could not proceed without the participation of silicon atoms from the substrate.

From a physico-chemical viewpoint [145-155], it is clear that, since the Co₂Si layer is the first to form in the Co–Si couple, the CoSi layer cannot grow in the Co–CoSi–Si specimens until the Co₂Si layer has reached a minimal necessary thickness. The CoSi phase is a reactant in the process of growth of the Co₂Si layer and therefore is gradually consumed until its complete disappearance. When the Co₂Si layer reaches the minimal necessary thickness, the CoSi layer can clearly re-appear and grow in the Co–Co₂Si–CoSi–Si system.

Thus, the explanation of this phenomenon lies in the ratio of the thickness of the CoSi and Co₂Si layers. In the natural course of the growth process, when both layers simultaneously grow in the Co–Si couple during prolonged isothermal annealing in the presence of sufficient amounts of cobalt and silicon, the Co₂Si layer is thicker than the CoSi layer. In artificially prepared Co–CoSi–Si specimens, the Co₂Si layer is either missing (in the initial state) or very thin (after short annealing), and the ratio of layer thicknesses is thus incorrect. Silicon from the Si substrate is indifferent only in the latter case, whereas in the former it is consumed during growth of the CoSi layer.

It should be emphasised that under conditions of diffusion control the Co₂Si layer grows in Co–Co₂Si–CoSi–Si specimens at the expense of diffusion across its bulk of only cobalt atoms and their subsequent partial chemical reaction with the CoSi compound at the Co₂Si–CoSi interface, while the CoSi layer grows at the expense of diffusion across its bulk of only silicon atoms and their subsequent partial chemical reaction with the Co₂Si compound at the same interface. This is due solely to the absence of a source of appropriate atoms (Si for Co₂Si and Co for CoSi), without any connection with the mobility of silicon atoms in the Co₂Si lattice or of cobalt atoms in the CoSi lattice, when each of these compounds is taken alone.

The same applies to Pt–Pt₂Si–PtSi–Si specimens. Under conditions of diffusion control the Pt₂Si layer grows only at the expense of diffusing platinum atoms, while the PtSi layer grows only at the expense of diffusing silicon atoms, though in those compounds taken alone both components may well happen to diffuse at close rates.

The exact law of growth of the layers of two chemical compounds in the late diffusional stage of their formation can be found, at least in principle, by solving the system of equations (2.46) with initial conditions $x = x_0$ and $y = y_0$ ($x_0 > 0$, $y_0 > 0$) at $t = 0$ (or $t = t_0$) without any additional assumptions. Indeed, dividing the second equation by the first yields an equation of the type $dy/dx = f(x, y)$. By solving this equation, y is obtained as a function of x . By substituting this dependence into equation (2.46₁), the expression $dx/dt = f(x)$ is

obtained. Its integration gives x as a function of t . It is then possible to determine the $y - t$ dependence from equation (2.46₂).

Unfortunately, every stage of finding the solution to the system of differential equations (2.46) leads to very complicated expressions. Therefore, the final result can hardly be represented in the form of a single simple function. However, these difficulties are not a serious obstacle for practical applications of the system of equations (2.46).

Indeed, the derivatives dx/dt and dy/dt at $t = t_i$ can readily be determined (for example, by graphic differentiation or any other means) from the experimental data. Then, the system (2.46) transforms into an ordinary system of algebraic equations containing two unknown quantities k'_{1A2} and k'_{1B2} :

$$\left(\frac{dx}{dt}\right)_{t=t_i} = \frac{k'_{1A2}}{x_i} - \frac{rg}{p} \frac{k'_{1B2}}{y_i}, \quad (2.53_1)$$

$$\left(\frac{dy}{dt}\right)_{t=t_i} = \frac{k'_{1B2}}{y_i} - \frac{q}{sg} \frac{k'_{1A2}}{x_i}. \quad (2.53_2)$$

Therefore, an attempt can be undertaken to describe the experimental dependence of the thickness of the layers upon time in terms of the diffusional constants k'_{1A2} and k'_{1B2} . If these prove to be indeed constant at all experimental values of the thicknesses of the A_pB_q and A_rB_s layers, then the system of equations (2.46) describes properly the process of growth of two chemical compound layers. Otherwise, this portion of the layer thickness-time dependence appears to be not purely diffusional, and use must be made of other mathematical equations giving a more adequate fit to the experimental data.

It is clear that in general the kinetic dependences considered in this chapter gradually transform into each other with passing time. In contrast to the diffusional theory, the physico-chemical approach thus gives a more complicated, not simply parabolic, relationship between the thickness of two chemical compound layers and the time, in accordance with the available experimental data in binary systems.

Note that the unjustified neglect of the step of chemical transformations in analysing the process of growth of two compound layers immediately leads to the loss of a few growth laws (linear, parabolic, asymptotic, *etc.*). Also, spreading the consequences following from diffusional equations into the region of small layer thicknesses, to which these are inapplicable at all, results in the misleading conclusion about the simultaneous beginning of parabolic growth of both layers in any binary system with two chemical compounds on the equilibrium phase diagram.

In application to chemical compounds, both the diffusional and physico-chemical theories consider the rate of chemical transformations (chemical reaction) in the late diffusional stage of layer formation as very high compared to that of diffusion. But the conclusion made from

this *quite correct* premise in the framework of diffusional considerations is *quite incorrect*, namely, the (rapid) step of chemical transformations is considered as non-existing at all.

In fact, chemical transformations taking place at the interfaces between reacting phases are responsible for the occurrence of the barriers to diffusing atoms at the critical values of the thickness of the A_pB_q and A_rB_s layers. Their rate is also decisive in determining the sequence of formation of the layers of those compounds in the A – B reaction couple.

Actually, the rate of chemical transformations affects the rate of growth of the layers at all stages from the start of the interaction of initial substances to the establishment of equilibrium in the system. The widespread opinion according to which the chemical transformations have no effect on the layer-growth kinetics, except in a very short initial period of time, is thus quite groundless.

As long as the components A and B are insoluble in each other and in the compounds A_pB_q and A_rB_s , equilibrium can only be established by means of sequential consumption of initial phases. After the substance A or B has been completely consumed, either A_pB_q or A_rB_s becomes another initial substance. Depending on the relative amounts of initial substances A and B , the following phases can remain in the equilibrium state:

- (i) substance A and adjacent layer A_pB_q ,
- (ii) substance B and adjacent layer A_rB_s ,
- (iii) layers of A_pB_q and A_rB_s ,
- (iv) layer of either A_pB_q or A_rB_s .

It should be noted that in general any inert marker only indicates the diffusing species in that compound layer in which it is embedded or with which it borders. From Fig. 2.12, it must be clear that in the case of two compound layers it is necessary to have inert markers inside *both* layers to *directly* decide of the diffusing species in their bulks. Indeed, the fact that the distance between any marker located within the A_rB_s layer growing under conditions of diffusion control and interface 3 remains unchanged, while the distance between this marker and interface 2 steadily increases in the course of reaction means that component B is the only diffusing species in *this* layer and nothing more, though component B is often regarded to be the main diffusing one in *both* layers. The latter conclusion is incorrect. The very presence of the A_pB_q layer growing under conditions of diffusion control provides *indirect* evidence that component A is the *only* diffusing species in this layer since it cannot grow at the expense of diffusion of the B atoms in view of their lack.

Evidently, in the course of layer formation the plane of inert markers cannot coincide with the initial interface between substances A and B . It would mean that compound layers could grow at the expense of *one* component. Chemically, this is impossible since any binary compound consists of two components. Position of the layers relative to the initial interface is mainly dependent upon the stoichiometry of chemical compounds, if both ends of a couple

are equally free to move. Coincidence of initial and marker planes provides evidence for the lack of contact between reacting phases at that place.

It must also be clear that in the case of two compound layers, even growing under conditions of diffusion control, the calculation of integrated diffusion coefficients produces fictitious, physically intractable quantities since the real mechanism of layer formation [1, 48, 49, 146-155] has little in common with the assumptions made when introducing the concept of an integrated diffusion coefficient and deriving basic mathematical equations [5, 50]. In fact, there is no *interdiffusion* during diffusional growth of two compound layers, with only *one* component diffusing across each layer. Any concentration-distance curve like that shown in Fig. 2.1 may of course be divided into two regions of equal area to formally define the Matano interface, but such a division can hardly be considered as sufficiently substantiated.

2.8.3: Simultaneous diffusional growth of the Al_3Mg_2 and $Al_{12}Mg_{17}$ intermetallic layers between aluminium and magnesium

Consider the results obtained by E.M. Tanguet Njiokep *et al.* [232] with Al–Mg couples as an example of diffusional parabolic growth kinetics. Consideration will mainly be restricted to a temperature of 400 °C, at which two intermetallic compounds, Al_3Mg_2 (also designated Al_8Mg_5) and $Al_{12}Mg_{17}$, are known to exist and which is much below both eutectic temperatures [157, 159, 231].

Polycrystalline aluminium (99.98 % Al) and magnesium (99.9 % Mg) rods were used as starting materials, of which discs, 6 mm in diameter and about 3 mm thick, were cut. A couple of discs was placed in a stainless steel holder and pressed together by screws to ensure intimate contact between polished faces.

Diffusion couples were encapsulated in quartz ampoules filled with argon. Their annealing was carried out in electric-resistance furnaces, with the temperature deviations from the required value not exceeding ± 1 °C. After annealing, the couples were cut along the cylindrical axis and polished mechanically. The cross-sections obtained were studied metallographically. An ARL electron probe microanalyser was employed to determine both the concentration profiles and the contents of the components in intermetallic layers formed.

Both intermetallic compound layers, Al_3Mg_2 and $Al_{12}Mg_{17}$, were found to grow simultaneously at the interface between aluminium and magnesium. A schematic diagram to illustrate their growth process is shown in Fig. 2.16a, while the microstructure of the Al–Mg transition zone in Fig. 2.16b.

Formation of the layers is likely to be due to partial chemical reactions



and



taking place at their common interface 2.

As seen in Fig. 2.17, the Al_3Mg_2 layer grows much faster than the $\text{Al}_{12}\text{Mg}_{17}$ layer, though the diffusional theory [5, 22] predicts the opposite relationship since the homogeneity range of Al_3Mg_2 is at least five times less than that of $\text{Al}_{12}\text{Mg}_{17}$. This provides additional support to the conclusion of Chapter 1 about the lack of direct proportionality between the rate of formation of a chemical compound and the width of its homogeneity range.

The layer-growth kinetics were found to be parabolic for both compounds (Fig. 2.18), indicative of diffusion control. This result could be expected since the layer thickness varied from about 10 μm to 300 μm for the $\text{Al}_{12}\text{Mg}_{17}$ intermetallic compound and from about 80 μm to more than 900 μm for the Al_3Mg_2 intermetallic compound.

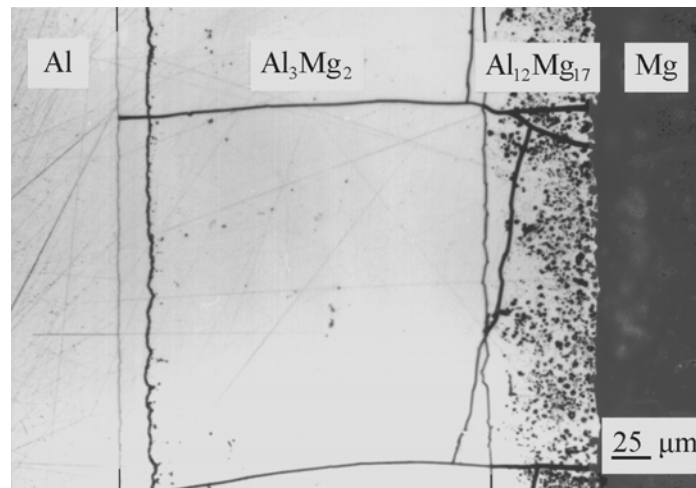
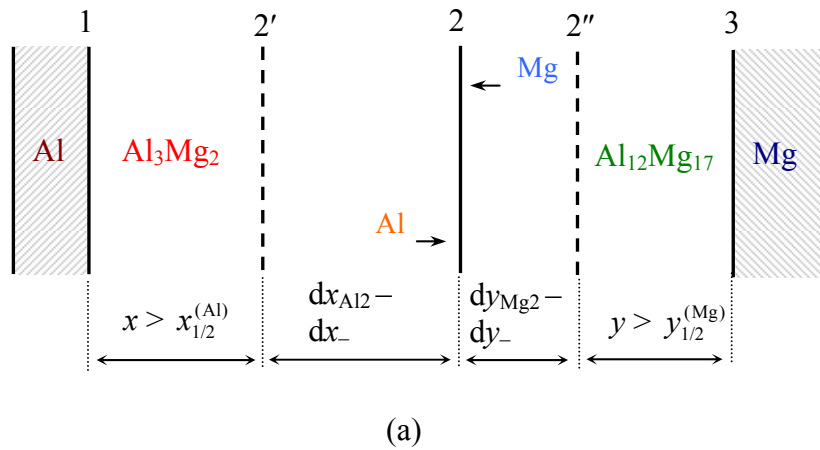


Fig. 2.16. Schematic diagram to illustrate the diffusional stage of the growth process of the Al_3Mg_2 and $\text{Al}_{12}\text{Mg}_{17}$ intermetallic compound layers (a), and microstructure of the transition zone between aluminium and magnesium after isothermal annealing at 400 °C for 172800 s (48 h) [232] (b). Photograph kindly provided by Prof. H Mehrer.

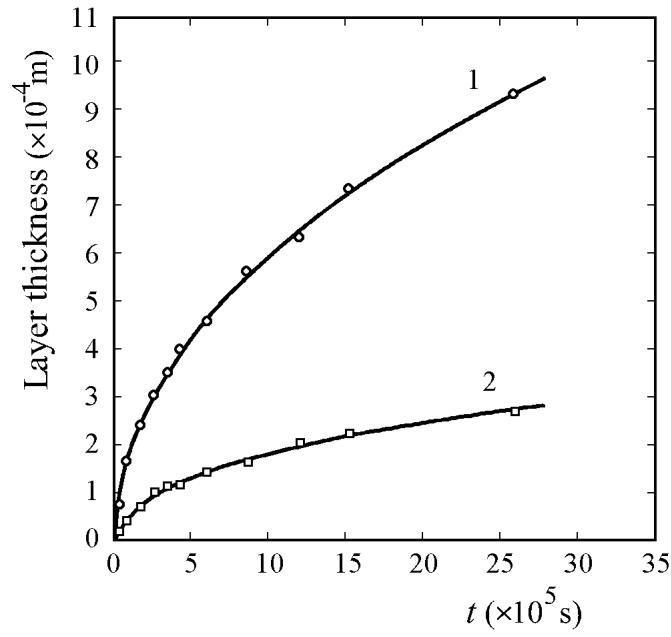


Fig. 2.17. Plots of layer thickness against annealing time of Al–Mg diffusion couples at 400 °C according to the data of E.M. Tanguép Njiokep *et al.* [232]. 1, Al_3Mg_2 ; 2, $\text{Al}_{12}\text{Mg}_{17}$.

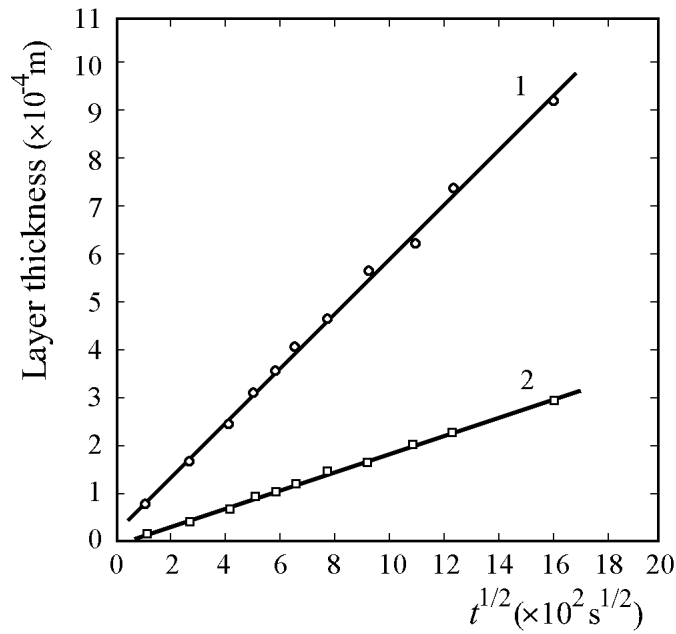


Fig. 2.18. Plots of layer thickness against the square root of the annealing time of Al–Mg diffusion couples at 400 °C according to the experimental data of E.M. Tanguép Njiokep *et al.* [232]. 1, Al_3Mg_2 ; 2, $\text{Al}_{12}\text{Mg}_{17}$.

Diffusional constants were calculated using parabolic equations of the type $x^2 = 2k_1t$. The temperature dependence of the diffusional constants was found by E.M. Tanguiep Njiokep *et al.* [232] to obey the Arrhenius relation:

$$k_1^{(\text{Al}_3\text{Mg}_2)} = 3.5 \times 10^{-8} \exp(-69 \text{ kJ mol}^{-1} / RT) \text{ m}^2 \text{ s}^{-1}, \quad (2.55_1)$$

$$k_1^{(\text{Al}_{12}\text{Mg}_{17})} = 0.1 \exp(-165 \text{ kJ mol}^{-1} / RT) \text{ m}^2 \text{ s}^{-1}. \quad (2.55_2)$$

Treatment of the experimental data on the layer-growth kinetics in the Al–Mg system with the use of the system of equations (2.46), which in this case assumes the form

$$\left(\frac{dx}{dt} \right)_{t=t_i} = \frac{k_{1\text{Al}_2}}{x_i} - \frac{rg}{p} \frac{k_{1\text{Mg}_2}}{y_i}, \quad (2.56_1)$$

$$\left(\frac{dy}{dt} \right)_{t=t_i} = \frac{k_{1\text{Mg}_2}}{y_i} - \frac{q}{sg} \frac{k_{1\text{Al}_2}}{x_i}, \quad (2.56_2)$$

and in which the strokes were omitted for simplicity, yields the following results [233].

Evaluation of the diffusional constants $k_{1\text{Al}_2}$ and $k_{1\text{Mg}_2}$ was first carried out directly using initial experimental values of layer thicknesses at a temperature of 400 °C, listed in Table 2.1. Those were read from a graph, shown in Fig. 2.17, because tabulated values are lacking in the work of Tanguiep Njiokep *et al.* [232]. From the chemical formulae of the Al_3Mg_2 and $\text{Al}_{12}\text{Mg}_{17}$ compounds, $p = 3$, $q = 2$, $r = 12$ and $s = 17$. The value of g was estimated from the densities of these compounds [231, 234] and their molecular masses as 0.94.

The derivatives, dx/dt and dy/dt , at each value of time, t_i , were found by the numerical three-point method using a conventional computer program (linear approximation). To find a derivative for any given experimental point, (x_i, t_i) , of Fig. 2.17, data for its two neighbouring points, (x_{i-1}, t_{i-1}) and (x_{i+1}, t_{i+1}) , were used. Left-hand and right-hand derivatives, $(x_i - x_{i-1})/(t_i - t_{i-1})$ and $(x_{i+1} - x_i)/(t_{i+1} - t_i)$, were first found for this point and their mean value was then calculated. The derivatives could thus be found for all experimental points, excepting clearly end ones, for which a neighbouring point is lacking.

The results of calculations are presented in Table 2.1. The average value of $k_{1\text{Al}_2}$ was determined to be $4.49 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ and that of $k_{1\text{Mg}_2}$ $9.41 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. As seen in Table 2.1, the accuracy of calculations of $k_{1\text{Al}_2}$ and $k_{1\text{Mg}_2}$ are strongly dependent upon a scatter of experimental points. To avoid the effect of this scatter on final results, approximation of the experimental data with any suitable analytical function is therefore advisable.

Table 2.1. Evaluation of diffusional constants k_{1Al2} and k_{1Mg2} from the system of equations (2.56) for the Al_3Mg_2 and $Al_{12}Mg_{17}$ intermetallic layers at a temperature of 400 °C [233] using the initial experimental data of Tanguiep Njiokep *et al.* [232]

$t (\times 10^3 \text{ s})$	$x (\times 10^{-4} \text{ m})$	$y (\times 10^{-4} \text{ m})$	$k_{1Al2} (\times 10^{-13} \text{ m}^2 \text{ s}^{-1})$	$k_{1Mg2} (\times 10^{-14} \text{ m}^2 \text{ s}^{-1})$
30	0.58	0.03	-	-
75	1.58	0.18	5.06	4.71
170	2.43	0.53	4.70	9.32
255	3.08	0.88	4.84	12.10
340	3.63	0.98	4.40	9.26
425	4.13	1.03	4.11	8.42
600	4.78	1.33	4.13	9.77
865	5.93	1.53	4.27	9.38
1205	6.73	1.98	4.40	11.20
1525	7.88	2.23	4.53	10.50
2596	10.00	2.73	-	-

Average values: $k_{1Al2} = 4.49 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, $k_{1Mg2} = 9.41 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$.

For example, the use of parabolic relations $x^2 = 2k_1t$ and equations (2.55), with the parabolic constant $k_1 = 1.57 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for the Al_3Mg_2 compound and $k_1 = 1.63 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ for the $Al_{12}Mg_{17}$ compound at a temperature of 400 °C, to approximate the layer thickness–time dependences and then to find the derivatives, yields another set of values of k_{1Al2} and k_{1Mg2} (Table 2.2). Since the experimental dependences become smoothed as a result of this procedure (solid lines of Fig. 2.17), all values of k_{1Al2} ($k_{1Al2} = 3.40 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$) thus found are identical. The same applies to k_{1Mg2} ($k_{1Mg2} = 9.37 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$).

Comparing these with the average values of k_{1Al2} and k_{1Mg2} found numerically from the experimental points by direct calculations, it may be concluded that both sets of the constants agree fairly well, providing evidence for the validity of the analytical treatment employed. Physically, the value of k_{1Al2} thus obtained is the reaction-diffusion coefficient, D_{Al} , of aluminium atoms in the Al_3Mg_2 compound lattice, whereas the value of k_{1Mg2} is the reaction-diffusion coefficient, D_{Mg} , of magnesium atoms in the $Al_{12}Mg_{17}$ compound lattice in the course of simultaneous growth of both compounds.

As the melting points of aluminium (660 °C) and magnesium (651 °C) are very close, the large difference in growth rates of the Al_3Mg_2 and $Al_{12}Mg_{17}$ intermetallic compound layers appears to be due to the difference in atomic radii of those elements. The atomic radius of aluminium (0.143 nm) is less than that of magnesium (0.160 nm) [166, 167]. Therefore, the Al_3Mg_2 layer growing at the expense of diffusion of smaller aluminium atoms can reasonably be expected to grow faster compared to the $Al_{12}Mg_{17}$ layer growing at the

expense of diffusion of greater magnesium atoms. Note that both intermetallic compounds have similar (cubic) structures.

Table 2.2. Evaluation of diffusional constants k_{Al_2} and k_{Mg_2} from the system of equations (2.56) for the Al_3Mg_2 and $\text{Al}_{12}\text{Mg}_{17}$ intermetallic layers at a temperature of 400 °C [233] using the smoothed experimental data of Tanguiep Njiokep *et al.* [232]

$t (\times 10^3 \text{ s})$	$x (\times 10^{-4} \text{ m})$	$y (\times 10^{-4} \text{ m})$	$k_{\text{Al}_2} (\times 10^{-13} \text{ m}^2 \text{ s}^{-1})$	$k_{\text{Mg}_2} (\times 10^{-14} \text{ m}^2 \text{ s}^{-1})$
30	0.97	0.31	3.40	9.37
75	1.54	0.49	3.40	9.37
170	2.31	0.74	3.40	9.37
255	2.83	0.91	3.40	9.37
340	3.27	1.05	3.40	9.37
425	3.66	1.18	3.40	9.37
600	4.34	1.40	3.40	9.37
865	5.21	1.68	3.40	9.37
1205	6.15	1.98	3.40	9.37
1525	6.92	2.23	3.40	9.37
2596	9.03	2.91	3.40	9.37

Average values: $k_{\text{Al}_2} = 3.40 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, $k_{\text{Mg}_2} = 9.37 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$.

The Al–Mg binary system is worth further investigation, especially in the region of non-parabolic layer-growth kinetics. Marker experiments are also desirable, with inert markers embedded in both intermetallic layers, to reveal directly the contributions of the components Al and Mg to the growth process of the Al_3Mg_2 and $\text{Al}_{12}\text{Mg}_{17}$ intermetallic compound layers.

2.9: Formation of boride layers at the interface of boron with Fe–Cr alloys

In many practical applications, specific physical, chemical or mechanical properties are only needed for a thin surface layer, a few tens of nanometres to a few tens of micrometres thick, while the main body of a part may be from a low-cost ordinary metal, alloy or steel. Boriding (or boronising) is one of thermochemical surface treatments aimed at improving service characteristics of metals, alloys and steels [235-240]. This kind of treatment provides a very high increase in resistance to abrasion, wear and corrosion, with a negligible change in dimensions of the original part. A variety of borided parts are routinely manufactured, from pipe fittings to impeller gears to critical aerospace components.

Iron borides FeB and Fe_2B are known to exist in the Fe–B binary system [157, 159, 241, 242], Fig. 2.19. With iron, its alloys and low-alloy steels, one (either FeB or Fe_2B) or two (both FeB and Fe_2B) boride phases can therefore form as separate continuous layers on the surface of a solid substrate, depending on boriding techniques employed and temperature-time conditions of a boriding procedure.

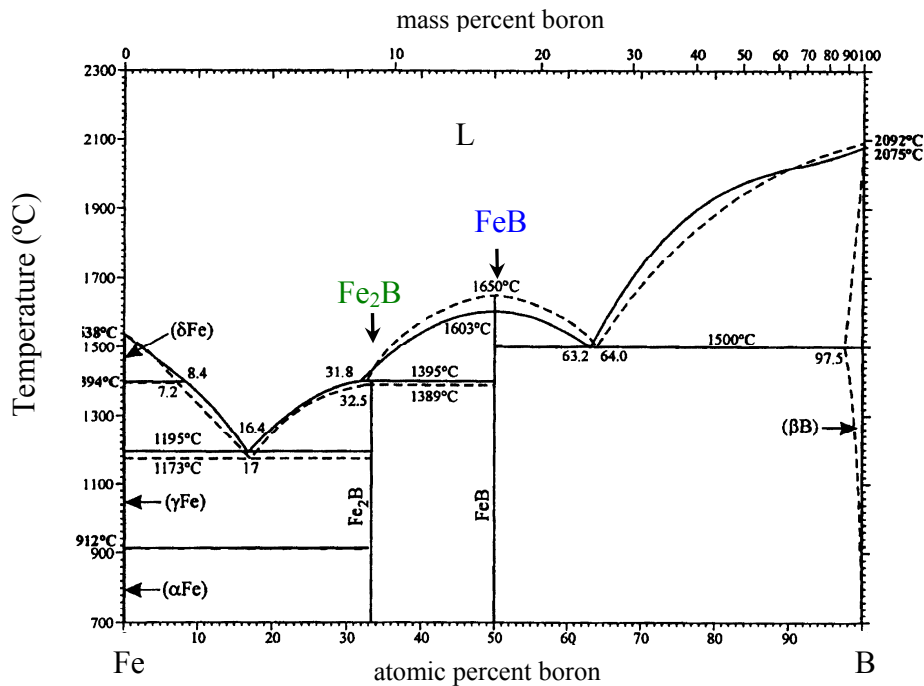


Fig. 2.19. Fe–B binary phase diagram [157, 159, 241, 242].

Physical, chemical, mechanical and other properties of boride layers formed are to a large extent dependent upon the amount of alloying elements and impurities present in the base material. In the case of materials of complicated chemical composition, such as steels or multi-component alloys with which the vast majority of experiments have hitherto been carried out (see, for example, [243–261], it is not always possible to separate the effect of a particular element from that of others. To facilitate this task, experiments with binary iron-based alloys on a systematic basis are therefore desirable.

In this section, comparative data on the interaction of five Fe–Cr alloys (chromium content: 5, 10, 15, 25 and 30 %) and also two industrial steels containing 13 and 25 % Cr with boron in a mixture of amorphous boron powder and KBF_4 (activator) in the temperature range of 850–950 °C are provided [262–269]. Main attention is paid to the mechanism of formation of boride layers and their growth kinetics. Also, the peculiarities of the microstructure of boride layers formed on high-chromium Fe–Cr alloys are discussed.

2.9.1: Experimental procedure and investigation methods

Materials used for the preparation of iron–chromium alloys included carbonyl iron powder (99.98 % Fe) and electrolytic-grade chromium platelets (99.98 % Cr). Reagents were amorphous boron powder (98.3 % B) and analytical-grade KBF_4 .

Cylindrical rods of Fe–Cr alloys were prepared by arc-melting of appropriate metals under argon, with subsequent casting of the melts into water-cooled copper crucibles. The rods were annealed at a temperature of 1100 °C for 2 h in an argon atmosphere at a pressure of 2.5×10^4 Pa to ensure their homogenisation.

Rods (16 mm diameter) of industrial steels (13 and 25 % Cr) were used in the as-received condition (without any additional heat treatment). The content of main components of 13 % Cr steel was 85.2 % Fe, 13.6 % Cr, 0.38 % C, 0.30 % Mn, 0.30 % Si and 0.20 % Ni. 25 % Cr steel contained 72.8 % Fe, 25.2 % Cr, 0.13 % C, 0.50 % Mn, 0.46 % Si, 0.45 % Ni and 0.28 % Ti. The microstructure of the steels consisted of the bodycentred cubic α -phase (ferrite) and fine inclusions of iron and chromium carbides.

Specimens in the form of tablets, 11.28 mm in diameter (1.0 cm² area) and 5.5 mm high, were machined from the Fe–Cr alloy and steel rods. Flat sides of the tablets were ground and polished mechanically.

The vacuum device VPBD-2S employed for boriding the Fe–Cr alloy samples has been described elsewhere [262]. Its experimental cell is shown in Fig. 2.20. Experiments were carried out in an alumina crucible, 13 mm inner diameter and 40 mm high.

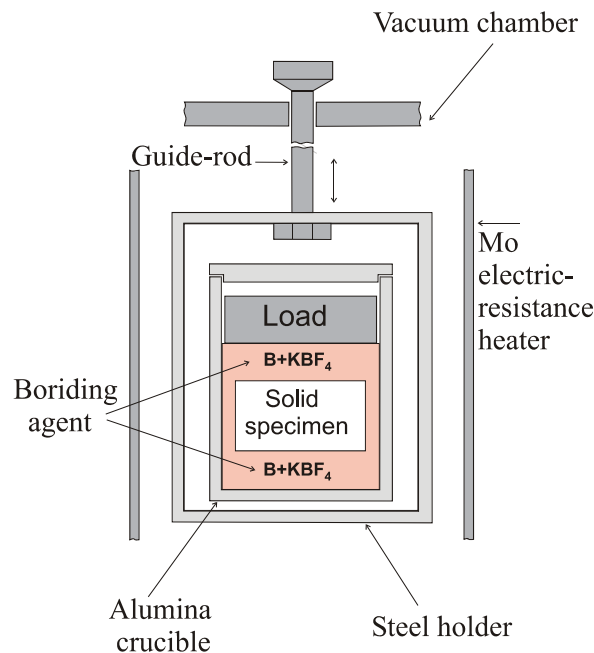


Fig. 2.20. Experimental cell of a device for boriding metals, alloys and steels.

An alloy or steel tablet was embedded into a mixture of boron powder with 5 % KBF_4 as an activator. This amount of KBF_4 appears to be optimum [1, 270]. The mixture was then slightly pressed, and a load of 8.5 g (a low-carbon steel cylinder) was placed on top. The crucible was closed with a low-carbon steel lid and placed into a steel-sheet holder, mounted to a guide rod capable of moving in the vertical direction.

The chamber was pumped to a pressure of about 10 Pa and filled with high-purity argon (99.999 vol.% Ar). This procedure was repeated twice. Then, the chamber was again pumped and filled with argon at a pressure of 2.5×10^4 Pa, and heating was started. During heating, the crucible with its contents was in the cold zone above the furnace. After the required temperature in the range of 850-950 °C had been reached in the furnace, the crucible, pre-heated to about 400 °C, was moved into its middle part.

After an initial drop, the temperature attained its pre-determined value in 4-5 min and was then maintained constant within $\pm 1^\circ\text{C}$ with the help of an automatic thermoregulator VRT-3. The temperature measurements were carried out using a Pt-PtRh thermocouple. The experiments were carried out at temperatures of 850, 900 and 950 °C. Their duration was 3600-43200 s (1-12 h).

After the experiment, the tablet with boride layers was cut along the cylindrical axis into two unequal parts (4 mm and 7 mm) using an electric-spark machine. Its greater part was embedded into a cold-setting epoxy resin and used to prepare a metallographic cross-section. The lesser part was used for X-ray diffraction investigations (plan-view samples).

Characterisation of initial materials and boride layers formed was carried out with the help of metallography, X-ray diffraction (XRD) and chemical analyses (CA), and electron probe microanalysis (EPMA). The thickness of boride layers was evaluated using the pictures obtained on an optical microscope MIM-7 equipped with an HP Photosmart 720 camera. Typically, six pictures were taken at different places of the interface (~ 1 cm long on any cross-section) between the reacting phases. The thickness of each boride layer was calculated by dividing the area occupied by that layer by the length of a region under examination, and the average value of six measurements was found.

Micrographs (backscattered electron images – BEI), contents of boron, iron and chromium in boride layers, and concentration profiles of these elements in the transition zone between reacting phases were obtained using an electron probe microanalyser JEOL Superprobe 733. Boron, iron and chromium standards (≥ 99.99 % each) were employed. Measurements of element contents were treated using a versatile ZAF (atomic number, absorption and fluorescence corrections) program PACM. All three elements (B, Fe and Cr) were determined simultaneously, and the composition was then normalized to 100 %. Non-normalized values usually fall in the range 98-102 %, providing evidence for a rather good accuracy of measurement, especially in view of the huge difference (more than two orders of magnitude) in intensity of radiation from boron and that from iron or chromium.

XRD patterns were taken immediately from the surface of tablet plan-view samples on a DRON-3 apparatus equipped with both a computer and a self-recording potentiometer KSP-4. Use was made of Cu-K α radiation.

When taking the first pattern, no polishing of a borided tablet sample was applied. The as-received flat surface of the tablet was considered to be section 0 of the sample. Then, 10 to 30 μm of the boride layer (depending upon its total thickness) was removed from the flat surface of the tablet by grinding and subsequent polishing, and another X-ray diffraction pattern was taken (section I). This procedure was repeated at a step of 30-50 μm until the base material was reached. Six to eight X-ray diffraction patterns were thus taken on each borided alloy or steel sample.

2.9.2: Microstructure, phase identity and chemical composition of boride layers

As could be expected from the Fe-B phase diagram, two continuous boride layers were found to form at the interface between reacting phases at a temperature of 850, 900 and 950 $^{\circ}\text{C}$ and rather long reaction times (up to 12 h). As evidenced in Fig. 2.21, two types of microstructure were revealed. Their constituent phases were identified by plan-view layer-by-layer X-ray diffraction analysis as shown in Fig. 2.22 for a Fe-30 % Cr alloy [269]. This was then followed by EPMA to find out the chemical composition of boride layers formed.

Comparison of experimental X-ray patterns with the literature data for iron and chromium borides [229, 230, 271-274] showed that in the case of Fe-5 % Cr, Fe-10 % Cr and Fe-15 % Cr alloys and 13 % Cr steel the outer boride layer bordering boron consists of the (Fe,Cr)B phase, whereas the inner boride layer adjacent to the solid substrate consists of the (Fe,Cr) $_2$ B phase (see Fig. 2.23). Each layer is a homogeneous phase, with the average chromium content varying, depending on the initial material, from around 2 to 8 at.% in (Fe,Cr)B and from 4 to 12 at.% in (Fe,Cr) $_2$ B. This is type I of microstructure shown in Fig. 2.21a and c.

Somewhat surprisingly, X-ray diffraction analysis indicated the presence only of the FeB and Fe $_2$ B phases and the absence of any chromium borides, even on the surface of borided Fe-25 % Cr and Fe-30 % Cr alloys and 25 % Cr steel. In view of the relatively high chromium content of these materials, of seven known compounds CrB $_4$, CrB $_2$, Cr $_2$ B $_3$, Cr $_3$ B $_4$, CrB, Cr $_5$ B $_3$ and Cr $_2$ B [275], the formation of at least CrB and Cr $_2$ B could be expected. Also, in this case the microstructure of both boride layers is readily seen in Figs. 2.21b and 2.22 to be two-phase. Nonetheless, even the most strong reflections of CrB (spacing, $d = 0.2350$, 0.1965 and 0.1255 nm) and Cr $_2$ B ($d = 0.2590$, 0.2158 and 0.2043 nm) [229, 230, 272] were missing from all experimental X-ray patterns obtained.

Subsequent microprobe investigations of borided samples used for XRD showed that with this second group of materials the outer boride layer comprises the (Fe,Cr)B and (Cr,Fe)B phases. The inner boride layer consists of the (Fe,Cr) $_2$ B and (Cr,Fe) $_2$ B phases. Both layers have a peculiar network-platelet morphology. This is type II of microstructure shown in Fig. 2.21b and d.

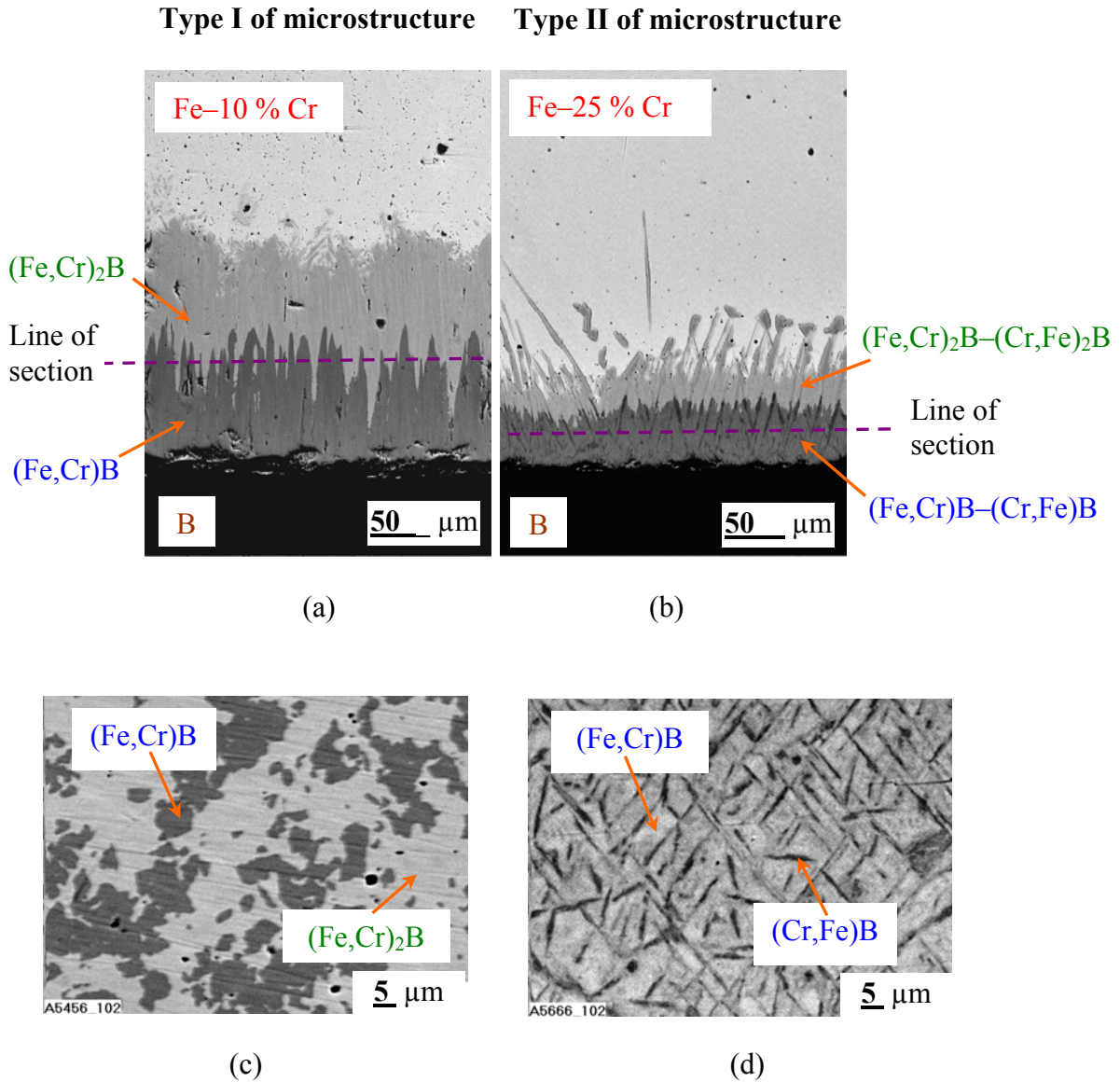


Fig. 2.21. Backscattered electron images (BEI) of the transition zone between reacting phases, (a) and (b), for the two types of microstructure of boride layers and those of plan-view sections crossing (c) both boride layers at the Fe–10 % Cr alloy–boron interface and (d) the outer boride layer at the Fe–25 % Cr alloy–boron interface. Boriding conditions: 950 °C, 21600 s (6 h) [269].

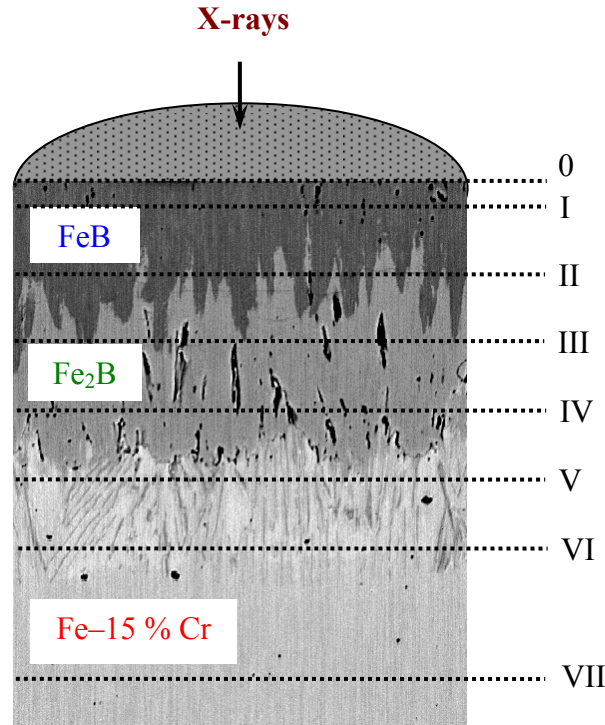


Fig. 2.22. Scheme of X-ray diffraction investigations of a borided Fe–15 % Cr alloy sample. Boriding conditions: 950 °C, 21600 s (6 h). Distance between successive sections of the sample (from top deeper inside its bulk): 10 μm (0-I), 30 μm (I-II), 30 μm (II-III), 30 μm (III-IV), 30 μm (IV-V), 30 μm (V-VI) and 50 μm (VI-VII).

Most probably, presence of the CrB phase in the boride layers can hardly be revealed by XRD or any other method of structural analysis such as electron diffraction because under highly non-equilibrium conditions the lattice rearrangement $\text{FeB} \rightarrow \text{CrB}$ is not completed in view of time limitations. Therefore, part of the iron sites of the FeB lattice, very similar to that of CrB, is simply replaced by chromium atoms, without any structural changes. In other words, the non-equilibrium CrB phase crystallises in the FeB lattice.

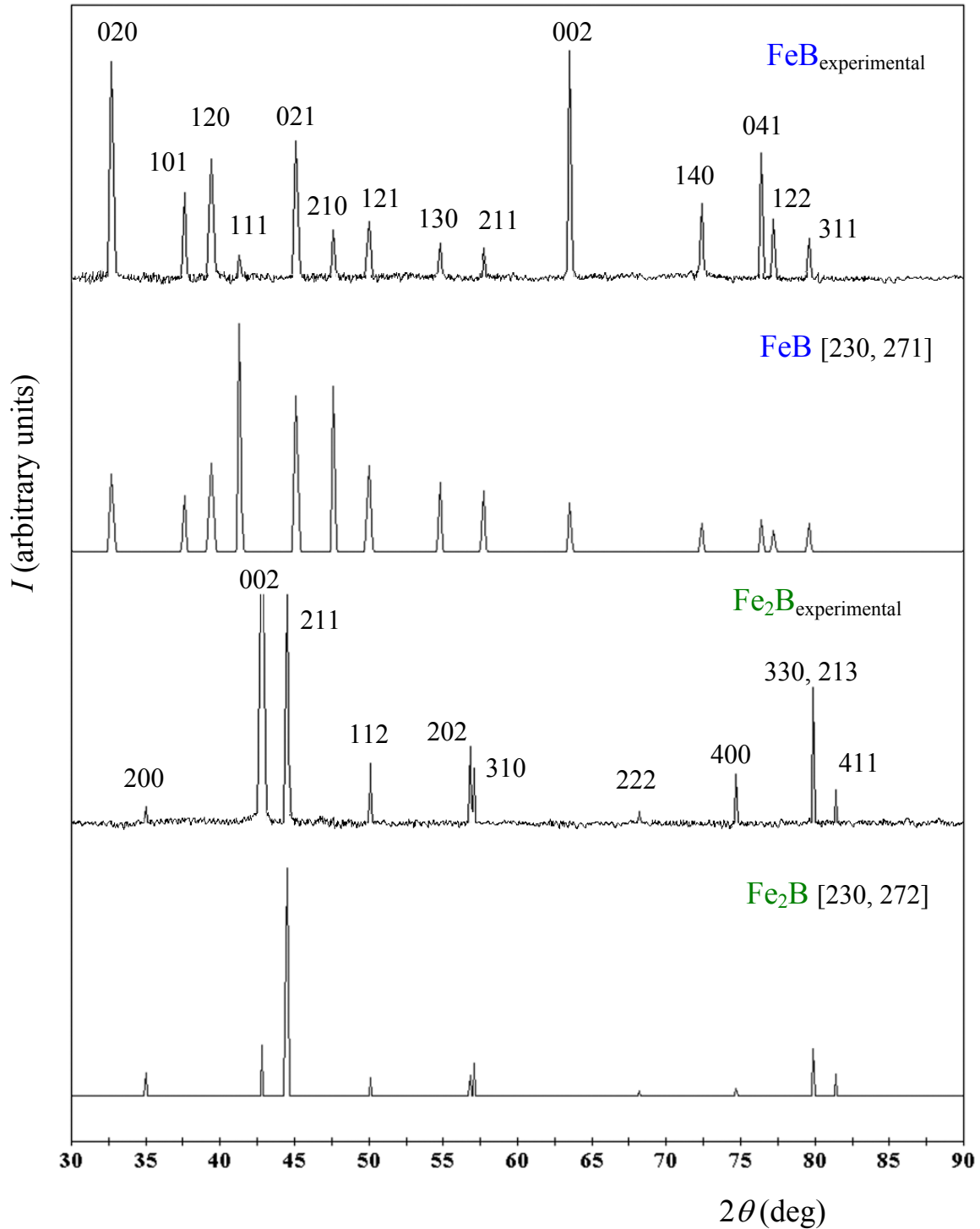


Fig. 2.23. Comparison of experimental X-ray diffraction patterns of the boride layers formed at the Fe–15% Cr alloy–boron interface after boriding at 950 °C for 21600 s (6 h) with the literature data for the FeB and Fe₂B phases [229, 230, 271, 272]. The experimental pattern of the FeB phase was taken from section 0, while that of Fe₂B phase from section IV – see Fig.2.22.

Hence, being far from equilibrium, the outer boride layer appears to be single-phase structurally (crystallographically) and two-phase compositionally (chemically). With materials of complicated chemical composition such as high-alloy steels (including 25 % Cr steel investigated), the two-phase microstructure of the outer boride layer is much less profound. Perhaps, just for these two reasons it was overlooked by previous researchers.

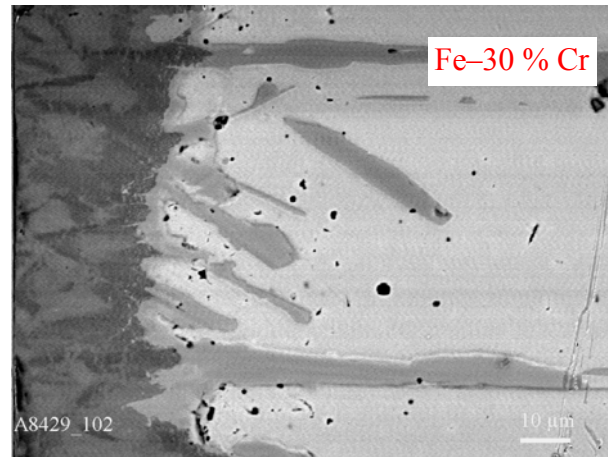
Similar considerations are also applicable to another pair Fe_2B and Cr_2B that are the constituents of the inner boride layer. The backscattered electron image and X-ray maps of iron and chromium shown in Fig. 2.24 and a micrograph of Fig. 2.25 provide additional evidence that both boride layers are indeed two-phase [269]. As an example, average chemical compositions of the constituent phases found by means of EPMA on a number of borided samples are provided in Table 2.3 for a Fe–30 % Cr alloy. Similar results were also obtained for a Fe–25 % Cr alloy [264] and 25 % Cr steel [267]. Therefore, formation of the $(\text{Cr,Fe})\text{B}$ and $(\text{Cr,Fe})_2\text{B}$ phases, readily seen visually in the microstructure of the boride layers occurred on the surface of these materials, can hardly be doubted.

The characteristic feature of the boride layers is a ragged morphology and pronounced texture. This is considered to be a consequence of the existence of paths of enhanced diffusion in the crystal lattices of FeB and Fe_2B [240, 259]. If such paths are not available (close rates of diffusion in all crystallographic directions), flat boride layers are formed (see, for example, [270]).

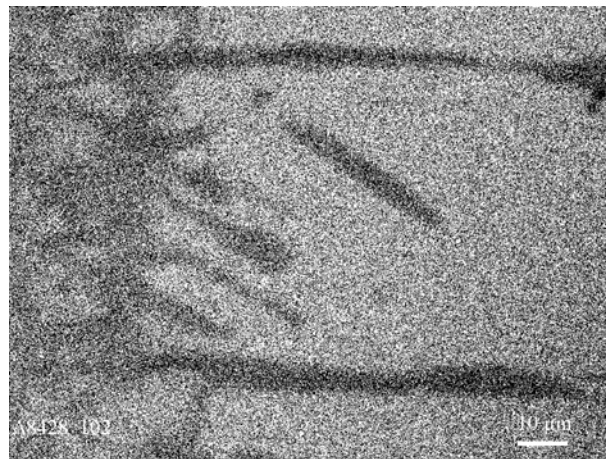
With a Fe–15 % Cr alloy samples, the strongest reflections were found to be $\{002\}$ ($2\theta = 63.1^\circ$ and spacing, $d = 0.1474$ nm) and, to a lesser extent, $\{020\}$ ($2\theta = 32.6^\circ$ and $d = 0.2744$ nm) for the orthorhombic FeB phase, and $\{002\}$ ($2\theta = 42.6^\circ$ and $d = 0.2125$ nm) for the tetragonal Fe_2B phase. The change in intensities of those reflections with increasing distance from the surface of a borided alloy tablet is illustrated schematically for this alloy in Fig. 2.26 as an example [263]. Similar results were obtained with other alloys and steels investigated. It should be noted that with isotropic microcrystalline samples the strongest reflections are $\{111\}$, $\{200\}$ and $\{210\}$ for FeB and $\{211\}$ for Fe_2B [229, 230, 271–274].

As evidenced from Fig. 2.26, the larger orientation order (higher peak intensity) is characteristic of the inner portions of both boride layers compared to their near-interface portions, in agreement with findings of other researchers [235, 246, 254]. This is easily explainable because near-interface portions of any boride layer are less equilibrated compared to its inner portions. Therefore, near-interface crystals have less time to align themselves in the preferred direction of growth.

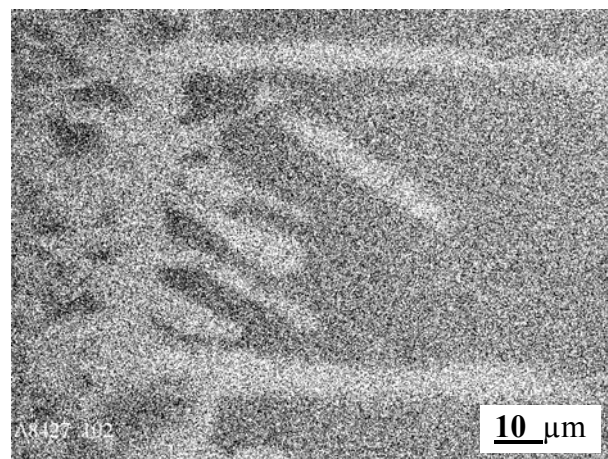
It is worth noting that boride layers with type II of microstructure possess much higher mechanical properties, wear resistance in particular, compared to those with type I of microstructure. The difference in wear resistance amounts to an order of magnitude [269].



BEI



X-ray Fe-K α



X-ray Cr-K α

Fig. 2.24. Cross-sectional backscattered electron image of the transition zone between a Fe–30 % Cr alloy and boron, and X-ray maps for iron and chromium. The brighter the region, the higher is the content of an appropriate element (Fe or Cr). Boriding conditions: 950 °C, 21600 s (6 h) [269].

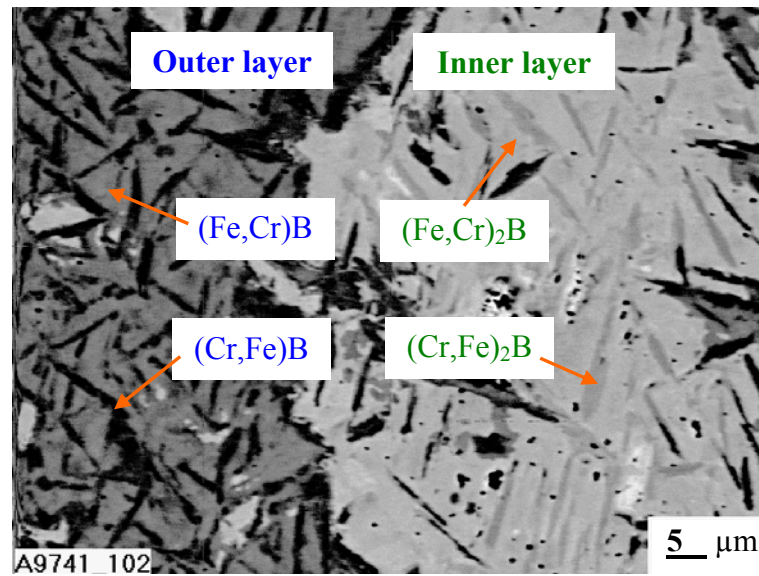


Fig. 2.25. Plan-view micrograph (BEI) corresponding to the second section, crossing both boride layers, for a Fe–30 % Cr alloy sample borided at 850 °C for 43200 s (12 h). The dark area is the outer boride layer. Its brighter regions are the (Fe,Cr)B phase, while the darker regions are the (Cr,Fe)B phase. The bright area is the inner boride layer. Its brighter regions are the (Fe,Cr)₂B phase, while the darker regions are the (Cr,Fe)₂B phase.

Table 2.3. Average Fe, Cr and B contents of boride phases, found by EPMA measurements on borided Fe–30 % Cr alloy samples used for X-ray diffraction investigations (see also Figs 2.22 and 2.25)

Region	Content (%/at.%)			Phase
	Fe	Cr	B	
Brighter of the outer boride layer (see Fig. 2.25)	65.4/38.4	18.0/11.4	16.5/50.2	(Fe,Cr)B
Darker of the outer boride layer	39.8/23.5	44.3/28.1	15.9/48.4	(Cr,Fe)B
Brighter of the inner boride layer	76.9/55.7	14.2/11.1	8.9/33.2	(Fe,Cr) ₂ B
Darker of the inner boride layer	28.1/19.7	62.8/47.3	9.1/33.0	(Cr,Fe) ₂ B

2.9.3: Sequence of formation of boride layers

Figure 2.27 provides evidence that the FeB and Fe₂B layers occur sequentially, with the Fe₂B layer being the first to form [262]. After a 3600 s (1 h) anneal at 950 °C, the FeB layer is seen in Fig. 2.27a to be missing from the Fe–10 % Cr alloy–boron interface, even though the Fe₂B layer has reached a thickness of around 70 µm. It means that a minimal thickness of the Fe₂B layer, necessary for the FeB layer to occur, is rather large, in contrast to the Pd–Al reaction couple where its value does not exceed a few micrometres (see Section 2.4). With a Fe–5 % Cr alloy at the same temperature, a continuous FeB layer is formed when the thickness of the Fe₂B layer exceeds 100 µm. A 3600 s (1 h) anneal in the temperature range of 850–950 °C was found to be sufficient for both boride layers to form on the surface of samples of other alloys and steels investigated.

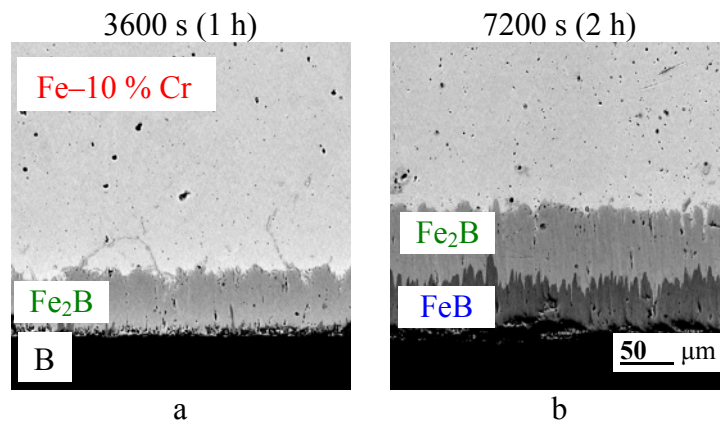


Fig. 2.27. Backscattered electron images (BEI) of the Fe–10 % Cr alloy–boron transition zone at 950 °C. The Fe₂B layer is the first to occur [262].

Initially, the Fe₂B layer can readily grow at the Fe–B interface by direct chemical reaction between the surface iron and boron atoms (Fig. 2.28)



as long as these are in immediate contact with each other.

To simplify the designations and further analytical treatment of kinetic data, iron and chromium will be considered as a single chemical element (Fe). In view of the close similarity of their physico-chemical properties, this simplification does not appear to cause any misleading results.

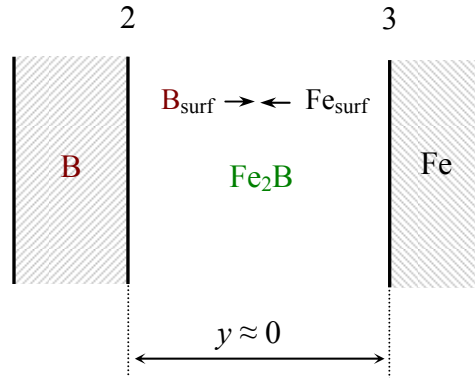


Fig. 2.28. Schematic diagram to illustrate the growth process of the Fe_2B layer by direct chemical reaction between the surface iron and boron atoms.

It is clear, however, that the formation of the Fe_2B layer, even one crystal-lattice thick, separates the reactants from one another, thereby making the further progress of the direct chemical reaction between the surface iron and boron atoms impossible. Subsequently, growth of the Fe_2B layer takes place at the expense of counter-diffusion of iron and boron atoms across its bulk and partial chemical reactions (see Section 1.2)



and



proceeding at the $\text{B}-\text{Fe}_2\text{B}$ and $\text{Fe}_2\text{B}-\text{Fe}$ interfaces, respectively, as shown in Fig. 2.29.

These reactions cause an increase in thickness of the Fe_2B layer during a time dt by $dy_{\text{Fe}_2\text{B}}$ at the former interface and by $dy_{\text{Fe}_2\text{B}}$ at the latter. Note that no reaction can take place between the diffusing iron and boron atoms in the bulk of the growing Fe_2B layer. As pointed out in Section 1.2, any chemical transformations (reactions) proceed entirely at phase interfaces.

After the continuous layers of both iron borides have formed, their subsequent growth under conditions of reaction (chemical) control, when the rate of diffusion of reacting atoms across their bulks exceeds the rate of interfacial transformations, is due to four partial chemical reactions (Fig. 2.30)

Layer	Interface	Reaction	
FeB	1	$\text{Fe}_{\text{dif}} + \text{B}_{\text{surf}} = \text{FeB},$	(2.59 ₁)
	2	$\text{B}_{\text{dif}} + \text{Fe}_2\text{B} = 2\text{FeB},$	(2.59 ₂)
Fe_2B	2	$\text{Fe}_{\text{dif}} + \text{FeB} = \text{Fe}_2\text{B},$	(2.60 ₁)
	3	$\text{B}_{\text{dif}} + \text{Fe}_{\text{surf}} = \text{Fe}_2\text{B}.$	(2.60 ₂)

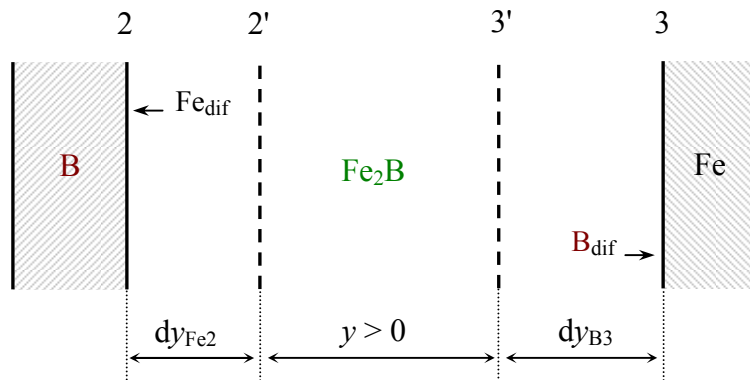


Fig. 2.29. Schematic diagram illustrating the growth process of the Fe_2B layer by partial chemical reactions between the diffusing iron atoms and surface boron atoms at interface 2 and between the diffusing boron atoms and surface iron atoms at interface 3. No reaction takes place between the diffusing iron and boron atoms in the bulk of the growing Fe_2B layer.

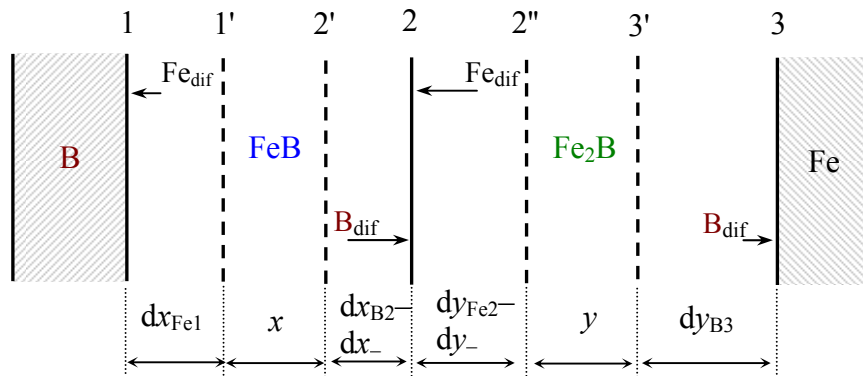


Fig. 2.30. Schematic diagram illustrating the growth process of the FeB and Fe_2B layers under conditions of reaction (chemical) control. Arrows of different length are employed to indicate the decrease in amount of diffusing atoms, available at a particular interface, with increasing distance from a given initial substance (B or Fe).

Both components (Fe and B) are supposed to be capable of diffusing in both layers. As a result of these reactions, the thickness of the FeB layer increases during a time dt by $dx_{\text{Fe}1}$ at interface 1 and by $dx_{\text{B}2}$ at interface 2, while that of the Fe_2B layer increases during the same time by $dy_{\text{Fe}2}$ at interface 2 and by $dy_{\text{B}3}$ at interface 3. Simultaneously, the thicknesses of the FeB and Fe_2B layers decrease at their common interface 2 due to the mutual consumption in reactions (2.59₂) and (2.60₁). This decrease is dx_- for the FeB layer and dy_- for the Fe_2B layer.

Arrows of different length are employed in Fig. 2.30 to indicate the decrease in amount of diffusing atoms, available at a particular interface, with increasing distance from a given initial substance (boron or iron). From considerations of Section 2, it must be clear that only those boron atoms which have not entered into partial chemical reaction (2.59₂) at interface 2 can diffuse further to interface 3 and enter there into partial chemical reaction (2.60₂). Similarly, only those iron atoms which have not entered into partial chemical reaction (2.60₁) at interface 2 can diffuse further to interface 1 and enter there into partial chemical reaction (2.59₁).

Reaction controlled growth kinetics of the FeB and Fe_2B layers are expected to be described by equations (2.27). As this kind of kinetics is typical of very thin boride layers (perhaps, of the order of 1 μm or less), it does not appear to have been investigated experimentally till now.

Thickening of the FeB and Fe_2B layers with passing time eventually results in a change of the regime of their growth from reaction controlled to diffusion controlled (see Sections 1.3.2 and 1.4.1), when the rate of interfacial transformations (reactions) becomes greater than the rate of diffusion of reacting atoms to the reaction sites (interfaces). After the FeB layer has reached its critical thickness, $x_{1/2}^{(\text{Boron})}$, with regard to boron, the Fe_2B layer loses the source of boron atoms and therefore stops growing at the expense of diffusion of this component. Note that the only source of boron atoms for both layers to grow is the initial boron phase (boron powder).

Again, after the Fe_2B layer has reached its critical thickness, $y_{1/2}^{(\text{Iron})}$, with regard to iron, the FeB layer loses the source of iron atoms and therefore stops growing at the expense of diffusion of this component. It must be clear that the only source of iron atoms for both layers to grow is the initial iron phase (Fe–Cr alloy or steel).

Hence, under conditions of diffusion control the FeB and Fe_2B layers are only able to grow at their common interface 2, as shown in Fig. 2.31. The FeB layer grows at the expense of diffusion of boron atoms across its bulk and their subsequent reaction with the Fe_2B compound. The Fe_2B layer grows at the expense of diffusion of iron atoms across its bulk and their subsequent reaction with the FeB compound. Thus, both boride layers grow at interface 2 by pushing each other in opposite directions.

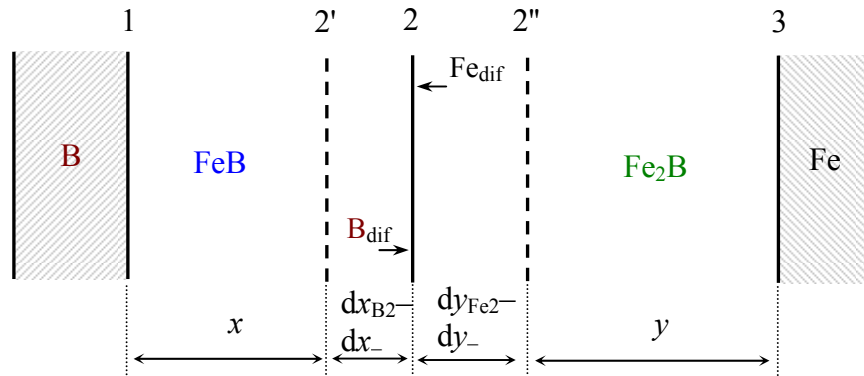


Fig. 2.31. Schematic diagram illustrating the growth process of the FeB and Fe₂B layers under conditions of diffusion control. Both layers only thicken at their common interface 2. No partial chemical reactions can take place at interfaces 1 and 3 due to the lack of appropriate diffusing atoms (Fe at interface 1 and B at interface 3).

Even though the FeB and Fe₂B layers are often considered to grow entirely at the expense of diffusion of the single component boron across their bulks, it is hardly possible with compact layers having no macroscopic defects and therefore growing by the volume-diffusion mechanism. During diffusional growth, by definition, diffusion across the layer bulks is the rate-determining step, the interfacial partial chemical reactions being very fast. It means that all the boron atoms reaching interface 2 react with Fe₂B to form FeB at that interface. Since under conditions of diffusion control the ability of interface 2 to combine those atoms exceeds their diffusional transport across the FeB layer (slow diffusion followed by fast reaction), none of them can diffuse further to interface 3 and react with Fe to form Fe₂B according to reaction (2.59₂): $B_{\text{dif}} + 2\text{Fe} = \text{Fe}_2\text{B}$. This reaction can only take place either under conditions of reaction control when the flux of boron atoms from the initial B-containing phase is sufficient for both boride layers to grow or if the FeB layer is non-protective, due to the presence of cracks, fissures and other macroscopic defects, while boriding is carried out from a vapour or liquid phase.

If boride layers are permeable to a vapour or liquid phase, direct chemical reactions between initial substances prove to be possible. Grain-boundary diffusion can also make a considerable contribution to the layer-growth process. If a few growth mechanisms are operative simultaneously, a complicated and hardly tractable microstructure of boride layers can readily be formed.

From a chemical viewpoint, it must thus be clear that the diffusionally growing compact FeB layer itself can by no means be a source of boron atoms for the Fe₂B layer to grow. It only serves as a transport media for these atoms. Suppose that two FeB molecules decompose at interface 2 to yield one molecule of Fe₂B and one diffusing boron atom: $2\text{FeB} = \text{Fe}_2\text{B} + B_{\text{dif}}$. However, this boron atom will be unable to diffuse from interface 2 to

interface 3 because under conditions of diffusion control the Fe_2B surface is undersaturated with boron atoms and therefore the just-released atom is immediately combined at interface 2 according to the reaction $\text{B}_{\text{dif}} + \text{Fe}_2\text{B} = 2\text{FeB}$. The net result of those reactions is zero.

In contrast, under conditions of reaction control the Fe_2B surface bordering the FeB layer is oversaturated with boron atoms and therefore part of them (not combined into the FeB phase at interface 2) can readily diffuse further to interface 3 and react with the iron atoms to form Fe_2B . As the source of boron atoms for both layers to grow is the boriding phase (boron powder), it is clear that sooner or later the flux of boron atoms, diminishing as the FeB layer thickens, becomes only sufficient for the FeB layer itself to grow, whereas the faraway Fe_2B layer must stop growing.

Note that in the absence of the boriding phase or if the contact of the FeB layer with it is lost, reaction $2\text{FeB} = \text{Fe}_2\text{B} + \text{B}_{\text{dif}}$ can readily proceed, resulting in degradation of the existing FeB layer and enhanced growth of the Fe_2B layer at the expense of diffusion of the released boron atoms [259, 262]. The reasons of such a behaviour of compound layers will be discussed in Chapter 4.

Similarly, under conditions of diffusion control all the iron atoms diffusing across the Fe_2B layer are combined into Fe_2B by their reaction with FeB at interface 2. Hence, iron atoms cannot take part in the formation of the faraway FeB layer at interface 1.

This conclusion is usually overlooked, if the process of formation of compound layers is treated without writing the equations of chemical reactions proceeding at the layer interfaces. In fact, at the diffusional stage of layer formation each of two compound layers without any macroscopic defects can grow only at the expense of diffusion of the atoms from a neighbouring initial phase. When one of the initial phases is exhausted, then the compound layer adjacent to this phase becomes a new initial phase. This is the only way (by successive consumption of initial substances) for binary systems without any solubility in the solid state, like Fe–B, to attain equilibrium.

2.9.4: Layer-growth kinetics

Diffusional growth kinetics of two continuous compound layers are conventionally treated using parabolic equations of the type $x^2 = 2k_1t$, where x is the layer thickness, k_1 is the layer growth-rate constant and t is time. In the case of boride layers, such equations indeed produce a quite satisfactory fit to the experimental data, as illustrated in Fig. 2.32 where both the thickness-time and the squared thickness-time plots are shown for a Fe–30 % Cr alloy as an example. Similar plots have been obtained by many researchers involved into the study of the boriding process (see, for example, Refs [235-240, 243-247, 251-254, 257-261]).

In view of a relatively large experimental error (around 5 to 20 %) in the determination of layer thicknesses, acceptable results are obtained not only for the outer FeB layer and the inner Fe_2B layer separately but also for the total thickness of both layers, even though the

sum of any two parabolas is clearly not a parabola. Since such data are of interest for practical purposes to estimate the thickness of boride coatings formed at intermediate values of temperature and time, they are also included in Fig. 2.32. Appropriate values of k_1 are listed in Table 2.4.

As evidenced from considerations of Section 2.8, however, growth kinetics of the FeB and Fe₂B layers boride layers at the diffusional stage of their formation are in fact somewhat more complicated and can alternatively be described by a system of two non-linear differential equations of the type (2.46):

$$\left(\frac{dx}{dt}\right)_{t=t_i} = \frac{k_{1B2}}{x_i} - \frac{rg}{p} \frac{k_{1Fe2}}{y_i}, \quad (2.61_1)$$

$$\left(\frac{dy}{dt}\right)_{t=t_i} = \frac{k_{1Fe2}}{y_i} - \frac{q}{sg} \frac{k_{1B2}}{x_i}, \quad (2.61_2)$$

where x is the outer FeB layer thickness, y is the inner Fe₂B layer thickness, k_B is the FeB layer growth-rate constant, k_{Fe} is the Fe₂B layer growth-rate constant, $g = 0.60$ is the ratio of the molar volumes of the FeB and Fe₂B compounds, $p = q = r = 1$ and $s = 2$ (factors from the chemical formulae of FeB (written as BFe) and Fe₂B (BFe₂), with boron being component A and iron component B).

It appears relevant to mention an essential distinction between parabolic equations and the system of equations (2.61). Indeed, parabolic equations only predict an inevitable increase in thickness of both layers with passing time. According to the system of equations (2.61), however, each of the layers can either grow or shrink, depending on the ratio of their initial thicknesses.

The latter is typical of the boride layers already present on the surface of a substrate before its subsequent heat treatment (for more detail, see Refs [153-155]). In such a case, the available layers adjust themselves (thickness of one of them is decreasing with time, while that of the other is increasing) until the ratio, x/y , of their thicknesses falls into the range predicted by an inequality of the type (2.48).

Note that the kinetic models of diffusional growth of boride layers are often based on an assumption of the existence of a rather wide range of homogeneity, HR , of appropriate borides, iron borides in particular. However, as follows from the available data on the phase equilibria in the binary system Fe–B [157, 159, 241, 242] and the ternary system Fe–Cr–B [275], iron borides FeB and Fe₂B have no noticeable homogeneity range. Therefore, theoretical considerations based on this assumption lack any experimental support. Besides, as evidenced from Section 1.9.1, such models are expected to yield the unrealistically high values of the diffusion coefficients of the components in growing boride layers because $D \rightarrow \infty$, as $HR \rightarrow 0$.

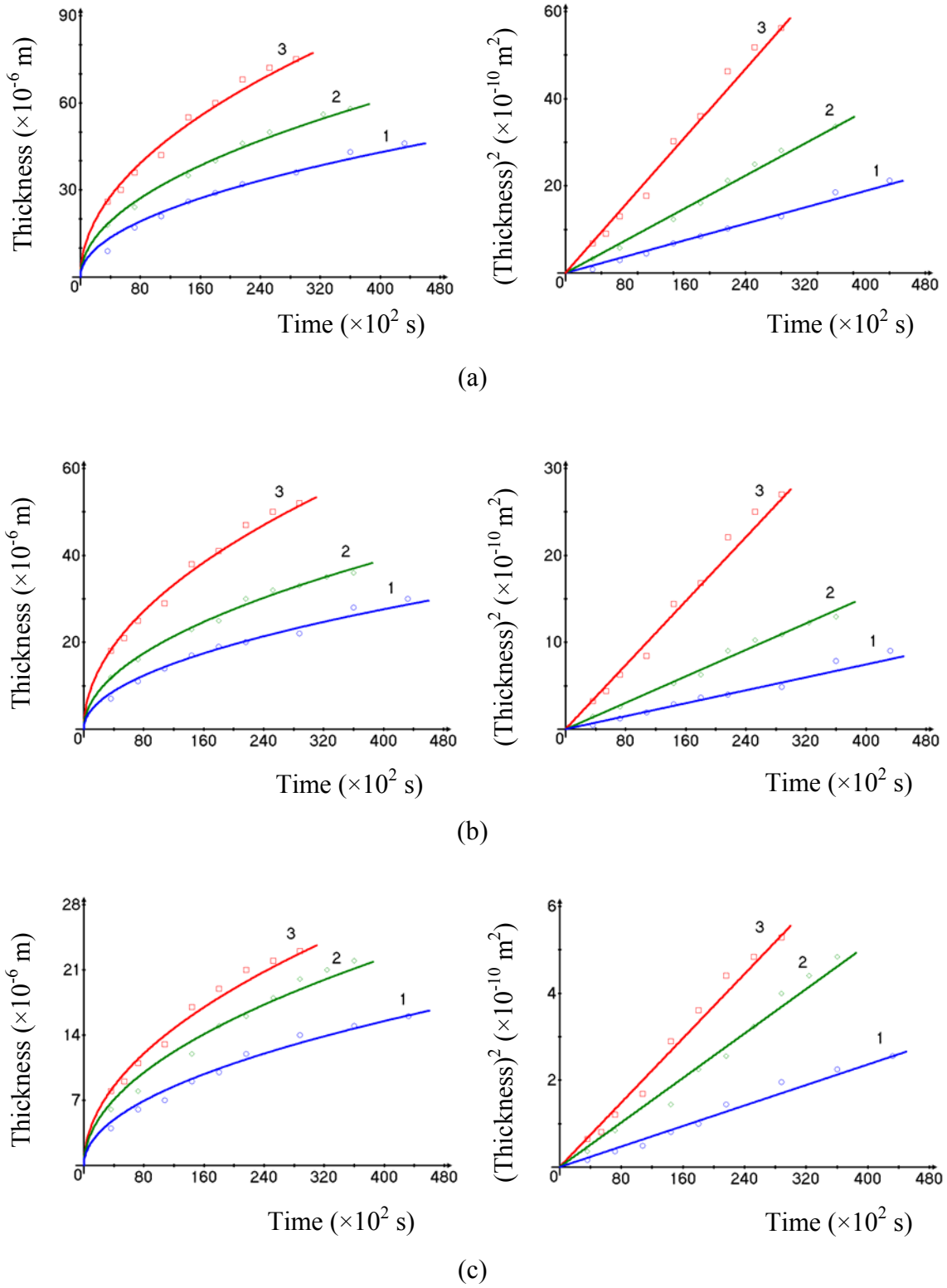


Fig. 2.32. Plots of layer thickness (left) and squared layer thickness (right) against time for (a) both boride layers, (b) the FeB layer and (c) the Fe₂B layer formed between a Fe–30 % Cr alloy and boron at a temperature of 850 °C (1), 900 °C (2) and 950 °C (3).

Table 2.4. Average values of layer growth-rate constants

Alloy or steel	Temperature (°C)	$k_1 (\times 10^{-14} \text{ m}^2 \text{ s}^{-1})$ from the equation $x^2 = 2k_1 t$	$k (\times 10^{-14} \text{ m}^2 \text{ s}^{-1})$ from the system of equations (2.61) using experimental points						$k (\times 10^{-14} \text{ m}^2 \text{ s}^{-1})$ from the system of equations (2.61) using approximated thickness-time dependences
		Total thicknes s	FeB	Fe ₂ B	k_B	k_{Fe}	k_B	k_{Fe}	
10 % Cr alloy	850	19.8	4.1	5.9	16.4	22.7	14.0	19.9	
	900	30.4	6.6	8.6	25.2	33.1	22.2	29.6	
	950	72.4	15.4	21.4	61.4	83.7	52.4	72.6	
15 % Cr alloy	850	13.1	2.9	3.6	11.3	14.5	9.64	12.5	
	900	20.6	4.6	5.9	14.7	18.3	15.4	20.4	
	950	35.3	7.2	10.6	22.4	30.9	24.8	35.6	
25 % Cr alloy	850	5.3	1.6	1.1	5.45	5.21	4.77	4.38	
	900	8.9	3.1	1.7	9.76	7.88	8.92	7.18	
	950	16.0	5.0	3.1	14.6	12.9	14.7	12.7	
30 % Cr alloy	850	2.23	0.93	0.27	3.01	1.79	2.45	1.37	
	900	4.60	1.90	0.58	5.39	3.13	5.04	2.89	
	950	9.56	4.58	0.82	11.2	5.00	11.4	4.84	
13 % Cr steel	850	8.8	1.6	3.0	7.35	12.2	5.81	9.60	
	900	17.3	3.5	5.3	15.4	22.2	12.1	17.7	
	950	28.1	5.9	8.3	19.6	27.6	20.1	28.1	

Like the case of the Al–Mg diffusion couple considered in the preceding section, the values of the derivatives dx/dt and dy/dt entering into the system of equations (2.61) were found from the experimental layer thickness-time dependences by the numerical three-point method. Calculation yielded the values of the diffusional constants, k_B and k_{Fe} , presented in Table 2. 4. Physically, k_B is the reaction-diffusion coefficient of boron atoms in the FeB layer, whereas k_{Fe} is the reaction-diffusion coefficient of iron atoms in the Fe₂B layer.

With 25 % Cr steel, the kinetic data obtained were treated using only parabolic equations and the values of the total thickness of both layers because the thickness of each of them

could hardly be measured separately with a sufficient degree of accuracy due to their extreme irregularity. In this case, the value of the diffusional constant, k_1 , was found to be $0.72 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ at 850 °C, $1.36 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ at 900 °C and $2.40 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ at 950 °C [267].

The results of calculations are strongly dependent upon a scatter of experimental points. To avoid this, preliminary approximation of the experimental data with any suitable analytical function is advisable. For example, the use of parabolic relations to approximate the layer thickness–time dependences and then to find the derivatives yields another set of values of k_B and k_{Fe} , also provided in Table 2.4.

Since these dependences become smoothed as a result of this procedure (solid lines on the left-hand plots of Fig. 2.32), all the values of k_B thus found prove identical. The same applies to k_{Fe} . Comparing these with the average values of k_B and k_{Fe} found directly from the experimental points, it may be concluded that both sets of the constants agree fairly well, providing evidence for the validity of the analytical treatment employed. Note that, in order to avoid a large computational uncertainty and to obtain acceptable results, the optimum number of experimental points must generally be nine or more.

The temperature dependence of the layer growth-rate constants obtained is described in the 850–950 °C range by a relation of the Arrhenius type $K = K_0 \exp(-E/RT)$, where K stands for any layer growth-rate constant, K_0 is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the absolute temperature. A plot of $\ln K$ against T^{-1} for a Fe–30 % Cr alloy is shown in Fig. 2.33 as an example. Values of K_0 and E found by the least-squares fit method are listed in Table 2.5. These are typical of diffusion-controlled processes. For the total thickness of both boride layers formed on the surface of 25 % Cr steel samples, the Arrhenius-type equation is $k_1 = 1.72 \times 10^{-8} \exp(-137.1 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}$.

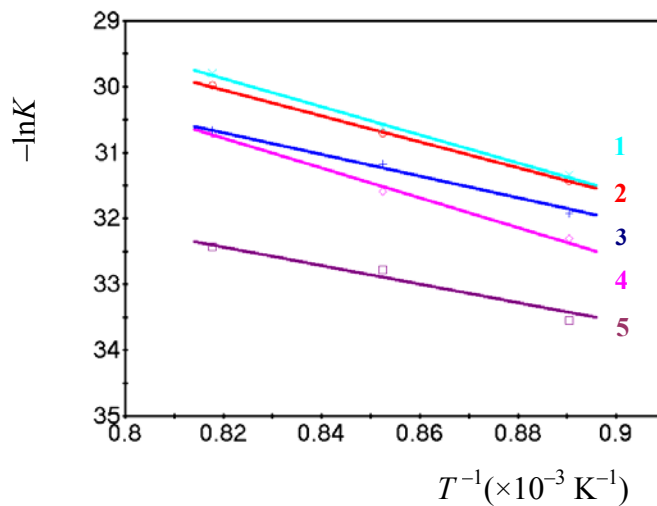


Fig. 2.33. Temperature dependence of the layer growth-rate constants, K , for a Fe–30 % Cr alloy: 1 ($\times$), k_B from the system of equations (2.61); 2 ($\circ$), k_1 from the equation $x^2 = 2k_1t$ for both boride layers; 3 ($+$), k_{Fe} ; 4 ($\diamond$) - k_1 for the FeB layer; 5 ($\square$) - k_1 for the Fe_2B layer [269].

Table 2.5. Values of K_0 and E of a relation of the Arrhenius type describing the temperature dependence of growth-rate constants of boride layers

Alloy or steel	k_1						k_B		k_{Fe}	
	Total thickness		FeB		Fe ₂ B		K_0	E	K_0	E
	K_0	E	K_0	E	K_0	E				
10 % Cr alloy	12.8 $\times 10^{-7}$	147.2	3.78 $\times 10^{-7}$	150.5	3.34 $\times 10^{-7}$	146.1	$\times 10^{-7}$	149.9	$\times 10^{-7}$	146.8
15 % Cr alloy	2.32 $\times 10^{-8}$	113.0	1.95 $\times 10^{-9}$	103.8	1.88 $\times 10^{-8}$	123.1	$\times 10^{-8}$	107.9	$\times 10^{-8}$	119.4
25 % Cr alloy	3.78 $\times 10^{-8}$	126.0	1.91 $\times 10^{-8}$	130.5	3.27 $\times 10^{-9}$	118.0	$\times 10^{-8}$	128.8	$\times 10^{-8}$	121.4
30 % Cr alloy	1.18 $\times 10^{-8}$	166.2	2.53 $\times 10^{-8}$	181.7	2.48 $\times 10^{-9}$	127.7	$\times 10^{-8}$	175.4	$\times 10^{-9}$	144.6
13 % Cr steel	1.37 $\times 10^{-8}$	132.9	1.49 $\times 10^{-7}$	149.5	7.90 $\times 10^{-9}$	116.4	$\times 10^{-7}$	142.2	$\times 10^{-8}$	122.9

Note: K_0 in $\text{m}^2 \text{s}^{-1}$, E in kJ mol^{-1} .

2.10: NiBi layer: missing or too thin?

As pointed out in Section 1.8.2, formation of the NiBi intermetallic layer is not observed in the Ni–Bi reaction couple for a very long period of time. At least, after a 70 h anneal at 250 °C no indication of its presence was found, though the NiBi₃ intermetallic layer has reached a thickness of almost 230 μm [163, 164]. This may seem somewhat surprising, especially in comparison with the Fe–B diffusion couple just considered, where the second layer FeB occurs after the first-formed layer Fe₂B has reached a thickness of the order of 100 μm .

The question whether the NiBi layer is indeed missing or only too thin to be observed could be answered by carrying out experiments with the artificially prepared Ni–NiBi–NiBi₃–Bi specimens. The disappearance of the already existing NiBi intermetallic layer would provide direct evidence for its kinetic instability. Such an attempt was undertaken by M.S. Lee *et al.* [276]. Unfortunately, the specimens they prepared proved to be not so easy to handle, and the final goal was not achieved to the full extent.

This example shows how difficult the reaction-diffusion experiments may be to carry out, even with *most suitable* binary systems. Most suitable systems are those in which (i) thermal expansion and (ii) volume effect associated with compound formation can be minimised. In the Ni–Bi couple, the coefficients of thermal expansion of the components are identical

[277-280], while the volume effect (see Ref. [276] is within a range typical of intermetallic compounds [234]. In regards to the influence of thermal expansion, the Ni–Bi system is preferable to the Al–Mg one in which the coefficients of thermal expansion of the components are slightly different.

Consider the growth process of the NiBi and NiBi₃ intermetallic layers between nickel and bismuth in more detail to explain the difference between diffusional and physico-chemical approaches to the same problem of the apparent absence of a chemical compound layer. This consideration differs little from that of the two preceding sections. From a physico-chemical viewpoint, in the reaction controlled regime ($x < x_{1/2}^{(Ni)}$, $y < y_{1/2}^{(Bi)}$) both layers can grow at the expense of diffusion of both components, as shown in Fig. 2.34a.

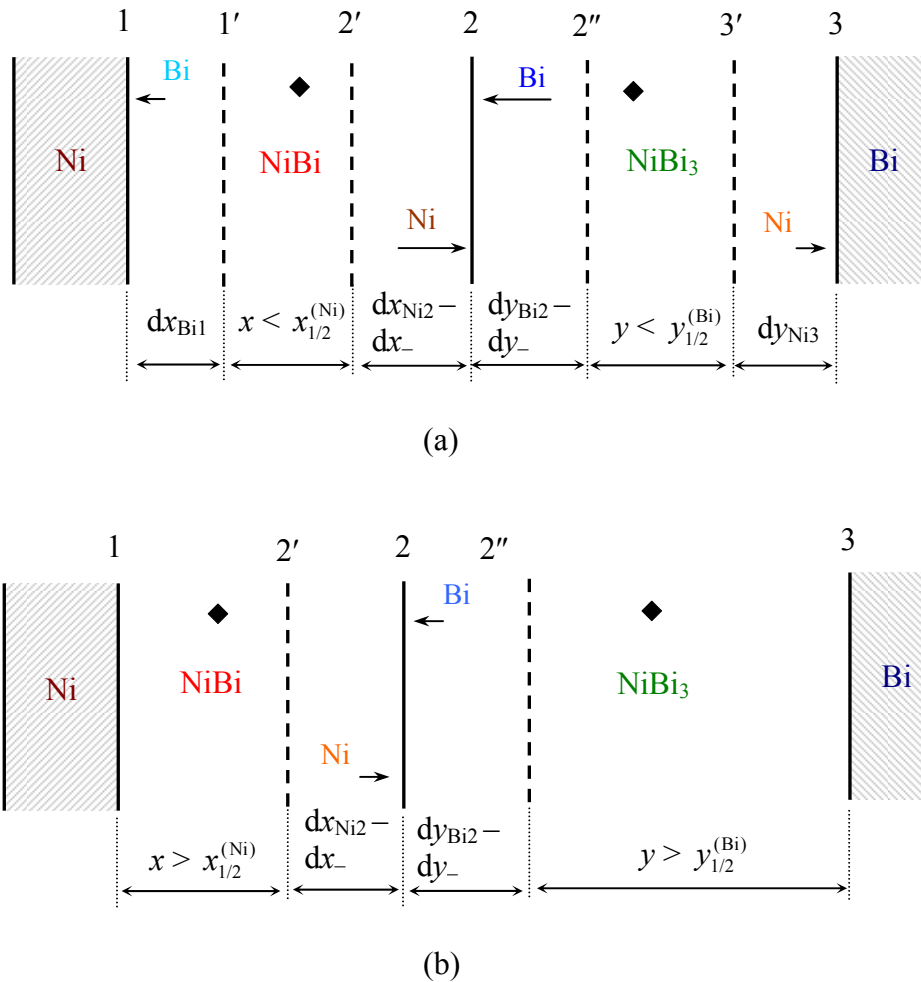


Fig. 2.34. Schematic diagram to illustrate the growth process of the NiBi and NiBi₃ intermetallic layers between nickel and bismuth: (a) reaction controlled regime of layer formation ($x < x_{1/2}^{(Ni)}$, $y < y_{1/2}^{(Bi)}$); (b) diffusion controlled regime of layer formation ($x > x_{1/2}^{(Ni)}$, $y > y_{1/2}^{(Bi)}$). The symbol ♦ designates an inert marker.

In the diffusion controlled regime ($x > x_{1/2}^{(\text{Ni})}$, $y > y_{1/2}^{(\text{Bi})}$) the NiBi layer grows at the expense of diffusion of the nickel atoms and their subsequent chemical reaction with the NiBi₃ compound at interface 2, whereas the NiBi₃ layer grows at the expense of diffusion of the bismuth atoms and their subsequent chemical reaction with the NiBi compound at the same interface 2, as illustrated in Fig. 2.34b. From a diffusional viewpoint, however, the NiBi and NiBi₃ layers are assumed to grow at the expense of diffusion of *both* components, *whatever* their thickness.

Another principal distinction concerns the time of occurrence of the NiBi and NiBi₃ intermetallic layers. In view of the very large difference in melting points of nickel (1451 °C) and bismuth (271 °C), at temperatures below 271 °C the mobility of the bismuth atoms in the NiBi₃ crystal lattice may reasonably be expected to be much greater than that of the nickel atoms in the NiBi crystal lattice.

From a physico-chemical viewpoint, the NiBi layer can hardly survive under such conditions, and therefore there must be a long delay with its occurrence between Ni and NiBi₃. According to diffusional considerations, it should occur from the very beginning of interaction of nickel and bismuth, but is supposed to be too thin to be observed experimentally. Though even now there is no doubt that the absence of the NiBi layer is a physical reality, to unambiguously judge of which of the two approaches is more correct in this particular case, long-term experiments with Ni–Bi couples, using refined techniques allowing the investigation of the layers a few lattice units thick, are badly needed.

From layer thickness-time plots presented by M.S. Lee *et al.* [276], the NiBi layer thickness in Ni–NiBi₃ couples after their annealing for 100 h can be estimated as about 10 µm at 330 °C, 25 µm at 370 °C, 40 µm at 410 °C and 50 µm at 450 °C. This provides evidence that the growth rate of the NiBi layer is indeed very low, though in those couples it can readily grow at the expense of diffusion of *both* components (Ni and Bi) and *additionally* at the expense of decomposition of the NiBi₃ compound (see Chapter 4).

In order to visualise the NiBi layer at temperatures below the melting point of bismuth, experiments with Ni–Bi couples must evidently be carried out in the 100–1000 h time range. At such annealing times, its thickness will probably exceed a few micrometers. The NiBi layer formed should therefore be seen even under optical microscope at moderate magnifications. A serious obstacle to performing such experiments may be the rupture of Ni–Bi specimens with thick NiBi₃ intermetallic layers.

2.11: Two compound layers: comparison of diffusional and physico-chemical approaches

Main distinctions between the conventional diffusional approach and the proposed physico-chemical one for the case of formation of two compound layers are briefly summarised in Table 2.5. To avoid misleading conclusions, it would be desirable to take account of these distinctions when studying the growth kinetics of two compound layers.

Most significant features of the mechanism of formation of two compound layers are partly visualised in Fig. 2.35 where a scheme for the case of formation of one compound layer is also included for comparison. Note that two compound layers can in principle grow simultaneously, whatever their growth regime (either reaction controlled or diffusion controlled).

From these schemes, it is seen that one compound layer can generally grow at the expense of diffusion of both components, whatever its growth regime (either reaction controlled or diffusion controlled). Two compound layers can grow at the expense of diffusion of both components only under conditions of reaction control. Under conditions of diffusion control, each of them grows exclusively at the expense of diffusion of one component (with which a given layer borders).

2.12: Two compound layers: short conclusions

1. In the reaction controlled regime, the layer of each of two chemical compounds A_pB_q and A_rB_s grows at the expense of two partial chemical reactions taking place at its interfaces with adjacent phases.

2. Each of two growing compound layers is a product in the two and a reactant in one of the four partial chemical reactions taking place in the $A-A_pB_q-A_rB_s-B$ system.

3. In most reaction couples, the layer formed first should reach a certain minimal thickness before the second layer can occur. Both compound layers will then grow simultaneously until one of initial substances A or B is entirely consumed.

4. In any binary system, the sequence of formation of compound layers is governed by the rate of chemical transformations (partial chemical reactions) at phase interfaces.

5. The layer thickness-time kinetic relationships are in general rather complicated, not merely parabolic. Depending on the values of the chemical and physical (diffusional) constants, their different portions can be described by linear, parabolic, asymptotic, parabolic and other laws.

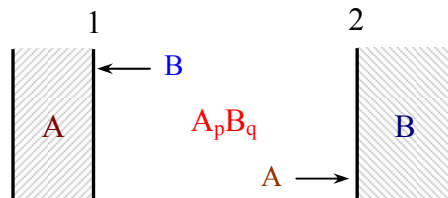
6. In the diffusion controlled regime, growth of each of two compound layers is due to one partial chemical reaction taking place at its common interface with another growing layer. In this case, only the A atoms diffuse across the A_pB_q layer adjacent to initial phase A , while only the B atoms diffuse across the A_rB_s layer adjacent to initial phase B . No partial chemical reactions proceed at the $A-A_pB_q$ and A_rB_s-B interfaces in view of the lack of appropriate diffusing atoms.

7. In the case of two compound layers, even growing under conditions of diffusion control, application of Matano's analysis and calculation of integrated diffusion coefficients do not seem to be sufficiently substantiated. Such quantities can hardly have any physical meaning.

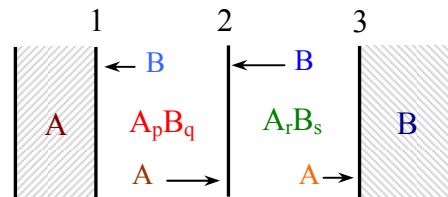
Table 2.5. Comparison of diffusional and physico-chemical approaches in the case of two compound layers

Diffusional approach	Physico-chemical approach
1. Both compound layers occur and grow simultaneously.	1. Occurrence of two compound layers is sequential rather than simultaneous.
2. Layer-growth kinetics are parabolic.	2. A variety of kinetic laws may be observed experimentally.
3. Both compound layers can always grow at the expense of diffusion of both components.	3. Under conditions of reaction control, both compound layers can generally grow at the expense of diffusion of both components. Under conditions of diffusion control, each of them grows only at the expense of diffusion of that component with which it borders.

1. One compound layer: reaction or diffusion control



2a. Two compound layers: reaction control



2b. Two compound layers: diffusion control

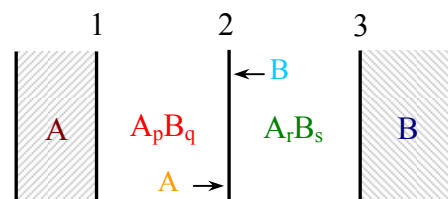


Fig. 2.35. Comparative schematic diagrams to illustrate the mechanism of growth of one and two compound layers.

3: Occurrence of multiple compound layers at the $A-B$ interface

Many binary systems are multiphase, with the number of chemical compounds on the $A-B$ equilibrium phase diagram reaching or even exceeding ten [157, 159, 281-290]. Therefore, the primary question the experimentalist faced when starting to investigate a particular reaction couple is how many and what compounds, of their variety shown on the phase diagram, can occur as separate layers at the interface between initial elementary substances A and B under given conditions of temperature and pressure.

In the framework of diffusional considerations all chemical compounds of a multiphase binary system, whatever their number, are assumed to simultaneously form individual layers which must grow according to a parabolic law during isothermal annealing of the $A-B$ reaction couple. Such misleading assumptions can readily be found in numerous papers, monographs and, unfortunately, even textbooks. Though often stated to follow from the equilibrium phase diagram, it appears to have no reasonable substantiation. Since now it is impossible (and perhaps not necessary) to find out who was the first to put forward this idea, no citation is made to avoid offending those researchers who have simply mentioned it in their works, following the others, even though their own experimental results provided sufficient evidence for opposite conclusions.

In fact, what follows from the equilibrium phase diagram of any binary system is (i) what compounds *may*, not *should*, form as individual layers at the interface between substances A and B and (ii) the final state of the $A-B$ reaction couple after prolonged isothermal annealing, which only depends on the amounts of initial substances taken. The phase diagram by no means dictates that those compound layers must necessarily occur simultaneously. Moreover, from the point of view of phase equilibria, the number of compound layers can be expected to decrease rather than to increase with passing time since only two phases must remain in the equilibrium state.

In most reaction couples, part of compound layers are known to be missing, with only one or two layers growing at the $A-B$ interface, irrespective of the number of chemical compounds on the appropriate phase diagram. The cases where three or more compound layers were *present* and the more so *grew simultaneously* between elementary substances A and B are very rare against the background of the cases where one or two layers were formed. Consider a few instructive examples.

Of eight intermetallics of the $Zr-Al$ binary system, only the $ZrAl_3$ layer is known to grow at the $Zr-Al$ interface at temperatures below the melting point of aluminium. This is typical of most transition metal-aluminium binary systems (see a review by E.G. Colgan [38]).

A single layer of the CuCd_3 compound was observed by Yu.E. Ugaste and P.A. Kyarsna [117] to occur between Cu and Cd (four intermetallics on the phase diagram). Though there are several oxides in the Ti–O binary system, the TiO_2 layer dominates during oxidation of titanium [13, 122-125].

As already mentioned in Chapter 2, two layers Ni_5Sb_2 and NiSb are formed at the Ni–Sb interface (five intermetallics on the phase diagram) [78]. According to V.I. Zmiy and A.S. Seryugina [222] and P.C. Tortorici and M.A. Dayananda [291], the Mo_5Si_3 and MoSi_2 layers occur in Mo–Si diffusion couples, while the formation of the Mo_3Si silicide is not observed. The Cu_5Zn_8 and CuZn_5 layers were found by V.V. Bogdanov *et al.* [292] and M.V. Yarmolenko *et al.* [293] to grow between Cu and Zn, with the third intermetallic compound CuZn of the Cu–Zn binary system being missing. Simultaneous growth of two intermetallic layers was also observed by T.C. Chou and L. Link [116] in Mo–Ni diffusion couples (three intermetallics on the phase diagram) and by E.K. Ohriner and E.P. George [294] in Mo–Ir diffusion couples (four intermetallics on the phase diagram). Compact layers of one or two compounds are known to form in almost all transition metal-silicon reaction couples [29, 126, 127]. The same applies to numerous other heterogeneous systems of different chemical nature [6, 10, 122-125, 295, 296].

Note that even in those cases where multiple compound layers were present at the A–B interface, two layers were dominating. For example, G. Hillmann and W. Hofmann [297] and O. Taguchi *et al.* [298] observed the formation of all six intermetallics shown on the equilibrium phase diagram in the Zr–Cu reaction zone, with two Cu-rich compounds occupying more than 90% of the total layer thickness and layer-growth kinetics deviating from a parabolic law. When investigating this system, K. Bhanumurthy *et al.* [299] have found only two (Cu-rich and Cu-poor) intermetallic layers growing parabolically. As evidenced from micrographs in those works, the specimens of G. Hillmann and W. Hofmann and O. Taguchi *et al.* contained cracks along the layer interfaces, while those of K. Bhanumurthy *et al.* did not. The TiCu and Ti_3Cu_4 layers are dominant in Ti–Cu diffusion couples, with the thickness of other compound layers being much less and in addition very irregular [300]. Multiple layers were also observed in Hf–Cu diffusion couples in which the intermetallics Hf_2Cu_7 , $\text{Hf}_{14}\text{Cu}_{51}$ and HfCu_5 occupied about 95% of their total width [301].

It should be emphasised that not always the multilayered structure of the transition zone between elementary substances *A* and *B* is a result of simultaneous isothermal growth of chemical compounds. Certain layers may occur during cooling, if slow, because the reaction usually takes place at elevated temperatures, while the layers grown are then investigated after cooling down to room temperature. Another main reason for the formation of additional layers may be the disruption of contact between the phases involved into the interaction, due to mechanical stresses associated with thermal expansion and volume effect. As a result, the examined reaction couple is split into at least two new independent couples. In those, the other compound layers, lacking from the previous couple, may readily occur. Clearly, in such a case, at least one of the former layers must shrink, up to its full disappearance, as was

observed, for example, by S.L. Markovski *et al.* [302] with the PtSb compound layer in Pt–Sb diffusion couples.

However, as evidenced from the available experimental data, not always even these secondary factors do lead to any significant increase in the number of chemical compound layers at the A – B interface. Not only the *simultaneous parabolic growth* of eight or ten compound layers, but even their *simultaneous presence* was never observed experimentally.

To explain the absence of certain compound layers between initial substances A and B , two reasons are put forward most frequently (see, for example, Ref. [22]).

(1) Difficulties with nucleating a new phase. This may take place in particular cases. However, generally the difficulties with nucleating new phases in a heterogeneous system appear to be too exaggerated. If sufficiently clean surfaces of initial phases capable of forming chemical compounds are brought into intimate contact, the interaction resulting in chemical bonding is known to start at relatively low temperatures even in reaction couples consisting of substances with very high melting points [126, 127, 303–310].

(2) The low layer-growth rate due to the small value of the product $D\Delta c$, where D is the diffusion coefficient and Δc is the width of the range of homogeneity of a chemical compound. Firstly, there is no straightforward relation between the width of the homogeneity range and the growth rate of the layer of a chemical compound. Secondly, if the absence of a given compound layer were a consequence of the low growth rate, its appearance in the A – B reaction couple would only depend on the duration of the interaction between initial substances.

The experiments are known in the literature, providing evidence that these reasons for the absence of some part of the compounds of a multi-phase system at the A – B interface are definitely not decisive [68, 72, 91, 96, 126, 311]. For example, F.J.J. van Loo [68] carried out isothermal annealing of Ti–Ti₃Al–TiAl–TiAl₂–TiAl₃–Al specimens consisting of all the phases of the Ti–Al binary system at 625 °C for 15 hours. Instead of the parabolic growth predicted by the diffusional theory, the layers of Ti₃Al, TiAl and TiAl₂ disappeared and only the TiAl₃ layer remained.

Note that all these intermetallic compounds are thermodynamically stable at 625 °C. This experiment has convincingly shown that, firstly, all the compound layers of a multiphase system present in the A – B reaction couple should not necessarily grow during its isothermal annealing and, secondly, the difficulties with nucleating new phases do not play in the solid-state systems that role which is ascribed to them. In the case under consideration, even the layers of the already existing compounds did not grow. Only the layer of the TiAl₃ intermetallic compound, which is known to be the first to occur at the Ti–Al interface [38, 68, 312], grew. The layers of the remaining compounds were consumed during its growth and therefore sequentially disappeared with passing time. Working with much thinner artificially prepared Ti–Ti₃Al–Al and Ti–TiAl–Al specimens, S. Wöhlert and R. Bormann [121] have confirmed the findings of F.J.J. van Loo [68] regarding the complete

disappearance of the initially existing Ti_3Al and TiAl intermetallic layers in the course of formation of the TiAl_3 layer.

It is worth noting that the intermetallic compound TiAl_3 is a stoichiometric phase without any noticeable range of homogeneity, whereas the other intermetallics of the Ti–Al binary system have the homogeneity ranges of 1 to 12 at.% [142, 145, 193]. Nonetheless, the TiAl_3 layer grows much faster than do these. In such a case, in order that the product $D\Delta c$ be a real reason for the fast growth of the TiAl_3 layer, the diffusion coefficient D must clearly have an infinitely high value. Physically, this is hardly possible.

It should be emphasised that according to the diffusional theory any chemical compound layer once formed cannot then disappear during isothermal annealing of the A – B reaction couple because its growth rate, $dx/dt \sim \partial c/\partial x$, increases with decreasing thickness and tends to infinity, as $x \rightarrow 0$. It is therefore usually assumed that the layers do not disappear completely, but their thickness decreases to such an extent that they become unobservable experimentally.

Until recently, when it was only possible to examine compound layers with a thickness of the order of 1 μm or greater, experimentalists were forced to believe in this explanation. At present, however, when the phase identity, chemical composition, crystallographic structure and rate of formation of chemical compound layers a few nanometers thick can readily be determined, this belief lost any experimental support. At smaller thicknesses of a growing layer the concept *phase* clearly loses its physical meaning since, in order to be identified as such, any phase must accommodate at least a few crystal-lattice units across the layer width.

Therefore, it appears much more reasonable to assume that if the layers of certain compounds cannot be revealed in the A – B reaction couple, both in thin films and massive specimens, with the help of sufficiently sensitive experimental techniques then they are simply *missing* from that couple, and to attempt to find out the most probable reasons for this phenomenon. Such an attempt will be undertaken in this chapter.

3.1: Partial chemical reactions at the layer interfaces of the A – B reaction couple

To understand the peculiarities of multiple layer formation, it suffices to consider the A – B binary system with three chemical compounds A_pB_q , A_rB_s and A_lB_n on the phase diagram (Fig. 3.1). Analysis of the process of their occurrence at the A – B interface is similar to that of two compound layers (see Chapter 2). First of all, the equations of partial chemical reactions taking place at phase interfaces must be written. These are as follows.

Layer	Interface	Partial chemical reaction	
A_pB_q	1	$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q,$	(3.1 ₁)
	2	$(sp - qr)A_{\text{dif}} + qA_rB_s = sA_pB_q,$	(3.1 ₂)

$$A_rB_s \quad 2 \quad (sp - qr)B_{\text{dif}} + rA_pB_q = pA_rB_s, \quad (3.2_1)$$

$$3 \quad (rn - ls)A_{\text{dif}} + sA_lB_n = nA_rB_s, \quad (3.2_2)$$

$$A_lB_n \quad 3 \quad (rn - ls)B_{\text{dif}} + lA_rB_s = rA_lB_n, \quad (3.3_1)$$

$$4 \quad lA_{\text{dif}} + nB_{\text{surf}} = A_lB_n. \quad (3.3_2)$$

As previously, all these reactions are assumed to be independent in the sense that the elementary act of each of them has no effect on the elementary acts of the others.

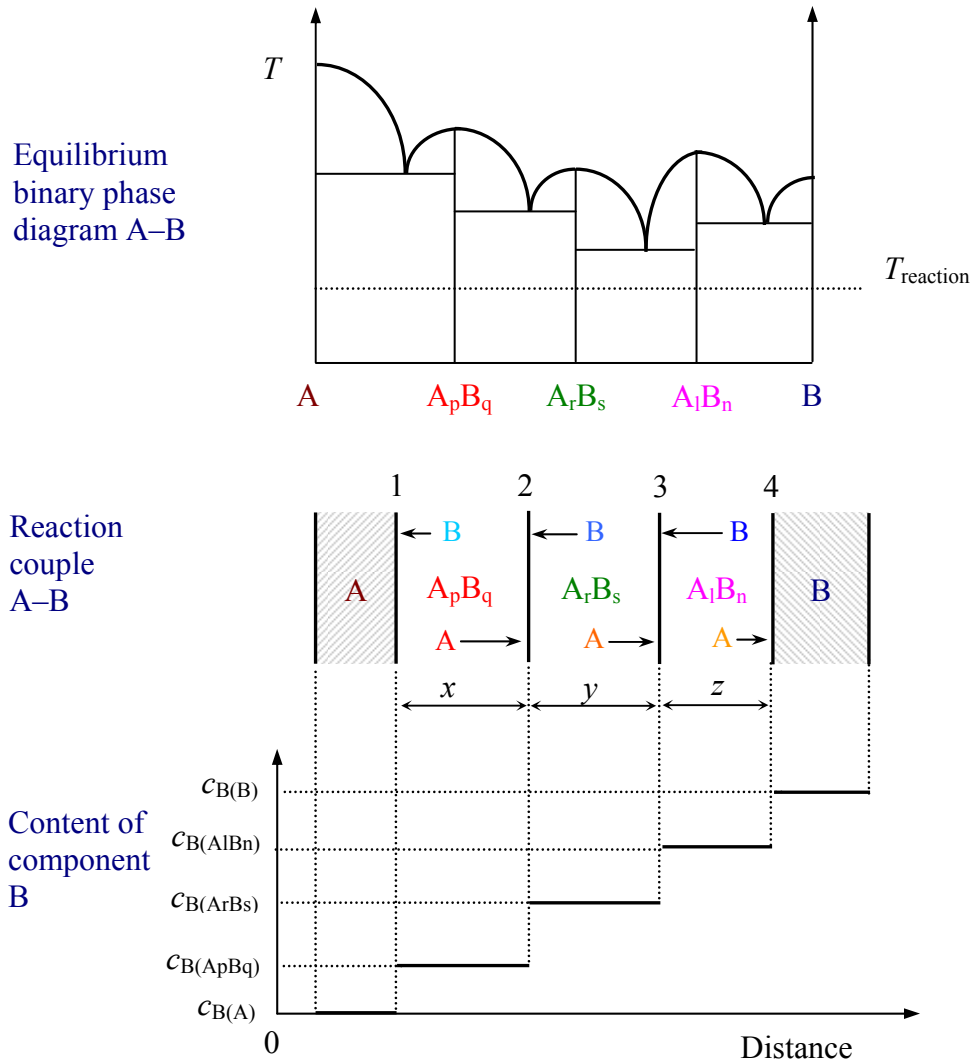


Fig. 3.1. Schematic diagram to illustrate the growth process of three chemical compound layers A_pB_q , A_rB_s and A_lB_n between mutually insoluble elementary substances A and B .

Partial chemical reactions (3.1₁)-(3.3₂) cause the changes in thickness of appropriate compound layers. During the time dt , reactions (3.1₁) and (3.1₂) lead to the increase of the

thickness of the A_pB_q layer by dx_{B1} at interface 1 and by dx_{A2} at interface 2 (Fig. 3.2). Reaction (3.2₁) resulting in the increase of the thickness of the A_rB_s layer by dy_{B2} at interface 2, leads simultaneously to the decrease in thickness of the A_pB_q layer by $dx_{-}^{(2)}$ at the same interface 2. The thickness of the A_rB_s layer also increases by dy_{A3} at interface 3 as a result of reaction (3.2₂). At the same time, its thickness decreases by $dy_{-}^{(2)}$ at interface 2 and by $dy_{-}^{(3)}$ at interface 3 since the A_rB_s phase is consumed in the course of reactions (3.1₂) and (3.3₁). Reactions (3.3₁) and (3.3₂) cause the increases of the thickness of the A_lB_n layer during dt by dz_{B3} and dz_{A4} at interfaces 3 and 4, respectively. Again, the thickness of this layer decreases by $dz_{-}^{(3)}$ at interface 3 as a result of reaction (3.2₂).

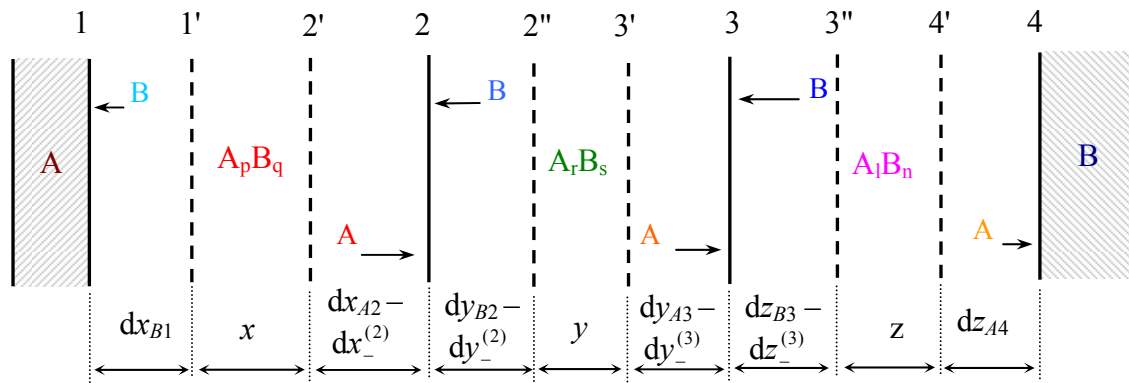


Fig. 3.2. Schematic diagram to illustrate the changes in thickness of three chemical compound layers A_pB_q , A_rB_s and A_lB_n growing between mutually insoluble elementary substances A and B at the expense of diffusion of both components (reaction control).

Position of interface 1 is seen to depend on the occurrence of only one partial chemical reaction (3.1₁). Similarly, position of interface 4 only depends on partial chemical reaction (3.3₂). Position of interface 2 is determined by two partial chemical reactions (3.1₂) and (3.2₁) taking place simultaneously. The same applies to position of interface 3, depending on partial chemical reactions (3.2₂) and (3.3₁).

The thickness of the A_pB_q layer as well as the A_lB_n layer is thus determined by the rate of occurrence of two partial chemical reactions. The thickness of the A_rB_s layer located between them depends on the rate of four partial chemical reactions. The same applies to any other compound layer of a multiphase system, having no direct contact with either of initial phases, if the number of compounds on the phase diagram exceeds three.

3.2: A system of differential equations describing the growth process of three compound layers between elementary substances *A* and *B*

Application of the postulate about the summation of the time of diffusion of reacting atoms and the time of subsequent chemical transformations with their participation yields

$$dt = dt_{\text{dif}}^{(B \rightarrow A_p B_q)} + dt_{\text{chem}}^{(B \rightarrow A_p B_q)}, \quad (3.4_1)$$

$$dt = dt_{\text{dif}}^{(A \rightarrow A_p B_q)} + dt_{\text{chem}}^{(A \rightarrow A_p B_q)}, \quad (3.4_2)$$

$$dt = dt_{\text{dif}}^{(B \rightarrow A_r B_s)} + dt_{\text{chem}}^{(B \rightarrow A_r B_s)}, \quad (3.5_1)$$

$$dt = dt_{\text{dif}}^{(A \rightarrow A_r B_s)} + dt_{\text{chem}}^{(A \rightarrow A_r B_s)}, \quad (3.5_2)$$

$$dt = dt_{\text{dif}}^{(B \rightarrow A_l B_n)} + dt_{\text{chem}}^{(B \rightarrow A_l B_n)}, \quad (3.6_1)$$

$$dt = dt_{\text{dif}}^{(A \rightarrow A_l B_n)} + dt_{\text{chem}}^{(A \rightarrow A_l B_n)}, \quad (3.6_2)$$

where the subscripts and superscripts have the former meaning (see Section 2.2 of Chapter 2).

Assuming that the time of diffusion of the *A* or *B* atoms is directly proportional to both the increase in thickness of the layer and its total thickness, while the time of chemical transformations in which these atoms then take part is directly proportional to the increase in thickness of the layer and is independent of its total thickness, one obtains the following relations:

$$dt_{\text{dif}}^{(B \rightarrow A_p B_q)} = \frac{x}{k_{1B1}} dx_{B1} \quad \text{and} \quad dt_{\text{chem}}^{(B \rightarrow A_p B_q)} = \frac{1}{k_{0B1}} dx_{B1}, \quad (3.7_1)$$

$$dt_{\text{dif}}^{(A \rightarrow A_p B_q)} = \frac{x}{k'_{1A2}} dx_{A2} \quad \text{and} \quad dt_{\text{chem}}^{(A \rightarrow A_p B_q)} = \frac{1}{k'_{0A2}} dx_{A2}, \quad (3.7_2)$$

$$dt_{\text{dif}}^{(B \rightarrow A_r B_s)} = \frac{y}{k'_{1B2}} dy_{B2} \quad \text{and} \quad dt_{\text{chem}}^{(B \rightarrow A_r B_s)} = \frac{1}{k'_{0B2}} dy_{B2}, \quad (3.8_1)$$

$$dt_{\text{dif}}^{(A \rightarrow A_r B_s)} = \frac{y}{k'_{1A3}} dy_{A3} \quad \text{and} \quad dt_{\text{chem}}^{(A \rightarrow A_r B_s)} = \frac{1}{k'_{0A3}} dy_{A3}, \quad (3.8_2)$$

$$dt_{\text{dif}}^{(B \rightarrow A_l B_n)} = \frac{z}{k_{1B3}} dz_{B3} \quad \text{and} \quad dt_{\text{chem}}^{(B \rightarrow A_l B_n)} = \frac{1}{k_{0B3}} dz_{B3}, \quad (3.9_1)$$

$$dt_{\text{dif}}^{(A \rightarrow A_l B_n)} = \frac{z}{k_{1A4}} dz_{A4} \quad \text{and} \quad dt_{\text{chem}}^{(A \rightarrow A_l B_n)} = \frac{1}{k_{0A4}} dz_{A4}. \quad (3.9_2)$$

Hence,

$$dt = \left(\frac{x}{k_{1B1}} + \frac{1}{k_{0B1}} \right) dx_{B1}, \quad (3.10_1)$$

$$dt = \left(\frac{x}{k'_{1A2}} + \frac{1}{k'_{0A2}} \right) dx_{A2}, \quad (3.10_2)$$

$$dt = \left(\frac{y}{k'_{1B2}} + \frac{1}{k'_{0B2}} \right) dy_{B2}, \quad (3.11_1)$$

$$dt = \left(\frac{y}{k'_{1A3}} + \frac{1}{k'_{0A3}} \right) dy_{A3}, \quad (3.11_2)$$

$$dt = \left(\frac{z}{k_{1B3}} + \frac{1}{k_{0B3}} \right) dz_{B3}, \quad (3.12_1)$$

$$dt = \left(\frac{z}{k_{1A4}} + \frac{1}{k_{0A4}} \right) dz_{A4}. \quad (3.12_2)$$

Since equations (3.10₁)-(3.12₂) are assumed to be independent of each other, the increases in thickness of the A_pB_q , A_rB_s and A_lB_n layers can be expressed from them as follows

$$dx_{B1} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} dt, \quad (3.13_1)$$

$$dx_{A2} = \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}} dt, \quad (3.13_2)$$

$$dy_{B2} = \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}} dt, \quad (3.14_1)$$

$$dy_{A3} = \frac{k'_{0A3}}{1 + \frac{k'_{0A3}y}{k'_{1A3}}} dt, \quad (3.14_2)$$

$$dz_{B3} = \frac{k_{0B3}}{1 + \frac{k_{0B3}z}{k_{1B3}}} dt, \quad (3.15_1)$$

$$dz_{A4} = \frac{k_{0A4}}{1 + \frac{k_{0A4}z}{k_{1A4}}} dt. \quad (3.15_2)$$

The increase of the thickness of the A_pB_q layer during the time dt , due to partial chemical reactions (3.1₁) and (3.1₂), is (see Fig. 3.2)

$$dx_+ = dx_{B1} + dx_{A2}. \quad (3.16)$$

The decrease of the thickness of this layer during the same time dt as a result of partial chemical reaction (3.2₁) in which the A_pB_q compound is a reactant, is equal to (see Section 2.2)

$$dx_-^{(2)} = \frac{rg_1}{p} dy_{B2}, \quad (3.17)$$

where $g_1 = V_{A_pB_q} / V_{A_rB_s}$, V is the molar volume of an appropriate compound. Thus, the total change, dx , of the thickness of the A_pB_q layer during the time dt is

$$dx = dx_+ - dx_-^{(2)} = dx_{B1} + dx_{A2} - \frac{rg_1}{p} dy_{B2}. \quad (3.18)$$

For the A_rB_s layer, the increase of its thickness during the time dt is

$$dy_+ = dy_{B2} + dy_{A3}. \quad (3.19)$$

Unlike the A_pB_q compound which is only consumed by one partial chemical reaction (3.2₁), the A_rB_s compound is a reactant of two partial chemical reactions (3.1₂) and (3.3₁). Therefore, during dt the thickness of the A_rB_s layer decreases by

$$dy_-^{(2)} = \frac{q}{sg_1} dx_{A2} \quad (3.20)$$

at interface 2 as a result of reaction (3.1₂) and by

$$dy_{-}^{(3)} = \frac{lg_2}{r} dz_{B3} \quad (3.21)$$

at interface 3 as a result of reaction (3.3₁), where $g_2 = V_{A_rB_s} / V_{A_lB_n}$.

Hence, the total change, dy , of the thickness of the A_rB_s layer during the time dt is

$$dy = dy_{B2} + dy_{A3} - \frac{q}{sg_1} dx_{A2} - \frac{lg_2}{r} dz_{B3}. \quad (3.22)$$

Evidently, for the A_lB_n layer,

$$dz_{+} = dz_{B3} + dz_{A4} \quad (3.23)$$

and

$$dz_{-}^{(3)} = \frac{s}{ng_2} dy_{A3}, \quad (3.24)$$

with the total change, dz , of its thickness during the time dt being

$$dz = dz_{B3} + dz_{A4} - \frac{s}{ng_2} dy_{A3}. \quad (3.25)$$

The required system of non-linear differential equations describing the growth rates of three chemical compound layers A_pB_q , A_rB_s and A_lB_n at the interface between two mutually insoluble solid elementary substances A and B is obtained by inserting the expressions for the layer-thickness changes from equations (3.13₁)-(3.15₂) into equations (3.18), (3.22) and (3.25), giving

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}} - \frac{rg_1}{p} \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}}, \quad (3.26_1)$$

$$\frac{dy}{dt} = \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}} + \frac{k'_{0A3}}{1 + \frac{k'_{0A3}y}{k'_{1A3}}} - \frac{q}{sg_1} \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}} - \frac{lg_2}{r} \frac{k_{0B3}}{1 + \frac{k_{0B3}z}{k_{1B3}}}, \quad (3.26_2)$$

$$\frac{dz}{dt} = \frac{k_{0B3}}{1 + \frac{k_{0B3}z}{k_{1B3}}} + \frac{k_{0A4}}{1 + \frac{k_{0A4}z}{k_{1A4}}} - \frac{s}{ng_2} \frac{k'_{0A3}}{1 + \frac{k'_{0A3}y}{k'_{1A3}}}. \quad (3.26_3)$$

Undertaking no attempt to find a general solution to this rather complicated system, let us analyse the most important consequences resulting immediately from the differential equations and their solutions in a few simplest limiting cases.

3.3: Initial linear growth of three compound layers

During certain initial period of time, the rates of diffusion of the A and B atoms do not play any significant role in determining the rates of formation of the A_pB_q , A_rB_s and A_lB_n layers. Their growth rates are only restricted by the rates of chemical transformations at the phase interfaces, both types of the diffusing atoms being in great excess for the growth of each of the layers. This does not necessarily mean, however, that they will all occur and grow simultaneously in any reaction couple $A-B$.

At small thicknesses of the A_pB_q , A_rB_s and A_lB_n layers, the terms of the type k_0x/k_1 are evidently negligible in comparison with unity. Hence, the system of equations (3.26) is simplified to

$$\frac{dx}{dt} = k_{0B1} + k'_{0A2} - \frac{rg_1}{p} k'_{0B2}, \quad (3.27_1)$$

$$\frac{dy}{dt} = k'_{0B2} + k'_{0A3} - \frac{q}{sg_1} k'_{0A2} - \frac{lg_2}{r} k_{0B3}, \quad (3.27_2)$$

$$\frac{dz}{dt} = k_{0B3} + k_{0A4} - \frac{s}{ng_2} k'_{0A3}. \quad (3.27_3)$$

From the system of equations (3.27), it follows that there may be a few ways of occurrence and further growth of the A_pB_q , A_rB_s and A_lB_n layers, depending on the values of the chemical constants k_0 , the stoichiometry of the compounds and the ratio of their molar volumes.

- (1) If the derivatives dx/dt , dy/dt and dz/dt are positive, then all three layers will occur and grow simultaneously according to a linear law from the very beginning of interaction of initial substances A and B (Fig. 3.3a).
- (2) If the condition $k_{0B1} + k'_{0A2} = (rg_1/p)k'_{0B2}$ happens to be satisfied, then the thickness of the A_pB_q layer, if present, remains constant (Fig. 3.3b) or is equal to zero if this layer was lacking in the initial $A-B$ couple.
- (3) If $k_{0B1} + k'_{0A2} < (rg_1/p)k'_{0B2}$, then the thickness of the A_pB_q layer present initially will decrease up to its disappearance because $dx/dt < 0$ (Fig. 3.3c). Only the A_rB_s and A_lB_n layers will grow between initial substances A and B . In the absence of the A_pB_q layer, their growth kinetics are described by a system of two differential equations similar to (2.30) (see Section 2.3)

$$\frac{dy}{dt} = k_{0B2} + k'_{0A3} - \frac{lg_2}{r} k_{0B3}, \quad (3.28_1)$$

$$\frac{dz}{dt} = k_{0B3} + k_{0A4} - \frac{s}{ng_2} k'_{0A3}. \quad (3.28_2)$$

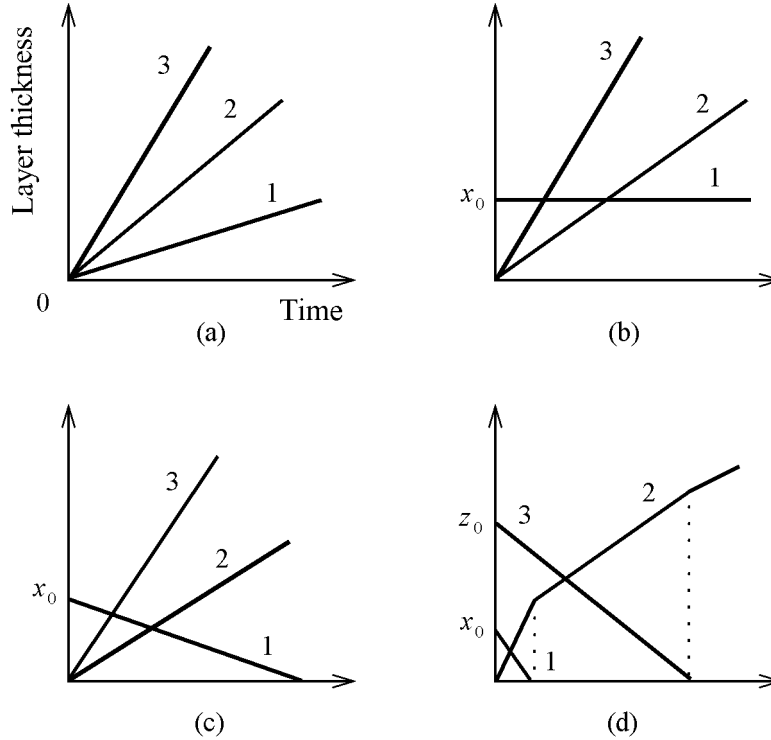


Fig.3.3. Typical dependences of the thickness of the layers of three chemical compounds A_pB_q (line 1), A_rB_s (line 2) and A_lB_n (line 3) upon the time in an initial period of interaction of elementary substances A and B : (a) simultaneous linear growth of all three layers; (b) thickness of the A_pB_q layer remains constant, while the A_rB_s and A_lB_n layers grow linearly; (c) thickness of the A_pB_q layer decreases up to its complete disappearance, while the A_rB_s and A_lB_n layers grow linearly; (d) only the A_rB_s layer grows, while the A_pB_q and A_lB_n layers are gradually consumed until their disappearance.

Note that k_{0B2} is not equal to k'_{0B2} since the chemical reactions at the A – A_rB_s and A_pB_q – A_rB_s interfaces in the reacting systems A – A_rB_s – A_lB_n – B and A – A_pB_q – A_rB_s – A_lB_n – B are different. Indeed, in the former system the B atoms diffusing across the A_rB_s layer react at interface 2 with phase A , while in the latter with phase A_pB_q . In order that not to change the numeration of all the interfaces shown in Fig. 3.1, both interfaces were designated by the same digit 2.

(4) If $dx/dt < 0$ and $dz/dt < 0$, then the A_pB_q and A_lB_n layers cannot occur at all and therefore only the A_rB_s layer will grow at the interface between substances A and B according to a

linear law (Fig. 3.3d). If the layers of all three compounds were present in initial specimens, the thickness of the A_pB_q and A_lB_n layers should decrease and they will disappear completely after some time, if of course the thickness of the A_rB_s layer does not exceed the minimal values necessary for the growth of these layers to start.

It should be noted that the disappearance of each of the A_pB_q and A_lB_n layers considerably reduces the rate of linear growth of the A_rB_s layer, as shown schematically in Fig. 3.2d, because the closer the compositions of adjacent non-growing phases to the composition of any growing compound layer, the greater is the growth rate of that layer. This question will be considered in more detail in Chapter 4.

3.4: Transition from linear to non-linear layer-growth kinetics

It is clear that the layer which has disappeared or was missing at the linear stage of reaction between substances A and B can then occur and grow again in the $A-B$ reaction couple. Assume that the A_pB_q layer present initially has disappeared (Fig. 3.4).

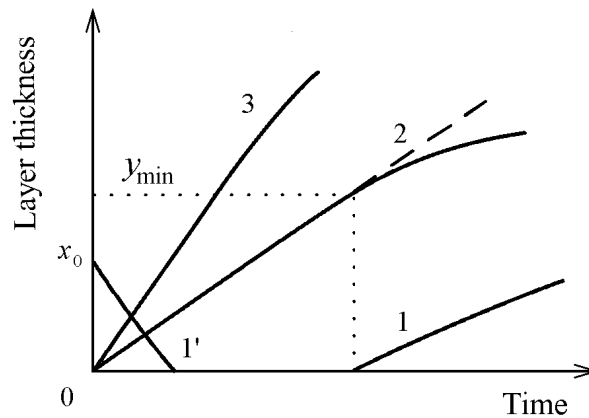


Fig. 3.4. Schematic illustration of the transition from the linear to non-linear stage of formation of the A_pB_q (lines 1' and 1), A_rB_s (line 2) and A_lB_n (line 3) layers between elementary substances A and B . The A_pB_q layer present initially first disappears and then occurs and grows again after the A_rB_s layer has reached the necessary minimal thickness, $y_{\min}$.

Since the A_rB_s and A_lB_n layers gradually thicken with increasing reaction time, at a certain moment of time the term $k'_{0B2}y/k'_{1B2}$ in the denominator of equation (3.26₁) becomes significant in comparison with unity and therefore should be taken into account. This may lead to a change in the number of growing compound layers.

Indeed, increasing the thickness, y , of the A_rB_s layer reduces the value of the third term

$$\frac{rg_1}{p} \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}}$$

on the right-hand side of equation (3.26₁). As its first two terms still remain almost constant and equal to k_{0B1} and k'_{0A2} , it is obvious that at a certain thickness, $y_{\min}$, of this layer the equality

$$k_{0B1} + k'_{0A2} = \frac{rg_1}{p} \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y_{\min}}{k'_{1B2}}} \quad (3.29)$$

will inevitably be satisfied.

Therefore, the derivative dx/dt becomes positive. This means that the A_pB_q layer will start to grow between the A and A_rB_s phases if, of course, the substance A is not consumed completely by that moment of time. The value, $y_{\min}$, is again a minimal thickness of the A_rB_s layer to be attained before the A_pB_q layer can start growing (see Section 2.4).

3.5: Critical thicknesses of compound layers and their influence on layer-growth kinetics

It seems more likely, however, that the number of growing compound layers will decrease, not increase, with increasing time of interaction of initial substances A and B . This is due to the existence of critical layer thicknesses (see Sections 1.3.1 and 2.2).

Evidently, at some thickness, say, of the A_pB_q layer the flux of the A atoms across its bulk and the reactivity of the surface of the A_rB_s layer towards these atoms become equal. This is a critical thickness of the A_pB_q layer at which the equality

$$dt_{\text{dif}}^{(A \rightarrow A_pB_q)} = dt_{\text{chem}}^{(A \rightarrow A_pB_q)}$$

is satisfied for the reacting A atoms.

By applying similar equalities to equations (3.7₁)-(3.9₂), one obtains the expressions for the critical layer thicknesses:

$$x_{1/2}^{(B)} = \frac{k_{1B1}}{k_{0B1}}, \quad (3.30_1)$$

$$x_{1/2}^{(A)} = \frac{k'_{1A2}}{k'_{0A2}}, \quad (3.30_2)$$

$$y_{1/2}^{(B)} = \frac{k'_{1B2}}{k'_{0B2}}, \quad (3.31_1)$$

$$y_{1/2}^{(A)} = \frac{k'_{1A3}}{k'_{0A3}}, \quad (3.31_2)$$

$$z_{1/2}^{(B)} = \frac{k_{1B3}}{k_{0B3}}, \quad (3.32_1)$$

$$z_{1/2}^{(A)} = \frac{k_{1A4}}{k_{0A4}}. \quad (3.32_2)$$

By comparing equations (1.17), (1.22), (2.28₁)-(2.29₂) and (3.30₁)-(3.32₂), it is easy to understand that some of the critical layer thicknesses are practically the same in all three reacting systems $A-A_pB_q-B$, $A-A_pB_q-A_rB_s-B$ and $A-A_pB_q-A_rB_s-A_lB_n-B$, while the others are definitely different. Practically and not precisely the same, because the value of any critical thickness is dependent, though probably to a negligible extent, upon where the reacting atoms are diffusing from.

For example, the critical thicknesses of the A_pB_q layer with regard to component B are the same since in all the systems the B atoms diffusing across its bulk react with the same phase A . However, the critical thicknesses of the same A_pB_q layer with regard to component A in the reacting systems $A-A_pB_q-B$ and $A-A_pB_q-A_rB_s-B$ are different, while in the reacting systems $A-A_pB_q-A_rB_s-B$ and $A-A_pB_q-A_rB_s-A_lB_n-B$ they are the same. To avoid confusion, in some cases it would be necessary to use more complicated designations for the critical layer thicknesses. For brevity, the simplified designations are nonetheless employed throughout, relying upon the comprehension of the reader.

At $x = x_{1/2}^{(A)}$, all the A atoms diffusing across the A_pB_q layer are combined by the surface of the A_rB_s layer into the A_pB_q compound at interface 2 according to reaction (3.1₂). Therefore, at $x \geq x_{1/2}^{(A)}$ none of these atoms is available for reaction (3.2₂) leading to the growth of the A_rB_s layer and even more so for reaction (3.3₂) resulting in the formation of the A_lB_n layer. Thus, the A_rB_s and A_lB_n layers cannot grow at the expense of diffusion of component A if the growth regime of the A_pB_q layer is diffusion controlled with regard to this component in the theoretical definition, *i.e.* if $x > x_{1/2}^{(A)}$.

An unambiguous criterion to distinguish between the growth regimes of any compound layer is the availability or lack of a given kind of diffusing atoms for other layers of a multiphase binary system. Under conditions of reaction (chemical) control these atoms are still available, while under conditions of diffusion control already not, and this is all that is necessary to explain the absence of some part of compound layers from the $A-B$ reaction couple.

If $x > x_{1/2}^{(A)}$, then the second terms of equations (3.26₂) and (3.26₃) and also the third term of equation (3.26₃) simply have no physical meaning and therefore should be omitted whatever y and z . At $x \gg x_{1/2}^{(A)}$, the system of equations (3.26) becomes

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k'_{1A2}}{x} - \frac{rg_1}{p} \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}}, \quad (3.33_1)$$

$$\frac{dy}{dt} = \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}} - \frac{q}{sg_1} \frac{k'_{1A2}}{x} - \frac{lg_2}{r} \frac{k_{0B3}}{1 + \frac{k_{0B3}z}{k_{1B3}}}, \quad (3.33_2)$$

$$\frac{dz}{dt} = \frac{k_{0B3}}{1 + \frac{k_{0B3}z}{k_{1B3}}}. \quad (3.33_3)$$

The growth process of the A_lB_n layer is seen to be quite independent of those of two other layers because equation (3.33₃) contains neither x , nor y . Note that in this case all three layers can still grow simultaneously. The A_pB_q layer will grow at the expense of diffusion of both components, whereas the A_rB_s and A_lB_n layers will grow only at the expense of diffusion of component B , as illustrated in Fig. 3.5.

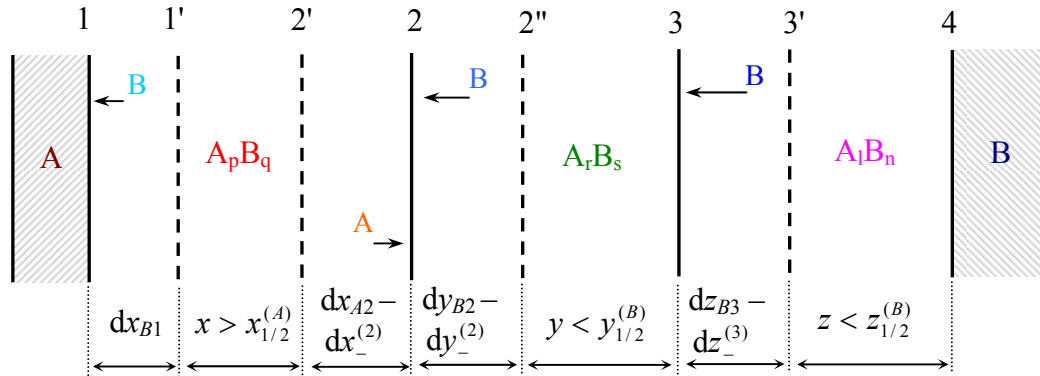


Fig. 3.5. Schematic diagram to illustrate the case where the A_pB_q layer grows at the expense of diffusion of both components, while the A_rB_s and A_lB_n layers grow at the expense of diffusion of only component B . The only source of diffusing A atoms for all the layers to grow is in fact substance A . Since the growth regime of the A_pB_q layer adjacent to phase A is diffusion controlled with regard to component A ($x > x_{1/2}^{(A)}$), the A_rB_s and A_lB_n layers lose the source of diffusing A atoms and therefore grow no longer at the expense of diffusion of this component, whatever their thicknesses and growth regimes. The growing compound layers readily supply to each other only the remaining diffusing atoms not consumed during their own growth process. In regards to the supply of diffusing A atoms, the A_lB_n layer is seen to be in the most unfavourable position.

Analysis of the kinetic dependence describing the simultaneous growth of compound layers in the $A-AB-AB_2-AB_3-B$ system can be found in the work by S.-L. Zhang and F.M. d'Heurle [313]. Even in the simplest case of diffusion of one component, this dependence is rather complicated.

3.6: Diffusional stage of formation of compound layers

The conditions of formation of the A_pB_q , A_rB_s and A_lB_n layers are changed drastically when at $z > z_{1/2}^{(B)}$ the growth regime of the A_lB_n layer becomes diffusion controlled with regard to component B . In such a case, all the B atoms crossing the A_lB_n layer are combined by the surface of the A_rB_s layer into the A_lB_n compound at interface 3 (Fig. 3.6). Therefore, the A_pB_q and A_rB_s layers lose a source of B atoms for their growth.

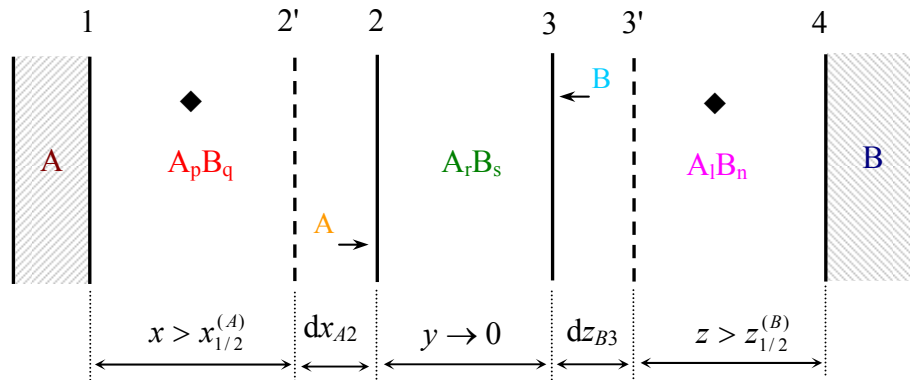


Fig. 3.6. Diffusional stage of formation of three chemical compound layers when $x > x_{1/2}^{(A)}$ and $z > z_{1/2}^{(B)}$. The A_pB_q layer grows only at interface 2 at the expense of diffusion of component A . At interface 1 its thickness does not increase because of the lack of diffusing B atoms. The A_lB_n layer grows only at interface 3 at the expense of diffusion of component B . At interface 4 its thickness does not increase because of the lack of diffusing A atoms. The A_rB_s layer having no source of both A and B atoms cannot grow at all and is therefore consumed until its full disappearance. The symbol $\blacklozenge$ designates an inert marker.

It is clear that at $x > x_{1/2}^{(A)}$ and $z > z_{1/2}^{(B)}$ the A_pB_q layer can still grow at the expense of diffusion of component A , whereas the A_rB_s layer having no source of diffusing A and B atoms cannot grow at all. Thus, in the diffusional stage the A_pB_q layer grows at the expense of diffusion of the A atoms across its bulk from interface 1 to interface 2 and subsequent partial chemical reaction (3.1₂), while the A_lB_n layer grows at the expense of diffusion of the B atoms across its bulk from interface 4 to interface 3 and subsequent partial chemical reaction (3.3₁). The middle layer A_rB_s is consumed during their growth until it entirely disappears (Fig. 3.7).

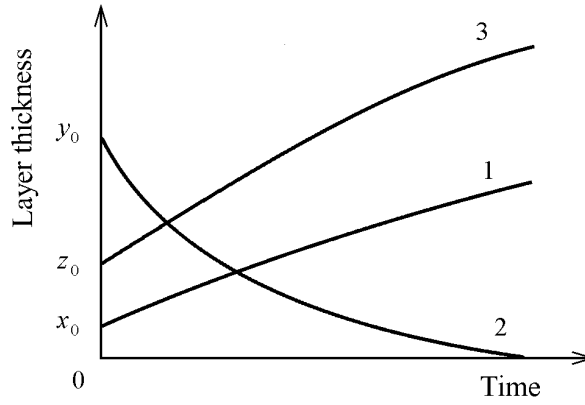


Fig. 3.7. Layer thickness-time plots for the A_pB_q , A_rB_s and A_lB_n layers in the diffusional stage of their formation at $x > x_{1/2}^{(A)}$ and $z > z_{1/2}^{(B)}$. The A_pB_q and A_lB_n layers grow (parabolically at $x \gg x_{1/2}^{(A)}$ and $z \gg z_{1/2}^{(B)}$), while the A_rB_s layer shrinks and eventually disappears completely.

In the late diffusional stage of formation of three compound layers ($x \gg x_{1/2}^{(A)}$ and $z \gg z_{1/2}^{(B)}$), the system of equations (3.26) becomes

$$\frac{dx}{dt} = \frac{k'_{1A2}}{x}, \quad (3.34_1)$$

$$\frac{dy}{dt} = -\frac{q}{sg_1} \frac{k'_{1A2}}{x} - \frac{lg_2}{r} \frac{k_{1B3}}{z}, \quad (3.34_2)$$

$$\frac{dz}{dt} = \frac{k_{1B3}}{z}. \quad (3.34_3)$$

The A_pB_q and A_lB_n layers are seen to grow parabolically, whereas the thickness of the A_rB_s layer will gradually decrease with passing time. Eventually, this layer disappears. It is easy to notice that in this case the values of the diffusional constants k'_{1A2} and k_{1B3} can readily be determined from the experimental dependences $x^2 - t$ and $z^2 - t$, respectively, using an artificially prepared specimen $A-A_pB_q-A_rB_s-A_lB_n-B$ or $A-A_rB_s-B$. It is essential to mention that both the A_pB_q and A_lB_n layers must be the first to occur at the A–B interface. The diffusional constant k'_{1A2} thus obtained is the reaction-diffusion coefficient of the A atoms in the A_pB_q lattice, while the diffusional constant k_{1B3} is the reaction-diffusion coefficient of the B atoms in the A_lB_n lattice (for their comparison with respective self-diffusion coefficients determined using radioactive tracers, see Section 1.9 of Chapter 1).

After the disappearance of the A_rB_s layer, the system $A-A_pB_q-A_lB_n-B$ remains. Growth kinetics of two compound layers have already been considered in Chapter 2.

During further isothermal holding, the A_pB_q and A_lB_n layers will grow until one of initial substances A or B is consumed completely. The A_rB_s layer can then form and grow either in the A_pB_q – A_rB_s – A_lB_n – B system or in the A – A_pB_q – A_rB_s – A_lB_n system.

To avoid any misunderstanding and confusion, it should be emphasised that it is only the *growth* of the third compound layer *between* the two compound layers already growing in the diffusion controlled regimes with regard to appropriate components, that is impossible. If, for example, the A_rB_s and A_lB_n layers grow between substances A and B , then the A_pB_q layer having an immediate contact with a source of A atoms, *i.e.* with substance A , may in principle occur and grow at the A – A_rB_s interface, whatever the growth regimes of the A_rB_s and A_lB_n layers. However, when the growth regimes of the A_pB_q and A_lB_n layers become diffusion controlled with regard to components A and B , respectively, then the A_rB_s layer proves “superfluous” and must inevitably disappear with passing time.

It is clear that if A_pB_q is the most A -rich compound and A_lB_n is the most B -rich compound of a binary multiphase system, then no other compound layer can grow in the A – B reaction couple until the full consumption of one of initial phases A or B , provided that the A_pB_q layer grows in the diffusion controlled regime with regard to component A and the A_lB_n layer grows in the diffusion controlled regime with regard to component B . Since in practice relatively thick layers of chemical compounds, already growing in the diffusion controlled regimes with regard to both components, are investigated, it becomes clear why in the majority of the A – B reaction couples the dominant growth of at most two layers is observed, irrespective of the total number of chemical compounds on the equilibrium phase diagram of a particular multiphase binary system.

3.7: Sequence of compound-layer formation at the A – B interface

From a theoretical viewpoint, predicting the sequence of layer occurrence at the A – B interface would present no difficulties if the values of all the chemical constants entering into a system of differential equations like (3.27) were known. For any multiphase binary system A – B , these values are determined by the physical and chemical properties of the elements A and B and their compounds. With their dependence on those properties established, the sequence of formation of compound layers would readily be predicted from the system of equations (3.27) or similar. Unfortunately, the theory of the reaction-diffusion process has not yet reached this stage of its development.

It is obvious that the simultaneous occurrence of all compound layers at the A – B interface is highly unlikely even from a formal statistical viewpoint. For example, with three compounds, the total probability of the cases where the derivatives dx/dt , dy/dt and dz/dt have different signs (+,–,–; –,+,–; –,–,+; +,+,–; +,–,+; –,+,+) is evidently much greater than the probability of the case in which all three derivatives are positive (+,+,+), with their ratio being 6:1. Therefore, formation of the A_pB_q , A_rB_s and A_lB_n layers must be sequential rather than simultaneous, in contrast to diffusional predictions but in accordance with experimental observations.

Exact laws governing the sequence of occurrence of compound layers in a particular reaction couple have not so far been established. What is available is a few empirical rules predicting this sequence at a probability level of about 60 to 90%. These are based either (i) on the main features of the equilibrium phase diagram of a binary system A – B or (ii) on the thermodynamic properties of its constituting phases.

3.7.1: Phase-diagram predictions

The equilibrium phase diagram of an appropriate binary or multi-phase system is doubtless one of the main sources from which the researcher obtains the required primary data when starting to investigate the kinetics of formation of chemical compound layers in a particular binary system. It immediately indicates what compounds *may* form as separate layers but clearly by no means dictates that those *must* necessarily occur at A – B interface *simultaneously*.

In the case of binary systems with three or more compounds, generally there is no full correspondence between the microstructure of the A – B transition zone and the appropriate equilibrium phase diagram, whatever the annealing time of reaction couples. Part of compounds will inevitably be missing, not simply too thin to be observed, for kinetic reasons. Therefore, to confidently judge of the structure of the A – B equilibrium phase diagram from reaction-diffusion experiments, it is necessary to investigate not only the A – B diffusion couple but also a few diffusion couples consisting of initial substances A and B and their compounds.

In binary systems with one chemical compound, there is a full correspondence between what is seen at the A – B interface and the equilibrium phase diagram in the sense that all the reacting phases are available in the microstructure of the A – B transition zone. During growth of any compound layer under conditions of diffusion control, boundary contents of the components in this layer may reasonably be expected to be equal to the limiting values of the homogeneity range of that compound, if any. Note that, even in this simplest case, there can be no equilibrium between all three reacting phases. One of them is “superfluous” since, according to the Gibbs phase rule, in any binary system only two phases can coexist under equilibrium at constant temperature and pressure.

In binary systems with two compounds, a full correspondence between the microstructure of the A – B transition zone and the appropriate equilibrium phase diagram can in principle be achieved at prolonged annealing. The only obstacle for this may be a very great difference in growth rates of compound layers. In such a case, one of them occurs after a considerable time delay and then over a long period of time is much thinner than the other.

As soon as both compound layers grow under conditions of diffusion control, boundary contents of the components in these layers are again equal to the limiting values of the homogeneity ranges of those compounds, if any. The concentration distribution within layer bulks must be close to linear.

It should be noted that both stable and metastable compounds may occur in reaction couples. Analysis of the available experimental data shows that the growth of metastable compound layers is observed relatively rarely. The possibility of formation of metastable compounds is usually mentioned in the explanatory note accompanying the equilibrium phase diagram of any system. For many systems, diagrams of both stable and metastable equilibria have been established [157, 159, 217, 281-290].

At a large difference in melting points of components *A* and *B*, the compound enriched in a low-melting component can evidently be expected to occur and grow first. According to an empirical correlation formulated by F.M. d'Heurle [34] as the ordered Cu₃Au phase rule, the first compound to occur should have the highest content of a component with a lower melting point and diffusion of atoms of that component prevails during formation of this compound. R.W. Walser and R.W. Bene [314] suggests that the first compound formed in a planar reaction couple must be the most stable, congruently melting compound bordering the lowest-melting eutectic on the equilibrium phase diagram of a binary system. If congruently melting compounds are present at both sides of this eutectic, the layer of the compound with a higher melting point will be the first to occur

According to a correlation established by B.Y. Tsaur *et al.* [79] when analysing the sequence of formation of transition metal silicides, the second compound to form is the nearest congruently melting compound enriched in the unreacted element. If all the compounds are non-congruently melting phases, then B.Y. Tsaur *et al.* suggest that a criterion for the sequence of their further formation should be the difference, ΔT , in temperatures between the liquidus curve and the peritectic horizontal, with the second phase to form being the compound having the lowest value of ΔT existing on the equilibrium phase diagram between the composition of the first phase and the unreacted element.

Clearly, if diffusion of one of the components (either *A* or *B*) prevails in all the compounds of a multiphase binary system, then only the layer of one of those compounds will grow. Probably, the previously mentioned Ti–Al system just belongs to such systems. Therefore, the results obtained by F.J.J. van Loo [68] with artificially prepared Ti–Ti₃Al–TiAl–TiAl₂–TiAl₃–Al specimens at 625 °C becomes easily explainable.

The melting point of titanium is 1670 °C, while that of aluminium is 660 °C [157]. In kelvins, these are 1943 K and 933 K, respectively. Thus, the temperature 625 °C (898 K) amounts to 0.46 T_{melting} of titanium and 0.96 T_{melting} of aluminium. Hence, at this temperature the aluminium atoms may be expected to be much more mobile in the crystal lattices of the titanium aluminides than the titanium atoms. This appears to be the case even with the Ti₃Al compound. The duplex structure of the Ti₃Al layer in the Ti–TiAl diffusion couple (see Fig. 5.13 of Ref. [68]) provides evidence that aluminium is the main diffusing species. Otherwise, its microstructure would be homogeneous. This point will be explained in more detail in the next chapter devoted to the consideration of growth kinetics of the same compound layer in various reaction couples of a multiphase binary system.

Under conditions of diffusion control, the TiAl_3 layer which is known to be the first to occur between titanium and aluminium, consumes all the Al atoms diffusing across its bulk exclusively for the growth of its own, not sharing them with the other intermetallic layers. Therefore, those or at least one of them can only grow at the expense of diffusion of the Ti atoms.

It seems likely that the self-diffusion coefficient of aluminium in the TiAl_3 lattice does not exceed its self-diffusion coefficient in pure solid aluminium. According to the data by L.N. Larikov *et al.* [168] (see also Ref. [315]), at 625 °C the value of this coefficient is on the order of $10^{-12} \text{ m}^2 \text{ s}^{-1}$.

On the other hand, by extrapolating the data of H. Nakajima and M. Koiwa [316], the self-diffusion coefficient of titanium in α -titanium at 625 °C is found to be of the order of $10^{-18} \text{ m}^2 \text{ s}^{-1}$. It is reasonable to assume that the self-diffusion coefficient of titanium in Ti_3Al and other titanium-enriched aluminides does not differ from this figure by more than one or two orders of magnitude. As, for any compound, the ratio of reaction-diffusion coefficients of its components may be expected to be close, if not equal, to the ratio of appropriate self-diffusion coefficients, it becomes obvious that the reaction-diffusion coefficient of aluminium in TiAl_3 is at least four orders of magnitude greater than the reaction-diffusion coefficient of titanium in titanium-enriched aluminides. Since (i) diffusional (physical) constants are identified with corresponding reaction-diffusion coefficients (see Section 1.9) and (ii) the ratio of layer thicknesses in the course of simultaneous growth of two compound layers is proportional to those constants (see equation (2.48)), the thickness of the TiAl_3 layer at 625 °C must be about four orders of magnitude greater than that of any other aluminide layer.

Thus, if the former is 100 μm , then the latter may (roughly) be estimated as 10 nm. Such layers are scarcely identifiable with the help of most frequently employed experimental techniques. Until recently, difficulties of studying the nanometer-range phases were used to justify the belief in invisible compound layers.

Experiments like those of S. Wöhlert and R. Bormann [121] clearly indicate, however, that there are no grounds for such a belief. When investigating the Ti– Ti_3Al –Al and Ti– TiAl –Al reaction couples with initial thicknesses of the deposited Ti_3Al and TiAl layers of around 200 nm, they found those layers to disappear completely during growth of the TiAl_3 layer, with no indication of formation of the TiAl_2 layer. Note that the beam spot had a diameter of about 2 nm. For comparison, lattice spacings of the titanium aluminides lie in the range of approximately 0.4–2.5 nm [157, 280]. Evidently, any really present intermetallic layer could hardly be overlooked by S. Wöhlert and R. Bormann.

From a physico-chemical viewpoint, those are indeed missing from the Ti–Al reaction couple. This is due mainly to large rates of their consumption in the formation of the TiAl_3 layer and not merely to small rates of diffusion of reacting atoms in their bulks.

Note that in the framework of purely diffusional considerations any diffusing atoms are assumed to be available for any growing compound layer. In other words, the existence of any interface barriers to prevent diffusion of appropriate atoms is not recognised. From this viewpoint, it would be more logical to compare the diffusion coefficients of aluminium, as the more mobile component, in all the titanium aluminides. In such a case, the absence of most aluminide layers becomes quite unexplainable. It is highly unlikely that the diffusion coefficients of aluminium in different titanium aluminides are so different as to exclude the formation, for example, of the TiAl_2 layer.

Definitely, more experimental work is desirable with thin films, but even already existing data provide sufficient evidence for rejecting the erroneous idea about the simultaneous formation of compound layers, with some being invisible due to their small thickness.

The second apparent factor influencing the mobility of the atoms and hence the sequence of compound-layer formation is atomic radii of reacting elements. Clearly, the direct juxtaposition of the melting points to decide which compound has a greater chance to occur first is only justified if the atomic radii are identical or close for both elements, as is the case of titanium and aluminium, the atomic radius being 0.146 nm and 0.143 nm, respectively [166, 167]. Similarly, the juxtaposition, with the same purpose, of the atomic radii is only valid if the melting points of both elements are close. An example of this kind is the Al–Mg binary system already considered in Section 2.8.3 of Chapter 2.

If both the melting points and the atomic radii of the elements are close, two compound layers may be expected to grow at comparable rates. The melting point of molybdenum is 2620 °C, while that of iridium is 2447 °C [166, 167]. Appropriate atomic radii are 0.139 nm and 0.135 nm. Therefore, as established by E.K. Ohriner and E.P. George [294], in the temperature range of 1200–1475 °C two intermetallic layers MoIr and MoIr_3 grow between iridium and molybdenum simultaneously at close rates.

Generally, these factors can act either in the same direction, strengthening the effect of each other, or in the opposite direction, thereby weakening this effect. In the former case, the final result is quite obvious, whereas in the latter it is hardly predictable *a priori*. For example, in the Ni–Bi binary system the melting point of nickel is 1455 °C, while that of bismuth is 271 °C. Atomic radii are 0.124 nm and 0.182 nm, respectively. From the point of view of melting temperatures, bismuth may be expected to be more mobile in the nickel bismuthides in the solid state, whereas from the point of view of atomic radii smaller nickel atoms must diffuse much faster. In this particular case, the effect of the difference in the melting points is known to prevail over that of the difference in the atomic radii [163, 164].

As the atomic radius of nickel is much less than that of titanium, not only NiAl_3 , but also Ni_2Al_3 can occur at the Ni–Al interface, especially at elevated temperatures. According to the data of E.G. Colgan *et al.* [91], X.-A. Zhao *et al.* [97, 98] and E. Ma *et al.* [317, 318], only one layer of the nickel aluminide NiAl_3 is formed between nickel and aluminium at temperatures of 300–425 °C. The layer of this compound is known to grow in the artificially prepared Ni–NiAl–Al specimens, whereas the existing NiAl layer disappears [91]. S.B. Jung

et al. [112] have observed the simultaneous growth of the Ni_2Al_3 and NiAl_3 layers between pure aluminium and the NiAl phase (49.5 at.% Ni) at temperatures of 550–635 °C, with the Ni_2Al_3 layer being much thicker than the NiAl_3 layer. According to M. Lieblisch *et al.* [319], the NiAl_3 layer is formed first in Ni_3Al –Al specimens at 350–500 °C, while then (either at longer times or at a higher temperature in that range) the Ni_2Al_3 layer starts to grow between the initial Ni_3Al phase and the growing NiAl_3 layer. A. Thevand *et al.* [77] found the Ni_2Al_3 layer to occur and grow in NiAl –Al specimens at temperatures of 760–1100 °C.

With purely ionic compounds, appropriate ionic radii must evidently be compared. Complications arise, however, with compounds formed by a metal with a non-metallic element, having partly covalent bonds. Though the values of covalent radii are available as well [166, 167], the precise nature of the chemical bond in any particular chemical compound is usually not known. It is yet unclear whether the conventional tabulated values can be used to predict the mobility of the components, for example, in the crystal lattices of transition-metal carbides, borides or silicides.

Therefore, even under close temperature and pressure conditions, the sequence of occurrence of silicide layers in metal-silicon reaction couples may be different. Indeed, A. Noya *et al.* [320] found that Ta_5Si_3 is the first compound to form in the Ta–Si thin-film couple at 650 °C. At 700 °C, in addition to Ta_5Si_3 , the TaSi_2 layer also occurs, whereas at higher temperatures only the latter grows. According to the data by T. Nakanishi *et al.* [321], the Nb_3Si compound is formed in the Nb–Si thin-film couple at 550 °C, while Nb_5Si_3 grows at 600 °C. At 650 °C, three phases Nb_3Si , Nb_5Si_3 and NbSi_2 were revealed, whereas only the NbSi_2 layer grew at 700 °C. The reason for the disappearance of the tantalum- or niobium-enriched layers is again kinetic. The TaSi_2 or NbSi_2 layer rapidly growing at the expense of diffusion of silicon fully consumes the layers of other silicides having insufficient growth rates.

At least with intermetallics, the effect of melting points and atomic radii on the sequence of occurrence of compound layers at the A–B interface appears to be more or less straightforward. On the contrary, the influence of the crystal structure of the compounds is rather obscure. Probably, those with less symmetrical and loosely packed structures may be expected to form first under highly non-equilibrium and stressed conditions typical of reaction-diffusion experiments.

Thus, by consulting the equilibrium phase diagram and knowing the physical and chemical properties of the elements A and B and their compounds, it is possible to draw certain conclusions about the sequence of compound-layer formation in a multiphase binary system. It must be remembered, however, that any predictions based on the above-mentioned or other criteria hitherto proposed are only the weak correlations rather than the firmly established rules. As both the researcher and technologist are always interested in knowing the sequence of occurrence of chemical compounds in a *particular* reaction couple, they can hardly be satisfied even with a correlation valid in 99 out of 100 cases, because it remains

unknown whether this couple falls into the range of those 99 or is the only exception. Further theoretical work in this direction is badly needed.

3.7.2: Thermodynamic predictions

The most stable compound of a multiphase binary system is often assumed to be the first to occur and grow at the A – B interface. The change, $\Delta_f G_T^0$, of the isobaric-isothermal potential (Gibbs free energy) in the reaction of formation of any compound from the elements under given conditions is usually considered to be a measure of its thermodynamic stability. The more negative the value of $\Delta_f G_T^0$, the more stable the compound is.

It should be noted, however, that the change in the free energy of formation of any compound can be calculated either per mole (or, in other words, per chemical formula), or per gram-atom (the former value should be divided by the total number of the atoms of both kinds in the molecule of the compound), or per unit volume of that compound. When the compounds are ranked according to those values, their different series will in general be obtained. In neither case, however, the juxtaposition of the experimental data on the thermodynamics of chemical reactions on the one hand and the kinetics of layer growth on the other reveals the existence of any simple, straightforward relationship between the value of $\Delta_f G_T^0$ and the sequence of occurrence of compound layers in reaction couples A – B .

In some works including textbooks, it is proposed to compare the values of the thermodynamic functions calculated per certain amount of a diffusing element. In such a case, however, it would be necessary first to identify this element. Furthermore, in the compounds of a given multiphase system, enriched in component A , diffusion of the A atoms often prevails, whereas in those enriched in component B diffusion of the B atoms is dominant. This makes any comparison of such values of the thermodynamic functions quite meaningless.

Consider the thermodynamic data on the formation of a few transition-metal silicides presented in Table 3.1. The values of $\Delta_f G_T^0$ were taken from the work by V.N. Yeremenko *et al.* [322]. When comparing the free energy changes calculated per mole of the compound, the silicides of the Me_5Si_3 type should be regarded as most stable. However, in none of the systems under consideration the compound of this composition was found to form first.

Rather, it can be concluded that more often the less stable compounds occur first (in this case, in the two out of the three systems, namely, V–Si and Mn–Si). Thus, the well-known rule of successive reactions or steps by W. Ostwald (see, for example, Ref. [324]), stating that the compound of the lowest thermodynamic stability must be expected to form first, may seem to give more adequate predictions.

Table 3.1. Gibbs free energy of formation of vanadium, chromium and manganese silicides [322] and the first phase to grow in the Me–Si reaction couples

Silicide	Temperature (°C)	$\Delta_f G_T^0$		First phase to grow	Reference
		(kJ mol ⁻¹)	(kJ g-atom ⁻¹)		
VSi ₂	650	–113	–37.7	VSi ₂	65, 69
V ₅ Si ₃		–398	–49.8		
V ₃ Si		–161	–40.3		
CrSi ₂	475	–82	–27.3	CrSi ₂	67, 89
CrSi		–61	–30.5		
Cr ₅ Si ₃		–270	–33.8		
Cr ₃ Si	475	–128	–32.0	MnSi	323
MnSi _{1.7}		–81	–30.0		
MnSi		–72	–36.0		
Mn ₅ Si ₃		–278	–34.8		
Mn ₃ Si		–104	–26.0		

However, these predictions are, firstly, not always correct, with the Cr–Si system being an exception. Secondly, if the values expressed in kilojoules per gram-atom are compared, the quite another sequences will be obtained. From this viewpoint, the MnSi compound is the most stable in the Mn–Si system, and it indeed grows first. In the two other systems, however, the least stable compounds VSi₂ and CrSi₂ are the first to form.

Hence, none of the two above-mentioned criteria can be used as a reliable basis for predicting the sequence of occurrence of chemical compound layers in multiphase binary systems. The experimental data on the formation of nickel and cobalt silicides provides additional evidence for the validity of this conclusion.

In both the Ni–Si and Co–Si systems, the compounds of the same type Me₂Si are known to be the first to grow. However, in the Ni–Si system the change in the free energy of formation is more negative for Ni₂Si than for NiSi, whereas in the Co–Si system it is more negative for CoSi than for Co₂Si [82].

It should be noted that the thermodynamic data for the same binary system often reveal a very considerable scatter. This can readily be seen from the results compiled by J. Gülpén [325] for the nickel silicides. At 850 °C, the literature values of $\Delta_f G_T^0$ vary from –28.6 to –37.4 kJ g-atom⁻¹ for Ni₃Si, from –31.2 to –39.8 kJ g-atom⁻¹ for Ni₅Si₂, from –32.2 to –41.8 kJ g-atom⁻¹ for Ni₂Si, from –30.3 to –43.8 kJ g-atom⁻¹ for Ni₃Si₂, from –27.3 to –42.3 kJ g-

atom⁻¹ for NiSi and from -20.0 to -30.5 kJ g-atom⁻¹ for NiSi₂. Clearly, it is not too difficult to select “suitable” data from this variety of the experimental values in order to validate almost any relationship.

Converting the values of the thermodynamic functions per unit volume of the compound formed does not appear to result in more adequate predictions of compound-layer sequences. Table 3.2 displays the data from the work by E.G. Colgan *et al.* [91] for the Ni–Al binary system at 350 °C.

Table 3.2. Gibbs free energy of formation of nickel aluminides (J cm⁻³) and the first phase to grow in reaction couples of the Ni–Al binary system at 350 °C [91]

Couples	Possible phases			
	NiAl ₃	Ni ₂ Al ₃	NiAl	Ni ₃ Al
Ni–Al	-4226*	-4937	-7155	-6736
Ni–NiAl–Al	-1506*	-1004	...	-2469
Ni ₃ Al–Al	-2427*	-2343	-2845	...
Ni–NiAl ₃	...	-1841*	-4058	-4853
Ni ₃ Al–NiAl ₃	...	-753*	-1339	...

*Phase observed experimentally.

In neither of reaction couples of this system the thermodynamically preferred phase is seen to form first. Again, Ostwald's rule is fulfilled in the three out of the five cases, assuming that the NiAl₃ phase is the first to occur in the Ni–Al couple. Similar results were obtained by E.G. Colgan [96] for the Pt–Al binary system with eight intermetallic compounds on the phase diagram [241]. Of the five types of reaction couples considered, in the four the intermetallic compound Pt₂Al₃ was the first to grow, although its formation was preferable thermodynamically only in one couple Pt₂Al–Al. Ostwald's rule was found to be fulfilled for the two couples Pt–PtAl₂ and Pt–Pt₂Al₃.

By combining the thermodynamic data with those on the structure of the equilibrium binary phase diagram, R. Pretorius *et al.* [326, 327] were able to improve the accuracy of predicting the sequence of compound-layer formation in the transition metal-aluminium systems. For this, they used the values of the standard enthalpies (heats) of formation of the compounds. It seems to be sufficiently justified because the change, $\Delta_f S^0$, in the entropy of solid-state formation of the ordered phases is relatively small. Hence, at low temperatures the term $T\Delta_f S^0$ of the equation $\Delta_f G^0 = \Delta_f H^0 - T\Delta_f S^0$ is insignificant in comparison with the value of $\Delta_f H^0$ and therefore can be neglected.

The approach of R. Pretorius *et al.* [326, 327] can briefly be explained as follows. Consider the formation of the Ni_2Al_3 compound between the pure nickel and aluminium phases as an example. For the purpose of illustration, let us arbitrarily assume that at the interface between those phases the effective concentration of nickel is 70 at.% and that of aluminium 30 at.%. It is clear that in this case the limiting element is aluminium, whereas nickel is in excess. The standard enthalpy of formation of the Ni_2Al_3 compound is $-57 \text{ kJ g-atom}^{-1}$. Hence, if the total number of the nickel and aluminium atoms is equal to the Avogadro number, N_A , then $57 \times 0.30 : 0.60 = 28.5 \text{ kJ}$ of heat is released in the system after consuming all the aluminium atoms in the reaction of formation of Ni_2Al_3 . Thus, R. Pretorius *et al.* introduce the concept of the effective heat, $\Delta H'$, of formation of a compound through the equation

$$\Delta H' = \Delta_f H^0 \times \frac{\text{effective concentration of limiting element}}{\text{concentration of limiting element in compound}},$$

where the enthalpies (heats) of formation is expressed in kilojoules per g-atom, while the concentrations in atomic per cent or atomic fractions.

Further, assuming that the highest mobility of the atoms and hence the most effective mixing at the interface must be expected at the composition of the eutectic with the lowest melting point according to the equilibrium phase diagram of the Ni–Al system, they selected the effective concentration to be equal to the composition of this eutectic (3.5 at.% Ni and 96.5 at.% Al). The limiting element is seen to be nickel, with its concentration being 3.5 at.%. Therefore, for Ni_2Al_3 ,

$$\Delta H' = -57 \frac{3.5}{60} = -4.98 \text{ kJ g-atom}^{-1}.$$

The values of $\Delta H'$ thus calculated are presented in Table 3.3. The standard enthalpies (heats) of formation of the nickel-aluminium compounds, expressed in kJ mol^{-1} and kJ g-atom^{-1} , are also given for comparison. It is seen that the most negative value of $\Delta H'$ is obtained for the NiAl_3 intermetallic compound which is indeed the first to form.

R. Pretorius *et al.* [326, 327] have formulated the following rules. The first phase to grow in the metal-metal interaction is a compound with the most negative effective heat, $\Delta H'$, of formation at the concentration of the eutectic (liquidus) with the lowest melting point of a binary system. After the formation of the first phase, the next phase growing between the resultant layer and the remaining element is a compound with a higher content of the unreacted element, having the most negative effective heat of formation.

Table 3.3. Standard enthalpies (heats) of formation of nickel aluminides and their effective heats of formation calculated for the effective concentration at the interface corresponding to the composition (3.5 at.% Ni, 96.5 at.% Al) of the eutectic with the lowest melting point in the Ni–Al binary system [326]. For all the intermetallic compounds, the limiting element is nickel

Compound	Chemical composition (at.%)		$\Delta_f H^0$		$\Delta H'$
	Ni	Al	(kJ mol ⁻¹)	(kJ g-atom ⁻¹)	(kJ g-atom ⁻¹)
NiAl ₃ *	25	75	–152	–38	–5.32
Ni ₂ Al ₃	40	60	–285	–57	–4.98
NiAl	50	50	–118	–59	–4.13
Ni ₃ Al	75	25	–164	–41	–1.91

*First phase to grow

Not always, however, application of these rules results in accurate predicting the sequence of layer formation, especially for compounds of complicated composition, containing the large number, Z , of the atoms in their unit cells. For example, for Pt₅Al₂₁ ($Z = 416$), $\Delta H' = -5.9$ kJ g-atom⁻¹, whereas for Pt₂Al₃ ($Z = 5$), $\Delta H' = -4.75$ kJ g-atom⁻¹ [326, 327]. Nonetheless, the first phase to occur is Pt₂Al₃ and not Pt₅Al₂₁.

Note that any mixing can hardly take place at either of the interfaces between reacting *solid* phases. Therefore, the basic assumptions of R. Pretorius *et al.* [326, 327] about a limiting element and its concentration at an interface seem to be somewhat artificial. In fact, in the reactions under consideration, there is no reaction volume, with all the interactions proceeding onto the phase surfaces exposed to each other. The distances between those surfaces scarcely exceed considerably the typical values of spacings in the crystal lattices of chemical compounds. Hence, the concept *concentration of a limiting element at an interface* does not appear to have any real physical meaning.

This does not mean, however, that the rules based on those assumptions must necessarily be incorrect. Though, for example, the original derivation of Evans' equation is definitely incorrect, the final equation itself is quite correct (see Chapter 1). Further work is required to check the applicability of the proposed rules to other binary systems of different chemical nature. Also, much effort is to be undertaken to find out other relationships between the thermodynamic properties of chemical compounds and the sequence of occurrence of their layers at the A – B interface. This sequence appears to be more dependent on the partial rather than the integral values of thermodynamic functions.

3.7.3: Reasons for the formation of multiple compound layers at the A–B interface

In some experimental works, the simultaneous presence of multiple compound layers was observed. Therefore, just as in the framework of diffusional considerations it is necessary to explain why the number of compound layers is in most cases so small, so in the framework of the physico-chemical approach proposed it is necessary to explain why in certain cases the number of those layers is so large. There are a few reasons for the formation of multilayered structures at the A–B interface. These may be summarised as follows.

(1) If the growth regimes of all the layers are reaction controlled (in the theoretical definition given in Chapter 1) at least with regard to one component, then they can in principle grow simultaneously, whatever their number. Note that in this case the layer-growth kinetics can hardly be expected to obey a parabolic law. This is characteristic of very thin compound layers, at most a few hundreds of nanometers thick.

Thus, many compound layers may occur in the A–B reaction couple of a multiphase system in the initial reaction controlled rather than in the late diffusional stage of their formation, although this seems to be somewhat paradoxical. Furthermore, initially their number may even happen to exceed the number of chemical compounds on the equilibrium phase diagram of a given binary system. This is so in the case of compounds with wide ranges of homogeneity. The layers of such compounds may consist of two sublayers of different composition.

The results of this kind have been obtained by R. Tarento and G. Blaise when studying the reactions in thin-film nickel-aluminium couples [101] (see also Ref. [328]). Using an ingenious variant of ion mass spectrometry, they were able to examine the nickel aluminide layers as thin as 5 nm. For comparison, the lattice spacings of the Ni–Al intermetallics lie in the range 0.3–0.7 nm [157, 234].

At 220 °C, the nickel aluminide layers were found to form sequentially, with the first to occur being Ni₃Al and NiAl₃. The number of the separate layers present simultaneously between nickel and aluminium was equal to six, whereas according to the equilibrium phase diagram there are only four intermetallic compounds Ni₃Al, NiAl, Ni₂Al₃ and NiAl₃ in the Ni–Al binary system [157, 217]. However, since the NiAl and Ni₂Al₃ phases have considerable ranges of homogeneity, each of them forms two sublayers of limiting compositions. These sublayers had the atomic percentages Ni₆₀Al₄₀ and Ni₄₄Al₅₆ for NiAl and Ni₄₀Al₆₀ and Ni₃₅Al₆₅ for Ni₂Al₃ [101, 328].

The upper and lower limits of the homogeneity range of the NiAl intermetallic compound are equal to 60 at.% and 45 at.% of nickel, respectively. For Ni₂Al₃, these values are 40.8 at.% and 36.3 at.% of nickel [157]. As the accuracy of measuring the width of the homogeneity range is within ±1 at.%, the agreement between the two sets of the experimental results should be regarded as fairly good.

Subsequent growth of the intermetallic layers is accompanied by a redistribution of the concentrations of the components in their bulks from stepwise to smooth, and eventually the

distribution close to linear is established. At the layer interfaces those concentrations correspond to the limiting values of the homogeneity range of a given compound.

If the equilibrium phase diagram were unknown, the data obtained by R. Tarento and G. Blaise could be interpreted in such a way, as if the Ni–Al binary system contains six intermetallic compounds. Again, judging from the late diffusional stage of growth of the nickel aluminide layers, it can be concluded that there are only two compounds in the system, namely, Ni_2Al_3 and NiAl_3 . Both conclusions are evidently incorrect. Therefore, great care is necessary not only when judging of the sequence of compound-layer formation from the phase diagram but also when constructing the phase diagram using the data of reaction-diffusion experiments.

(2) Restrictions on the number of simultaneously growing compound layers, following from physico-chemical considerations [146, 149, 151, 153-156], are not applicable to the phases with extremely wide ranges of homogeneity, similar to the ϵ -phase of the Ag–Zn binary system [56]. This phase has a homogeneity range extending from 55.1 to 81.6 % Zn.

For such phases, the condition of a quasi-stationary distribution of the concentrations of the components across the width of the layer formed is usually not fulfilled, as was observed by D.S. Williams *et al.* [56]. Note that this type of phase is not regarded as chemical compounds. During their formation, considerable part of diffusing atoms may either remain within the layer due to the existence of a wide range of homogeneity or, on the contrary, may leave that layer without the loss of stability of a given phase.

Therefore, firstly, the physical (diffusional) constants become strongly dependent upon the layer thickness and consequently vary with annealing time. Secondly, the chemical constants also become time-dependent due to the variation of boundary concentrations of the components in that layer.

In such a case, growth of other layers is possible not only at the expense of consumption of a given phase, but also at the expense of variation of the average composition of its layer. The latter is clearly impossible with typical chemical compounds having no homogeneity ranges. Since the phases with a very wide range of homogeneity are something intermediate between chemical compounds and extended solid solutions, the description of their growth kinetics requires a more detailed consideration, the theoretical basis of which is still obscure.

(3) Since compound layers are polycrystalline, grain boundary diffusion may to some extent affect both their morphology and growth kinetics. Grain boundary diffusivities of the components of any compound are known to be a few orders of magnitude higher than appropriate lattice ones.

Therefore, an excess of diffusing atoms may build up in the vicinity of the boundaries of any grain adjacent to the other phase. Part of these atoms, not consumed completely at a given interface in view of its insufficient local combining ability, are then able to diffuse further and are consumed in the formation of additional compound layers.

This must result in the formation of the layers with uneven interfaces, *i.e.* the layer thickness becomes irregular. The effect of grain boundary diffusion is clearly most profound in compound layers of columnar structure, with the grains extending from one layer interface to another. In fine-grained structures of constant grain size, it can hardly play any significant role.

(4) The effect produced by cracks in growing layers, located in the direction of atomic diffusion, is largely similar to that of grain boundary diffusion, with the main contribution to mass transport in the vicinity of any crack arising from surface diffusion. Less obvious and predictable is the effect of cracks located along and at the layer interfaces, especially of those continuously forming and disappearing in the course of annealing the reaction couples. Such cracks appear to be the main reason for the occurrence of thick multiple compound layers at the A–B interface. Therefore, this point will be analysed in more detail.

Consider first the primary causes of crack formation. These appear to be (i) the difference in the coefficients of thermal expansion of the constituents of a given reaction couple and (ii) the volume effect associated with the formation of a chemical compound, the volume of the reaction products formed being in general not equal to that of the reactants consumed.

The difference of thermal expansion coefficients of the interacting phases causes their considerable lateral displacement relative to each other, if the temperature is changed. As these are usually not free either to move laterally or to bend, great mechanical stress arisen results in the formation of cracks, mainly at the layer interfaces. Clearly, the cracks due to this cause most frequently occur during heating the reaction couples from room temperature up to the experiment temperature and then during their cooling down from that temperature again to room temperature.

As seen in Table 3.4 where the room-temperature (20 °C) coefficients, α_{20} , of thermal expansion for some elementary substances are presented, there are very few couples with identical or at least close values of α_{20} . For most substances, those values are known to slightly increase with increasing temperature [279].

The couples like Ni–Bi ($\alpha_{20} = 13.5 \times 10^{-6} \text{ K}^{-1}$ for both metals) readily withstand a few heating-cooling cycles without any indication of rupture, whereas those like Ni–Zn ($\alpha_{20} = 30.0 \times 10^{-6} \text{ K}^{-1}$ for zinc) crack along one of the interfaces between reacting phases during the first cooling-down from experimental temperatures to room temperature. With Ni–Zn, in a temperature interval of 20–400 °C the ratio of the lengths, $L_{\text{Zn}} : L_{\text{Ni}}$, of the couple constituents increases from 1 to about 1.007, *i.e.* by 0.7 %.

With Cu–Zr, in an interval of 20–1000 °C it amounts to 1 %. If initial dimensions, L_{Cu} and L_{Zr} , are 1 cm each, then the relative displacement of the phases is 100 μm which value is close on the order of magnitude to layer thicknesses encountered in reaction-diffusion experiments. With brittle compound layers formed and insufficiently ductile initial phases, this appears to be more than sufficient to cause any couple to rupture.

Table 3.4. Room-temperature coefficients, α_{20} , of thermal expansion for some elementary substances used as the constituents of reaction couples [278-280]

Chemical symbol	α_{20} ($\times 10^{-6} \text{ K}^{-1}$)	Chemical symbol	α_{20} ($\times 10^{-6} \text{ K}^{-1}$)	Chemical symbol	α_{20} ($\times 10^{-6} \text{ K}^{-1}$)
Ag	18.9	In	33.0	Sc	9.5
Al	24.0	Ir	6.4	Se	37.0
As	4.7	La	5.0	Sm	6.5
Au	14.4	Mg	25.7	Sn	16.3
B	2.0	Mn	23.0	Sr	23.0
Be	12.3	Mo	5.1	Ta	6.5
Bi	13.5	Nb	7.2	Te	16.8
C*	7.9	Nd	6.0	Th	12.3
Cd	29.8	Ni	13.5	Ti	7.1
Ce	5.5	Os	6.1	Tl	28.0
Co	12.5	Pb	29.5	U	15.0
Cr	8.1	Pd	11.7	V	7.5
Cu	16.5	Pt	8.9	W	4.0
Fe	11.9	Re	6.0	Y	10.0
Ga	18.3	Rh	8.9	Yb	24.0
Gd	6.0	Ru	8.5	Zn	30.0
Hf	6.0	Sb	11.3	Zr	6.3

*Graphite

The formation of chemical compounds is usually accompanied by a decrease of the couple volume and relatively rarely by its increase. For illustration, let us make calculations for the formation of NiBi_3 through the overall chemical reaction $\text{Ni} + 3\text{Bi} = \text{NiBi}_3$, assuming that the room-temperature density of any substance is not too different from that at experimental temperatures.

The pyknometric density of NiBi_3 is $10.1 \times 10^3 \text{ kg m}^{-3}$ [165, 282]. As the molar volume is the quotient of dividing the molecular or atomic mass by the density,

$$V_{\text{NiBi}_3} = 67.9 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}.$$

For nickel and bismuth, appropriate values are $V_{\text{Ni}} = 6.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ and $V_{\text{Bi}} = 21.3 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$.

Hence, the value of the volume change is

$$V_{\text{NiBi}_3} - V_{\text{Ni}} - 3V_{\text{Bi}} = (67.9 - 70.5) \times 10^{-6} = -2.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}.$$

Thus, relative to the total volume of the nickel and bismuth phases consumed, the volume decrease is 3.7 %.

If the compounds are formed through reactions between elementary substances, close values are obtained for NiAl_3 (3.6 %), TaAl_3 (4.9 %), TiAl_3 (4.2 %) and ZrAl_3 (4.8 %). The relative volume decrease is much greater for NiAl (12.7 %) and NiBi (17.6 %). For nickel and cobalt silicides, its value exceeds 20 %.

The volume decrease gives rise to considerable mechanical stresses. If the *A–B* couple is allowed to freely contract, these will lead to the occurrence of numerous regular cracks across the layer bulks. If not, the couple will in all probability rupture along the whole reaction front. In the latter case, a continuous crack may be located either at one of the interfaces or in the bulk of one of compound layers formed.

Note that the cracks due to volume changes occur immediately in the course of layer growth. To prevent their formation, external pressure is often applied. It is not so easy, however, to choose its optimum value. If insufficient, it will obviously produce no desirable effect. If too high, compound layers may simply be crushed.

During the whole course of annealing the *A–B* couple under pressure, contacts between initial and occurring phases may well be lost and renewed several times, giving rise to a hardly tractable microstructure of the *A–B* transition zone. Thus, in many cases the compound-layer formation actually takes place in a few independent couples. Though in each of those couples no more than two compound layers can grow under conditions of diffusion control, multiple compound layers will ultimately be seen between *A* and *B*. Evidently, the newly occurred layers can only grow at the expense of the former ones whose thickness must therefore decrease.

In some cases the crack is apparent (Fig. 3.8), while in the others not (Fig. 3.9a). Shown in Fig. 3.8 is the microstructure of the transition zone between cobalt and silicon after annealing at 800 °C for 64 h in vacuum [329]. All the phases present on the phase diagram [241, 288, 330] are readily seen as distinct layers. However, since the Co_2Si and CoSi layers are known to be the first to occur, with Co_2Si being the very first [73, 74], the CoSi_2 layer was most probably formed after the occurrence of a crack between Co and Co_2Si . According to G.J. van Gurp and C. Langereis [73], the growth process of this layer is always accompanied by a decrease of the thickness of either the Co_2Si or CoSi layer or both. In the absence of cracks all these compound layers cannot occur simultaneously. Note that up to 500–600 nm the silicide layers are known to grow linearly [65, 73, 74].

When without the plots of Fig. 3.9b, the microstructure of Fig. 3.9a [302] might provide indisputable evidence for the simultaneous occurrence of all the platinum antimonides between platinum and antimony in the course of isothermal annealing the Pt–Sb reaction couple. Layer thickness-time plots clearly show, however, that this is far from being the case. The PtSb layer is seen to shrink. Therefore, though no crack is visible due to application of pressure, the Pt–Sb couple was evidently split at some (uncertain) moment of

time into at least two independent couples in which the other platinum antimonide layers could readily occur. Generally, in perfect reaction couples any compound layer survived in the initial linear stage of interaction can hardly be expected to shrink on its own during the further course of the reaction.

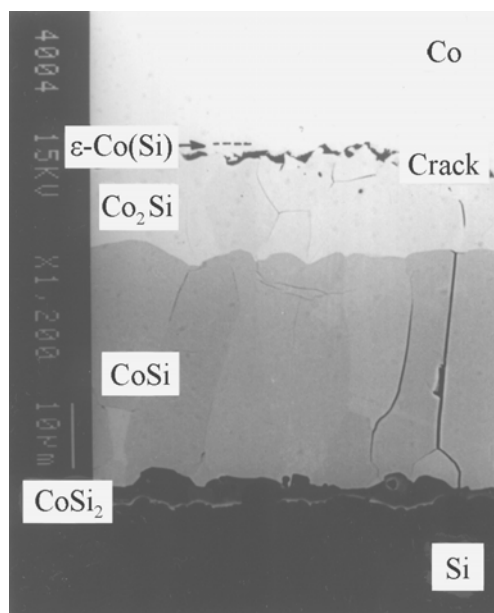
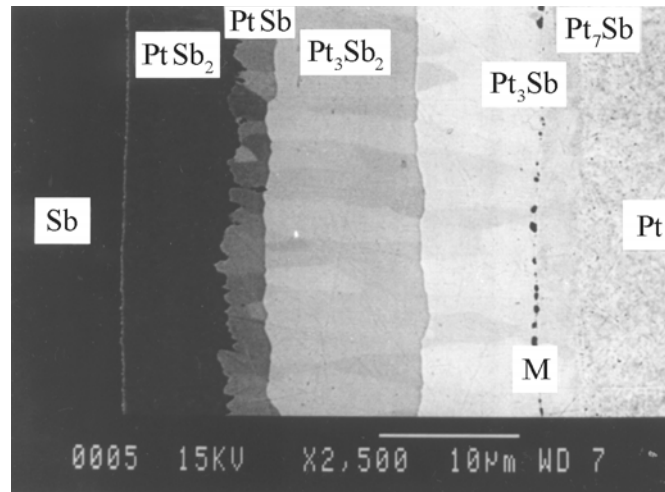


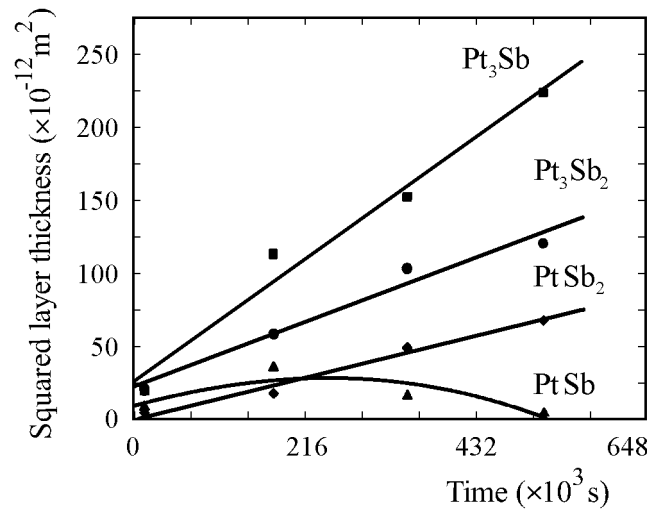
Fig. 3.8. Backscattered electron image of the transition zone between cobalt and silicon after annealing at 800 °C for 230400 s (64 h) in vacuum [329]. The microstructure reveals all the phases available on the equilibrium phase diagram of the Co–Si binary system. A continuous crack is seen between Co and Co₂Si. Photograph kindly provided by Dr. A.A. Kodentsov.

Microstructures like those in Figs 3.8 and 3.9 are often invoked to oppose massive specimens with multiple compound layers to thin-film ones with one or two compound layers. For binary systems without any considerable solubility in the solid state, however, the dimensions of reaction couples, if of course not of the order of the lattice spacing, play no role in determining layer-growth kinetics. Growing compound layers can scarcely feel whether a particular reaction couple is 100 nm or 1 cm thick, if the difference in chemical composition of the materials is negligible.

Though often invoked, the Kirkendall effect has in fact no relation to the crack occurrence in multi-layered structures where some part of compound layers grow at the expense of diffusion of only one component, while the other part do not grow at all. Also, in the case of multiple layers occurring in the actually independent couples any calculations of interdiffusion coefficients prove to be meaningless.



(a)



(b)

Fig. 3.9. Microstructure of the transition zone between platinum and antimony after annealing at 500 °C for 345600 s (96 h) (a) and plots of the squared layer thickness against time (b). The Pt₇Sb layer is extremely thin. The letter M designates inert markers. Experimental data from the work by S.L. Markovski *et al.* [302]. Photograph kindly provided by Dr. A.A. Kodentsov.

This is so even with perfect A–B couples. Initially, when interdiffusion is still taking place, layer-growth kinetics are non-parabolic and therefore the purely diffusional considerations are inapplicable. Then, when the layer growth becomes diffusion controlled, there is no interdiffusion in any of the layers present, and in some of them there is no diffusion at all, excepting random walk of atoms never resulting in compound formation.

In the diffusional stage of interaction of initial substances, interdiffusion is only possible if a single compound layer is formed between *A* and *B*. With two compound layers, only monodiffusion in each of the layers takes place. With multiple compound layers, even monodiffusion in all the layers is not possible. It takes place only in two of them.

To visualise the diffusing species, inert markers should be embedded in each of compound layers. From Figs 3.2 and 3.6, it must be clear that one marker is insufficient to make far-reaching conclusions regarding the diffusing species in multiple layers.

Position of the layers grown relative to the initial *A–B* interface only depends upon the amounts of *A* and *B* consumed or, in other words, upon the stoichiometry of chemical compounds and layer thicknesses. It does not indicate whether *A* or *B* is diffusing faster.

3.8: Formation of intermetallic layers in Ni–Zn and Co–Zn diffusion couples

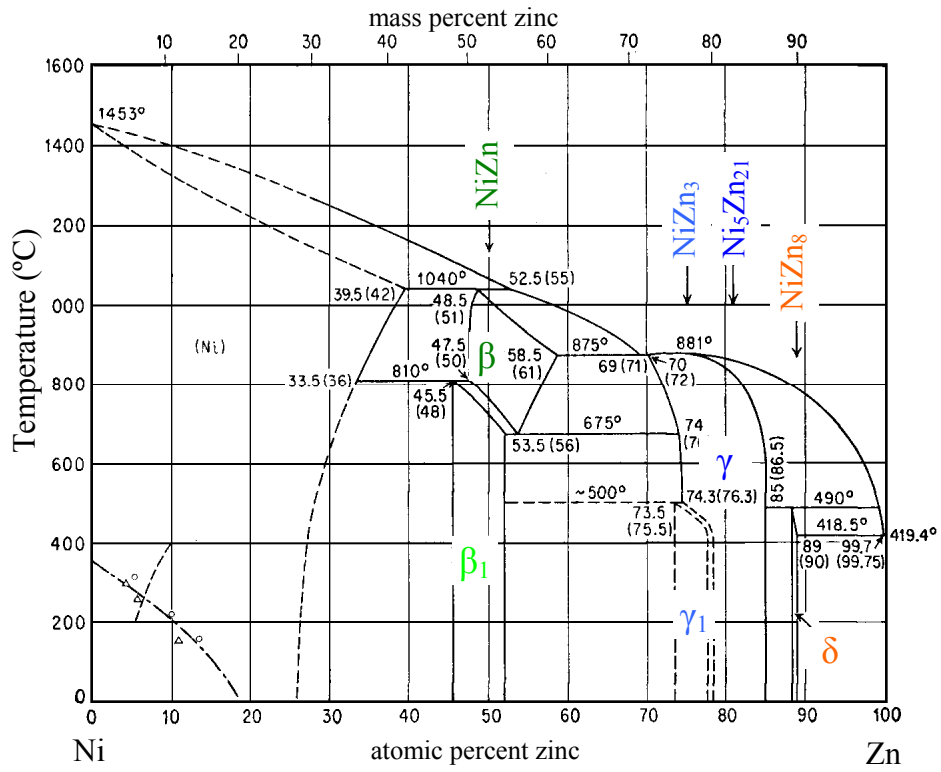
As seen from the preceding section, complicated microstructures occur even with compounds having almost no range of homogeneity. Further complications arise with compounds of close composition, having in addition wide homogeneity ranges, like those of the Ni–Zn or Co–Zn binary system.

Growth kinetics of intermetallic layers in these systems, mainly at temperatures above the melting point of zinc (420 °C) or at high pressures, have been investigated by S. Trajkov [331], N.M. Gumen and M.D. Rarog [332], S. Budurov *et al.* [333], G.P. Vassilev and S. Budurov [111] and other researchers. The results obtained when investigating Ni–Zn and Co–Zn reaction couples in the solid state at 250–400 °C [334–339] will be presented in this section.

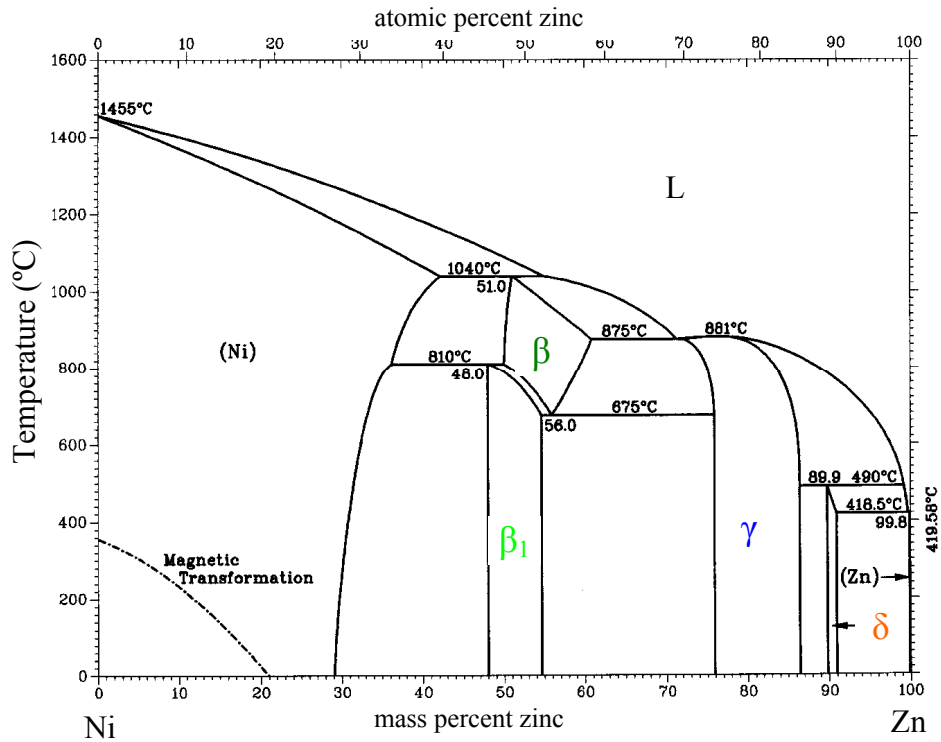
3.8.1: Ni–Zn and Co–Zn phase diagrams

The equilibrium phase diagrams of both systems are very similar. According to the handbook by M. Hansen [157], four intermetallic phases exist in the Ni–Zn binary system at temperatures below the melting point of pure zinc (Fig. 3.10a), those being β_1 , γ_1 and γ with the homogeneity ranges of 43–50, 76–77 and 82–86 at.% Zn, respectively, and δ whose composition is tentatively shown as ~89 at.% Zn. On the phase diagrams assessed by P. Nash and Y.Y. Pan [340] and reproduced in the handbook edited by T.B. Massalski *et al.* [241], three intermetallics (β_1 , γ and δ) are indicated (Fig. 3.10b), with γ having the homogeneity range of 74.3–85 at.% Zn. The range of homogeneity of the δ phase was not established due presumably to its narrowness [241, 340].

Four intermetallic compounds of the Co–Zn binary system are known to exist in the solid state (Fig. 3.11) [157, 340]. There is, however, some ambiguity regarding their ranges of homogeneity. Two sets of the composition ranges are given in the handbook by M. Hansen [157]. The first is β_1 , 47.9–56.5 at.% Zn; γ , 75.2–85.4 at.% Zn; γ_1 , 87.4–88.6 at.% Zn; γ_2 , 91.0–92.8 at.% Zn, while the second is β_1 , 55.5–59.0 at.% Zn; γ , 83.2–87.7 at.% Zn; γ_1 , 89.0 at.% Zn; γ_2 , 91.0 at.% Zn.

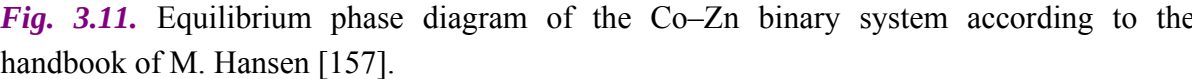


(a)



(b)

Fig. 3.10. Equilibrium phase diagram of the Ni–Zn binary system according to the handbooks of (a) M. Hansen [157] and (b) T.B. Massalski *et al.* [241].



3.8.2: Materials, specimen preparation and experimental methods

The materials used were electrolytic-grade nickel (>99.98 % Ni) and cobalt (>99.98 % Co) plates and granules of chemically pure zinc (>99.94 % Zn). To ensure intimate contact between their constituents and favourable conditions for phase nucleation, the Ni–Zn and Co–Zn reaction couples were prepared by the interaction of solid nickel or cobalt and molten zinc, with their subsequent joint cooling until the liquid phase solidified.

Polished nickel or cobalt plates were mounted in cylindrical graphite forms (11 mm inner diameter), rapidly heated up to about 450 °C and then filled with a molten flux (~475 °C) consisting of the eutectic mixture 82 % ZnCl₂ – 18 % NaCl. After 60 s holding the plates under the flux for cleaning their surfaces from possible contaminations, the forms were filled with molten zinc at 450–475 °C. Solid nickel or cobalt and liquid zinc were allowed to react for about 30 s. Then, the forms were cooled down to room temperature during 180 s.

The bimetallic specimens obtained (Fig. 3.12a) were cut in two ways, as shown in Figs 3.12b and 3.12c. Use was made of an electric-spark machine to avoid their damage during cutting. Further specimen preparation, annealing procedure and investigational methods have already been described in Section 1.8.1 (for more detail, see also Refs [334–339]).

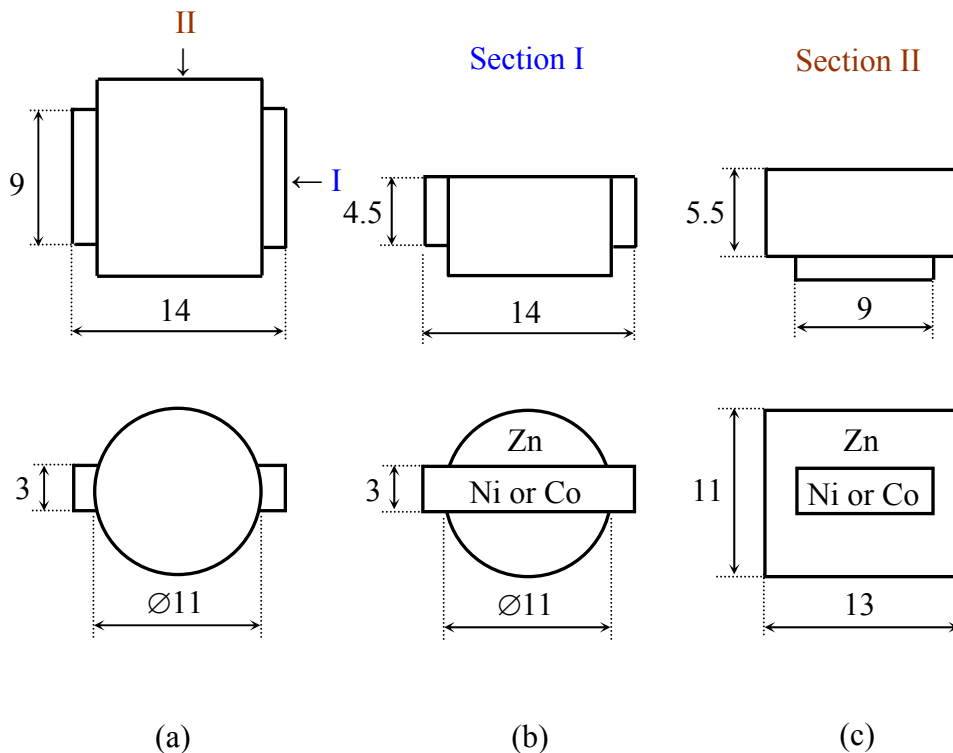


Fig.3.12. Ni–Zn or Co–Zn bimetallic specimen (a) in the as-received condition and after its cutting (b) normal and (c) parallel to the cylindrical axis. All dimensions are given in millimetres.

3.8.3: Layer identification

Figure 3.13 displays a backscattered electron image of the Ni–Zn transition zone after a 2 h anneal at 400 °C. Upon superficial metallographical examination, four intermetallic layers appear to be distinguishable in the microstructure of the Ni–Zn transition zone, giving an impression of the formation of all the compounds known from the equilibrium phase diagram by M. Hansen [157]. The same applies to Co–Zn reaction couples (Fig. 3.14a). However, upon more close examination this first impression proves to be erroneous, with only two of the four intermetallic compounds actually occurring.

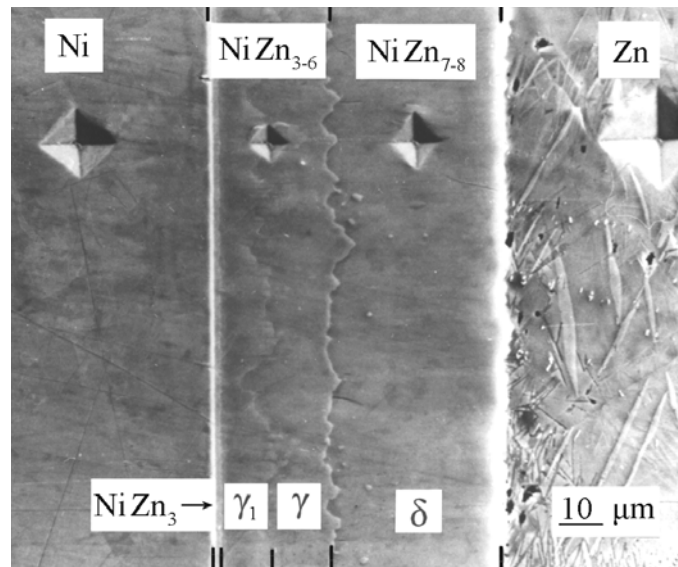
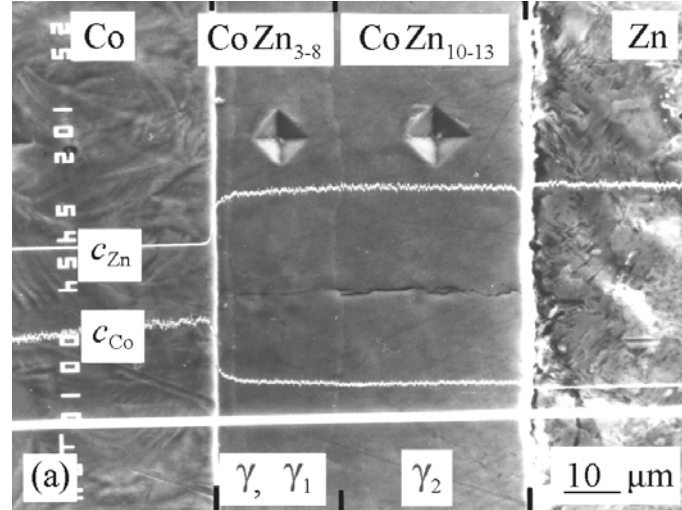


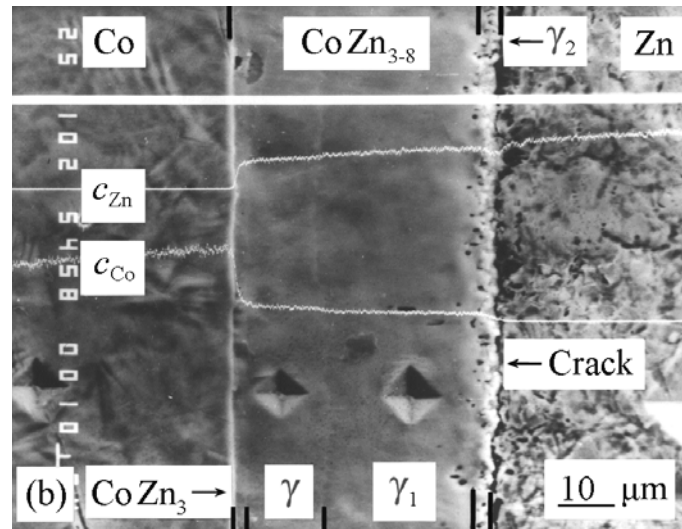
Fig. 3.13. Backscattered electron image of the Ni–Zn transition zone [334]. Annealing conditions: 400 °C, 7200 s (2 h). The Ni-bordering layer, NiZn₃₋₆, visually consists of three sublayers (NiZn₃, γ₁ and γ₂), whereas the Zn-bordering layer, NiZn₇₋₈, is quite homogeneous in appearance, being entirely the δ phase. Microhardness indentations were put onto the cross-section surface at a load of 0.196 N (20 g).

To identify the phases formed, X-ray patterns were taken immediately from the polished surfaces of the Ni–Zn and Co–Zn cross-sections. Annealing and subsequent cooling the specimens of the type shown in Fig. 3.12b in most cases resulted in their rupture along the interface between the zinc phase and the intermetallic layers, with the latter remaining strongly adherent to nickel or cobalt plates. Therefore, preparation of the cross-sections for X-ray analysis presented no difficulties. These could readily be prepared by successive grinding and polishing the plate surface until the Ni or Co phase was reached. In total, four layer sections parallel to the initial interface were examined for each cross-section.

Simultaneously, chemical composition of each section of the interaction zone was determined by electron probe microanalysis.



(a)



(b)

Fig. 3.14. Secondary electron image of the Co–Zn transition zone with the Co and Zn concentration profiles [337]. Temperature 350 °C. Time: (a) 18×10^3 s (5 h); (b) 72×10^3 s (20 h), cracked Co–Zn reaction couple with an uncertain time of crack occurrence. The γ and γ_1 layers grew at the Co– γ_2 interface in the absence of any contact between γ_2 and Zn. Microhardness indentations were put onto the surface of the cross-sections at a load of 0.196 N (20 g).

Interplanar distances (d -spacing) found from experimental X-ray patterns obtained were compared with those calculated from the available literature data on the crystal-lattice parameters. The X-ray patterns from the first two of the four sections were very similar and identifiable as the δ phase of the Ni–Zn binary system. The first section corresponded to a layer composition of 12.1 at.% Ni and 87.9 at.% Zn, while the second to 12.4 at.% Ni and 87.6 at.% Zn. Comparison showed the experimental values to be in better agreement with the d -spacing calculated from the monoclinic lattice parameters of $a = 1.337$ nm, $b = 0.747$ nm, $c = 0.765$ nm, and $\beta = 111.3^\circ$ (space group $C2/m$) reported by J.K. Critchley and S. Denton [341] than with the d -spacing calculated from the hexagonal lattice parameters of $a = 0.8873$ nm, $c = 1.4632$ nm of W. Heike *et al.* [342] or from the tetragonal lattice parameters of $a = 0.8922$ nm, $c = 0.9254$ nm of K. Tamaru and A. Osawa [343].

It should be noted that it is not so easy to distinguish between these lattices because almost all strong diffraction peaks for all the three are either in very close proximity or coincide. The total number of peaks of each X-ray pattern exceeds eighty [340].

The X-ray patterns taken from the two sections of the intermetallic layer adjacent to the Ni phase were also similar, though this layer is visually seen in Fig. 3.13 to consist of three sublayers. One of these sections corresponded to a layer composition of 16.0 at.% Ni and 84.0 at.% Zn, while the other to 19.0 at.% Ni and 81.0 at.% Zn. The experimental interplanar distances were found to be in better agreement with the calculated values from the orthorhombic lattice parameters of $a = 3.3326$ nm, $b = 0.8869$ nm and $c = 1.2499$ nm reported by G. Nover and K. Schubert [344] than from the cubic lattice parameter $a = 0.892$ nm [157, 340]. Moreover, a few diffraction peaks, including the strong peak corresponding to an interplanar distance of 0.207 nm, could not be indexed on the basis of the cubic structure.

Microhardness, HV_{20} , of the Zn-bordering intermetallic layer was found to be 4.0 ± 0.2 GPa. Within the Ni-bordering intermetallic layer, its value gradually decreases from 6.7 GPa to 4.6 GPa, indicative of a considerable change in chemical composition across the layer width. For comparison, HV_{20} was 1.7 ± 0.1 GPa for nickel and 0.6 ± 0.1 GPa for zinc.

Similar X-ray data were obtained with Co–Zn reaction couples. The intermetallic layer adjacent to the zinc phase was identified as the γ_2 phase. According to P.J. Brown [345], the monoclinic unit cell of this intermetallic compound, containing 26 zinc atoms and 2 cobalt atoms (space group $C2/m$), has the parameters $a = 1.3307$ nm, $b = 0.7535$ nm, $c = 0.4992$ nm, and $\beta = 126.8^\circ$. The intermetallic layer adjacent to the cobalt phase was mainly the γ_1 phase with a distorted γ -brass structure [157].

The average microhardness value for the Co-bordering layer was $HV_{20} = 3.6 \pm 0.3$ GPa. A change in microhardness with distance could be measured within the Zn-bordering layer which was much thicker than the Co-bordering layer. In the Zn-bordering layer, the microhardness increases with increasing distance away from the Zn phase from 2.8 GPa to 3.3 GPa. For cobalt, $HV_{20} = 3.7 \pm 0.4$ GPa.

3.8.4: Chemical composition of intermetallic layers

Electron probe measurements were carried out across the layer widths from one interface to the other to determine their chemical composition. With Ni–Zn couples, a gradual change of nickel and zinc contents was observed within the Zn-bordering intermetallic layer, indicative of the existence of a noticeable homogeneity range of the δ phase. Typical results are presented in Table 3.5. Statistical treatment of all EPMA data obtained at 350 and 400 °C showed this phase to have the homogeneity range extending from 87.5 ± 0.2 to 89.0 ± 0.2 at.% Zn.

This explains why numerous chemical formulae were ascribed to the δ phase, namely, $\text{Ni}_3\text{Zn}_{22}$ (88.0 at.% Zn), $\text{Ni}_2\text{Zn}_{15}$ (88.2 at.% Zn), $\text{Ni}_4\text{Zn}_{31}$ (88.6 at.% Zn), NiZn_8 (88.9 at.% Zn) and NiZn_9 (90 at.% Zn) [157, 340]. From the point of view of chemical composition, all these formulae are correct within the accuracy of experimental techniques employed for the investigation of phase equilibria in the Ni–Zn binary system. To these, one more formula may be added, namely NiZn_7 (87.5 at.% Zn), corresponding to the lower limit of the homogeneity range of the δ phase. Thus, the chemical composition of this phase varies from NiZn_7 to NiZn_8 . However, its basic stoichiometry is most probably $\text{Ni}_3\text{Zn}_{22}$, with two formula units per unit cell [341].

Table 3.5. Data of electron probe microanalysis for the Zn-bordering intermetallic layer of the Ni–Zn reaction couple annealed at 400 °C for 7200 s (2 h)

Distance from the γ – δ interface (μm)	Content			
	Ni		Zn	
	%	at.%	%	at.%
2	11.3	12.4	88.7	87.6
5	11.1	12.2	88.9	87.8
10	11.0	12.1	89.0	87.9
15	10.8	11.9	89.2	88.1
20	10.7	11.0	89.3	88.2
25	10.5	11.5	89.5	88.5
30	10.0	11.0	90.0	89.0

Note: The last measurement was made at a distance of about 2 μm away from the interface between the δ phase and zinc.

Typical EPMA data for the Ni-bordering intermetallic layer are given in Table 3.6. Within its bulk, the zinc content was found to gradually increase with increasing distance away from the Ni phase, the limiting values being 73.1 ± 0.3 and 86.2 ± 0.3 at.% Zn.

Table 3.6. Data of electron probe microanalysis for the Ni-bordering intermetallic layer of the Ni–Zn reaction couple annealed at 350 °C for 216 ks (60 h)

Distance from the Ni– γ interface (μm)	Content			
	Ni		Zn	
	%	at.%	%	at.%
2	24.8	26.9	75.2	73.1
3.5	23.9	25.9	76.1	74.1
5	21.6	23.5	78.4	76.5
12.5	17.2	18.9	82.8	81.1
17.5	16.9	18.5	83.1	81.5
27.5	16.7	18.2	83.3	81.8
37.5	15.6	17.1	84.4	82.9
47.5	15.5	17.0	84.5	83.0
62.5	14.0	15.3	86.0	84.7
72.5	12.6	13.8	87.4	86.2

Note: The last measurement was made at a distance of about 2 μm away from the end of the layer.

Measurements in the middle part of a very thin sublayer (around 5 μm thick) bordering immediately the Ni phase (see Fig. 3.13) indicated that its composition well corresponded to the chemical formula NiZn_3 . This can be illustrated by the following values of the Ni and Zn contents, c_{Ni} and c_{Zn} , obtained on a 400 °C, 2h anneal specimen (at.%):

$$c_{\text{Ni}} \quad 24.6 \quad 25.0 \quad 25.8$$

$$c_{\text{Zn}} \quad 75.4 \quad 75.0 \quad 74.2$$

with measurements made along the sublayer at a distance of 5 μm from each other and of 2.5 μm away from the Ni phase.

Note that in the concentration range of 73.1–86.2 at.% Zn only one (γ) or two (γ_1 and γ) phases are shown on the Ni–Zn phase diagram (see Fig. 3.10). However, the number of visible sublayers in the Ni-bordering intermetallic layer of Fig. 3.13, covering this concentration range, is three. This apparent inconsistency is most probably due to ordering in the solid state [346] (or, in other words, to a compositional polymorphism) of the NiZn_3 -based intermetallic phase with the range of homogeneity of 73.1–86.2 at.% Zn.

Compositional polymorphism is readily observable with intermetallics having very wide homogeneity ranges, like CuAu, Fe_3Al or TiIr [346, 347]. For example, though four phases ($\text{Ti}_{65}\text{Ir}_{35}$, $\text{Ti}_{55}\text{Ir}_{45}$, $\text{Ti}_{50}\text{Ir}_{50}$ and $\text{Ti}_{45}\text{Ir}_{55}$) were previously revealed in the concentration range of 35–57 at.% Ir of the Ti–Ir binary system, these were shown by V.N. Yeremenko *et al.* [347] to be nothing more than the various forms of the TiIr intermetallic phase possessing slightly

different crystal structures. With ZrRh, compositional polymorphism is known to be combined with the temperature polymorphism, giving rise to very complicated phase relations in the solid state [347].

Chemical composition of the Ni-bordering intermetallic layer is seen to vary approximately from NiZn_3 to NiZn_6 . Therefore, from a chemical viewpoint, all the formulae proposed in the literature for the intermetallic phases of the Ni–Zn binary system in the 73.1–86.2 at.% Zn concentration range, namely, NiZn_3 (75.0 at.% Zn), $\text{Ni}_3\text{Zn}_{10}$ (76.9 at.% Zn), $\text{Ni}_5\text{Zn}_{21}$ (80.8 at.% Zn) and $\text{Ni}_4\text{Zn}_{22}$ (84.6 at.% Zn), are quite substantiated. At least part of these compounds may happen to be the compositional polymorphous forms of the NiZn_3 -based intermetallic phase, with their structure changing from orthorhombic for $\text{Ni}_4\text{Zn}_{22}$ to cubic for NiZn_3 of near-stoichiometric composition. This explanation is compatible with the physico-chemical mechanism of layer formation.

Indeed, in the diffusion controlled regime the fresh portions of the Ni-bordering intermetallic layer are formed at its interface with the Zn-bordering intermetallic layer, with Ni being the diffusing species in Ni-bordering intermetallic layer and Zn in the Zn-bordering intermetallic layer. These portions will evidently have the highest Zn content and the structure of lowest symmetry due to the highly non-equilibrium conditions of compound formation. By contrast, the earlier-formed portions of the layer already have some time to order, with the degree of ordering increasing with increasing distance away from the reaction site, *i.e.* towards the Ni phase, thus giving rise to the orthorhombic ($\text{Ni}_4\text{Zn}_{22}$) $\rightarrow$ distorted cubic ($\text{Ni}_5\text{Zn}_{21}$, $\text{Ni}_3\text{Zn}_{10}$) $\rightarrow$ cubic (NiZn_3) transformation and hence the complicated microstructure of the intermetallic layer, shown in Fig. 3.13.

The formation of the β_1 phase in Ni–Zn couples was never observed. The layer of this phase, around 3 μm thick, was revealed in Ni– γ couples after a 30 h anneal at 400 °C. It contained 49.1 ± 0.4 at.% Zn.

The results obtained with Co–Zn reaction couples were largely similar. From the EPMA data presented in Table 3.7, it follows that the Zn-bordering intermetallic layer grown in the Co–Zn diffusion couple at 350 °C consists of the γ_2 phase, with boundary values of the Zn content being 91.6 to 93.3 at.%. For the other temperatures investigated, these values were found to be 91.2 to 93.2 at.% Zn at 400 °C, 91.0 to 92.1 at.% Zn at 300 °C and 90.6 to 92.4 at.% Zn at 250 °C.

The average boundary contents 91.1 to 92.8 at.% Zn, obtained for this layer, are in excellent agreement with the data on the width of the γ_2 -phase homogeneity range 91.0 to 92.8 at.% Zn (see the first set of composition ranges in Section 3.8.1). Thus, its composition varies approximately from CoZn_{10} to CoZn_{13} . Note that the chemical formula CoZn_{13} (92.86 at.% Zn) was established by P.J. Brown [345], when performing X-ray analysis of the crystals isolated from the zinc melt after its reaction with solid cobalt. As zinc was in excess, their composition corresponded to the upper Zn limit of the homogeneity range of the γ_2 phase.

As seen in Fig. 3.14a, two sublayers are visually distinguishable in the microstructure of the Co-bordering layer. The sublayer adjacent immediately to the Co phase was only 1 to 4 μm thick. Any thickness-time relation could hardly be established for this sublayer. The other sublayer was much thicker and continuously grew with increasing annealing time.

From the EPMA data in Table 3.7 (see also Fig. 3.14a), it follows that the Co-bordering layer consists of γ and γ_1 phases, with the last phase being dominant. Another important point is a smooth concentration distribution within the bulk of this layer, without any discontinuity due to the existence of the two-phase $\gamma + \gamma_1$ field of 85.4-87.4 at.% Zn on the phase diagram, indicative of a diffusionless transformation.

Note that the restrictions on the number of simultaneously occurring layers, following from physico-chemical considerations, are clearly inapplicable to compounds that are formed by a diffusionless (shear) mechanism.

No evidence for the presence of the β_1 -phase layer in Co–Zn reaction couples was found. This applies to all the temperatures investigated.

It is noteworthy that, due to the formation of a crack between the γ_2 and Zn phases, some Co–Zn reaction couples actually transformed into Co– γ_2 reaction couples. In the latter, the layers of γ and γ_1 phases grow simultaneously (Fig. 3.14b). One set of the EPMA data for such a reaction couple is given in Table 3.8. The Zn content changes from 76.0 to 85.4 at.% in the γ -phase layer and from 87.7 to 89.1 at.% in the γ_1 -phase layer. These values are in good agreement with those given in Section 3.8.1 (see the first set of homogeneity ranges for the γ and γ_1 phases). Again, the β_1 -phase layer was not revealed in Co– γ_2 reaction couples.

It should be emphasised that in Co– γ_2 reaction couples the γ -phase layer was in turn found to consist of two sublayers. The chemical composition of the sublayer adjacent immediately to the Co phase was close to CoZn_3 . Therefore, if the Co-bordering layer of Co–Zn reaction couples, in which the zinc content changes from the lower limit of the γ -phase homogeneity range to the upper limit of γ_1 -phase homogeneity range, is considered as a whole, then three sublayers may be distinguished within its width.

In this respect, the Co–Zn binary system is similar to the Ni–Zn binary system in which the Ni-bordering layer (73.1 to 86.2 at.% Zn) consists of three sublayers. Note that in the Ni–Zn binary system the γ_1 - and γ -phase regions were even combined by P. Nash and Y.Y. Pan [340] into a single region of the γ phase.

Let us leave to the researchers in the field of phase equilibria to argue whether these are individual phases or compositional polymorphs of the same phase. The results presented appear to be sufficient for the reader to appreciate how complicated phase relations may be and how careful it is necessary to be when interpreting any experimental data on both phase diagrams and compound-layer formation in diffusion couples, especially in those cases where the two-phase fields are narrow compared to the homogeneity ranges of chemical compounds.

Table 3.7. Data of electron probe microanalysis of the Co–Zn diffusion zone. Temperature 350 °C, annealing time 18 ks (5 h)

Phase	Place of measurement	Content				Remarks
		Co		Zn		
		%	at.%	%	at.%	
At distance l away from the Co-intermetallic interface						
Co	$l = -5 \text{ }\mu\text{m}$	99.45	99.50	0.55	0.50	<Co>
Co-bordering layer	3	13.00	14.22	87.00	85.78	γ, γ_1
	6	12.45	13.62	87.55	86.38	
	9	12.22	13.38	87.78	86.62	
	12	11.80	12.92	88.20	87.08	
	15	10.05	11.03	89.95	88.97	
						About 2 μm away from the interface between γ_1 and γ_2
Zn-bordering layer	21	7.63	8.39	92.37	91.61	γ_2
	26	7.68	8.45	92.32	91.55	
	31	7.52	8.27	92.48	91.73	
	36	7.74	8.51	92.26	91.49	
	41	7.52	8.27	92.48	91.73	
	45	6.10	6.72	93.90	93.28	
At distance l away from the intermetallic-Zn interface						
Zn	$l = 5 \text{ }\mu\text{m}$	0.69	0.76	99.31	99.24	<Zn>
	15	0.05	0.06	99.95	99.94	
	50	0.00	0.00	100.00	100.00	

Table 3.8. Data of electron probe microanalysis of the Co–Zn diffusion zone. Cracked Co–Zn reaction couple, with the time of crack occurrence being uncertain. The layers of the γ and γ_1 phases grew between cobalt and the γ_2 phase. Temperature 350 °C, annealing time 72 ks (20 h)

Phase	Place of measurement	Content				Remarks
		Co		Zn		
		%	at.%	%	at.%	
At distance l away from the Co-intermetallic interface						
Co	$l = -100\text{ }\mu\text{m}$	100.00	100.00	0.00	0.00	<Co>
	-25	100.00	100.00	0.00	0.00	
	-5	99.79	99.81	0.21	0.19	
Co-	3	20.14	21.86	79.86	78.14	γ
bordering	7	16.92	18.42	83.08	81.58	
layer	11	15.96	17.40	84.04	82.60	
	15	15.47	16.87	84.53	83.13	
	19	14.86	16.22	85.14	83.78	
	23	13.32	14.56	86.68	85.44	About 3 μm away from the interface between γ and γ_1
γ_2 -	30	11.10	12.17	88.90	87.73	γ_1
bordering	35	10.09	11.07	89.91	88.93	
layer	40	10.26	11.25	89.74	88.75	
	45	9.82	10.78	90.18	89.22	
	50	9.83	10.78	90.17	89.22	
	55	9.20	10.10	90.80	89.90	
	60	9.21	10.11	90.79	89.89	
γ_2 - layer	65	8.41	9.24	91.59	90.76	γ_2
At distance l away from the crack between γ_2 and zinc						
Zn	$l = 5\text{ }\mu\text{m}$	0.53	0.59	99.47	99.41	<Zn>
	10	0.12	0.14	99.88	99.86	
	25	0.00	0.00	100.00	100.00	

3.8.5: Layer-growth kinetics

Kinetic data obtained with Ni–Zn and Co–Zn reaction couples have been treated using parabolic equations of the type

$$k_1 = (x_i^2 - x_0^2) / 2t_i,$$

where x_i and x_0 are the layer thickness at time t_i and $t = 0$, respectively. The total thickness of all the sublayers was measured for the nickel-bordering or cobalt-bordering layers. The squared layer thickness-time dependence at 400 °C for the Ni–Zn binary system is shown in Fig. 3.15.

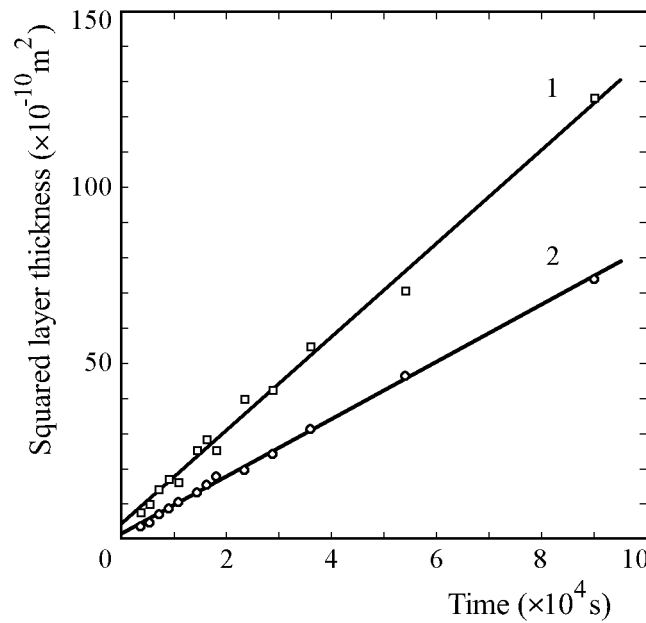


Fig. 3.15. Squared layer thickness-time plot at 400 °C. 1, NiZn₇₋₈; 2, NiZn₃₋₆.

Though the experimental points produce sufficiently straight lines in the $x^2 - t$ coordinates, deviations from a parabolic growth law are nonetheless noticeable, to a greater or lesser extent, at all four temperatures. As seen in Table 3.9, the diffusional constants, especially those for the Zn-bordering intermetallic layer, tend to decrease with increasing annealing time. This agrees with the physico-chemical approach that predicts small deviations from a parabolic law in the case of simultaneous growth of two compound layers of a binary system (see Section 2.8.2). It is also possible that these deviations are partly due to the effect of dissolution on the layer-growth kinetics (see Chapter 5) since the solid-state solubility of nickel and cobalt in zinc is perceptible.

For the purpose of further discussion, the average values of the diffusional constants presented in Table 3.10 will be used. As seen in Fig. 3.16 and Table 3.11, their temperature dependence obeys the Arrhenius relation.

Table 3.9. Diffusional constants, k_1 , for the Ni–Zn and Co–Zn binary systems calculated from the experimental data according to parabolic equations of the type $k_1 = (x_i^2 - x_0^2) / 2t_i$, where x_i and x_0 are the layer thickness at time t_i and $t = 0$, respectively. Temperature 400 °C

System	Time (s)	Ni-or Co-bordering layer		Zn-bordering layer	
		x ($\times 10^{-6}$ m)	k_1 ($\times 10^{-15}$ m ² s ⁻¹)	y ($\times 10^{-6}$ m)	k_1 ($\times 10^{-14}$ m ² s ⁻¹)
Ni–Zn	3600	18	4.3	27	9.6
	5400	21	3.9	31	8.6
	7200	26	4.6	37	9.3
	9000	29	4.6	41	9.1
	10800	32	4.7	40	7.2
	14400	36	4.4	50	8.6
	16200	39	4.6	53	8.6
	18000	42	4.9	50	6.8
	23400	44	4.1	63	8.4
	28800	49	4.1	65	7.3
	36000	56	4.3	74	7.6
	54000	68	4.3	84	6.5
	90000	86	4.1	112	6.9
Co–Zn	3600	15	3.1	23	6.0
	7200	21	3.1	31	6.0
	10800	26	3.1	37	5.9
	18000	32	2.8	46	5.6
	21600	33	2.5	52	6.0
	28800	38	2.5	56	5.3

Table 3.10. Experimental values of the diffusional constants, k_1 , for the Ni–Zn and Co–Zn binary systems

Temperature		$k_1 (\times 10^{-14} \text{ m}^2 \text{ s}^{-1})$			
		Ni–Zn		Co–Zn	
(°C)	(K)	Ni-bordering layer	Zn-bordering layer	Co-bordering layer	Zn-bordering layer
250	523	0.27	0.042	0.014	0.16
300	573	1.2	0.16	0.14	0.67
350	623	2.8	1.0	0.62	2.2
400	673	4.4	8.0	2.9	5.8

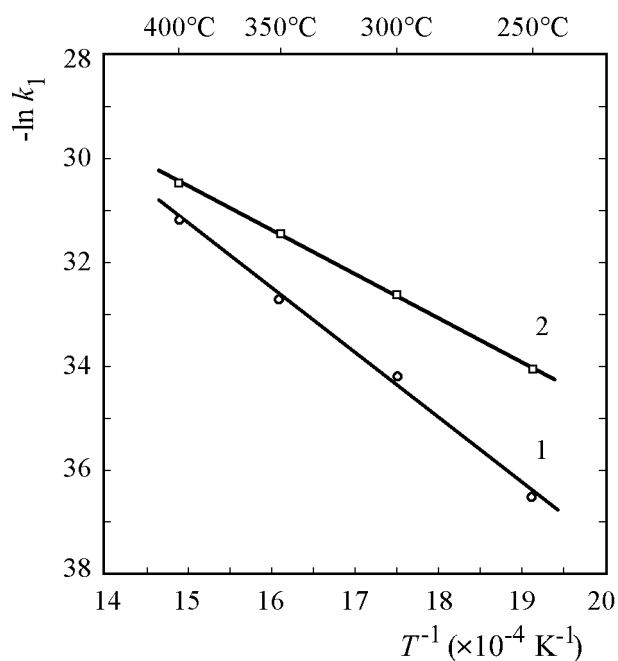


Fig. 3.16. Temperature dependence of the diffusional constants for the Co–Zn binary system. 1, Co-bordering layer; 2, Zn-bordering layer.

Both systems are suitable to check whether or not there is a directly proportional relationship between the width of the homogeneity range of a compound and the growth rate of its layer, predicted by the diffusional theory [22]. It is clear that in view of the presence of the liquid zinc phase during preparation of Ni–Zn and Co–Zn reaction couples, all the intermetallic phases had equal and favourable conditions to form their nuclei at the interface between nickel or cobalt and zinc, which could then readily grow during subsequent isothermal annealing.

Table 3.11. Parameters of the Arrhenius equation for the Ni–Zn and Co–Zn binary systems

Parameter	System			
	Ni–Zn		Co–Zn	
	Ni-bordering layer	Zn-bordering layer	Co-bordering layer	Zn-bordering layer
Pre-exponential factor ($\text{m}^2 \text{s}^{-1}$)	$(1.1^{+0.4}_{-0.3}) \times 10^{-9}$	$(6.4^{+5.5}_{-3.4}) \times 10^{-6}$	$(3.8^{+0.8}_{-0.7}) \times 10^{-6}$	$(2.06^{+0.13}_{-0.12}) \times 10^{-8}$
Activation energy (kJ mol^{-1})	55.4 ± 1.7	103.3 ± 3.1	104.1 ± 1.0	71.1 ± 0.4

The homogeneity ranges of the intermetallics of the Ni–Zn and Co–Zn binary systems are known to vary very little in the 250–400 °C temperature range, if at all (see Figs 3.10 and 3.11). Their widths are presented in Table 3.12. The values of the diffusional constants at a temperature of 250 °C, calculated from appropriate temperature dependences (see Table 3.11), are also included in Table 3.12.

Table 3.12. Comparison between the width of the homogeneity range and the diffusional constant for the intermetallic compounds of the Ni–Zn and Co–Zn binary systems at a temperature of 250 °C

Ni–Zn couple			Co–Zn couple		
Phase	HR (at.%)	$k_1 (\times 10^{-15} \text{ m}^2 \text{s}^{-1})$	Phase	HR (at.%)	$k_1 (\times 10^{-15} \text{ m}^2 \text{s}^{-1})$
β_1	8	missing	β_1	8.6	missing
γ_1	4	} 3.2	γ	10.2	} 0.15
γ	6.5		γ_1	1.2	
δ	1.5	0.31	γ_2	1.8	1.6

If there were a direct proportionality between the width of the homogeneity range of a given compound and the growth rate of its layer at the interface of elementary substances, then the layer of the β_1 -phase ($HR = 8$ at.%) might be expected to grow in Ni–Zn diffusion couples at a higher rate than the layer of any other phase. Similarly, the growth rate of the γ -phase layer ($HR = 10.2$ at.%) in Co–Zn diffusion couples would exceed those of other phases.

In fact, however, formation of the β_1 -phase was not observed experimentally in either Ni–Zn or Co–Zn diffusion couples. Again, the data in Table 3.12 do not reveal even a weak correlation between the width of the homogeneity range of an intermetallic compound and the growth rate of its layer. Indeed, when without the second half of this table, its first half might provide evidence for the existence of direct proportionality between these quantities because in Ni–Zn diffusion couples the diffusional constant for the Ni-bordering layer comprising the γ_1 and γ phases ($HR = 4 + 6.5 = 10.5$ at.%) is seen to be ten times greater than that for the Zn-bordering layer consisting only of the δ phase ($HR = 1.5$ at.%). However, the second half shows the quite opposite relationship to exist for Co–Zn diffusion couples, the growth rate of the Co-bordering layer comprising the γ and γ_1 phases ($HR = 10.2 + 1.2 = 11.4$ at.%) being ten times less than that of the Zn-bordering layer consisting only of the γ_2 phase ($HR = 1.8$ at.%). Any regularity of this relationship for both systems under consideration may hardly be found at other temperatures as well (see Tables 3.10–3.12).

It is worth noting that the layers of intermetallic compounds without any noticeable homogeneity range, like NiBi_3 , grow at a rate comparable or even higher than that of those with a wide homogeneity range. For example, at 250 °C the diffusional constant, k_1 , for the NiBi_3 intermetallic compound ($HR \approx 0$) is equal to $9.5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. This value far exceeds any one in Table 3.12. Hence, generally there is no directly proportional relationship between the width of the homogeneity range of a chemical compound and the growth rate of its layer at the interface of elementary substances. This equally applies both to compounds formed by different substances and to different compounds of the same binary system. Occasional regularity is of course not excluded.

All attempts to carry out marker experiments with Ni–Zn and Co–Zn diffusion couples in the same manner as with Ni–Bi ones (see Section 1.8 of Chapter 1) failed because of crack formation, not allowing an unambiguous determination of the diffusing species in the growing intermetallic layers. These proved, however, extremely useful for understanding the mechanism of multiple layer formation. Namely, it became quite clear that this phenomenon is most frequently a result of secondary reactions occurring in cracked couples.

The decrease in volume of the Ni–Zn and Co–Zn diffusion couples accompanying formation of intermetallic compounds produces a bulk dilation stress over the whole width of growing layers. Thermal expansion of the couple constituents during heating up as well as their contraction during cooling down in the course of successive anneals of the same couple produces a shear stress. These inevitably lead to the rupture of diffusion couples, with the latter effect being most disastrous.

In the type of couple shown in Fig. 3.12b, the cohesion between dissimilar metals after prolonged isothermal annealing was so poor that the nickel or cobalt plate could be taken out from the zinc matrix by hand without any effort. Therefore, more or less acceptable kinetic data were only obtained with the type of couple shown in Fig. 3.12c, in which the nickel or cobalt plate was surrounded by the zinc phase. However, even with this type of couple the percentage of evidently incorrect results yielding irregular thickness-time plots was rather large in comparison with Ni–Bi couples.

Needless to say that the Ni–Zn and Co–Zn diffusion couples have never withstood the second anneal and subsequent cooling down without cracking. Even if the crack was not visible after the run due to renewing the contact between reacting phases, its formation at one moment of time or another was quite evident from (i) splitting of a line of the microhardness indentation markers located in all the phases into two parallel lines, providing clear evidence for the longitudinal displacement of the phases relative to each other, (ii) irregular layer thicknesses not following a general trend to increase with increasing time and (iii) occurrence of a complicated microstructure of the transition zone.

In the great majority of cases, a line of the markers located in the zinc phase displaces a few micrometers aside from a line located in the other phases, indicative of the crack formation at the interface with zinc. To understand the further course of the reaction-diffusion process after the rupture of any reaction couple, it is necessary first to consider the growth kinetics of the same compound layer in different reaction couples of a multiphase binary system. This will be done in the next chapter.

3.9: Multiple compound layers: comparison of diffusional and physico-chemical approaches

Most essential distinctions between the conventional diffusional approach and the proposed physico-chemical one for the case of formation of multiple compound layers at the interface of elementary substances *A* and *B* are briefly listed in Table 3.13. These are partly visualised in Fig. 3.17.

3.10: Multiple compound layers: short conclusions

1. Though there are no restrictions on the number of compound layers growing simultaneously in the reaction controlled regimes, from a physico-chemical viewpoint their formation in the *A–B* reaction couple of any multiphase binary system is likely to be sequential and not simultaneous.

2. The sequence of occurrence of compound layers is determined by the rates of chemical transformations at the interfaces. It cannot yet be theoretically predicted with confidence for any particular reaction couple *A–B*. Having sufficient information on the equilibrium phase diagram, thermodynamics of chemical reactions, and the crystallographic structure and physico-chemical properties of the compounds, it is possible to indicate those of them, which are most likely to occur and grow first at the *A–B* interface.

3. The layers of no more than two compounds can grow simultaneously in the diffusion controlled regimes. The layer adjacent to substance *A* or the *A*-enriched phase only grows at the expense of diffusion across its bulk of *A* atoms. The layer bordering substance *B* or the *B*-enriched phase only grows at the expense of diffusion across its bulk of *B* atoms. Both layers thicken at their common interface by pushing each other in the opposite direction.

4. Under conditions of diffusion control, all other compound layers of a multiphase binary system, located between the two growing ones, are kinetically unstable. If these other layers were initially missing from the *A–B* couple, they will not occur in it until at least one of initial substances (either *A* or *B*) is completely exhausted. If present, they must disappear completely during further isothermal annealing.

5. In general, there can be no full correspondence between the equilibrium phase diagram of a multiphase binary system and the microstructure of the *A–B* transition zone occurred after isothermal annealing of the *A–B* reaction couple.

6. If observed, formation of multiple compound layers at the *A–B* interface is most likely a result of secondary reactions taking place after the occurrence of cracks in and between reacting phases. Crack formation is due to volume changes accompanying layer growth and the difference in the coefficients of thermal expansion of the couple constituents. Though often invoked, the Kirkendall effect is in principle unobservable with growing compound layers and therefore has no relation to the crack occurrence both in layer bulks and at the interfaces between reacting phases.

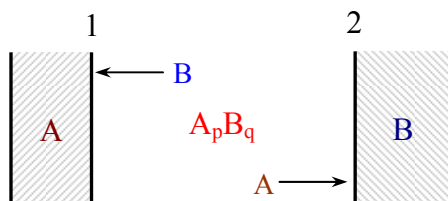
7. One inert marker only indicates the diffusing species in that compound layer in which it is embedded or with which it borders. If this layer grows under conditions of diffusion control, then the very presence of other compound layers provides in itself evidence that another component is diffusing across their bulks.

8. In view of the lack of interdiffusion in the course of multiple layer formation at the *A–B* interface and because of complicated mechanism of this process, calculation of integrated diffusion coefficients appears in most cases to be quite formal and hence meaningless, yielding figures of doubtful physical significance (like the average temperature of patients over the hospital).

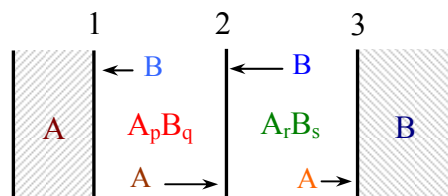
Table 3.13. Comparison of diffusional and physico-chemical approaches in the case of multiple layer formation

Diffusional approach	Physico-chemical approach
1. All compound layers, whatever their number on the $A-B$ phase diagram, can occur and grow simultaneously.	1. Compound layers occur in sequence that can as yet hardly be predicted with confidence theoretically.
2. Layer-growth kinetics are parabolic for all the layers, whatever their thickness.	2. Kinetic laws are rather complicated and in general can hardly be expressed by any simple mathematical relation.
3. All compound layers always can grow at the expense of diffusion of both components.	3. All compound layers always can grow at the expense of diffusion of both components only under conditions of reaction control. Under conditions of diffusion control, at most two compound layers will grow simultaneously, each at the expense of diffusion of one component. Artificially prepared “superfluous” layers must disappear with time.

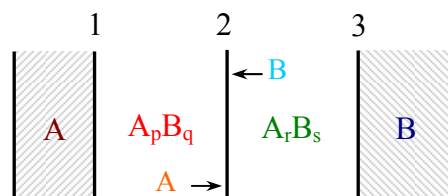
1. One compound layer: reaction or diffusion control



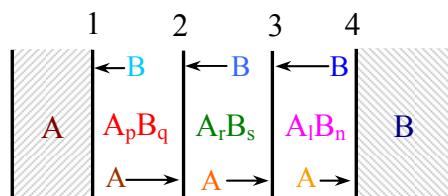
2a. Two compound layers: reaction control



2b. Two compound layers: diffusion control



3a. Three compound layers: reaction control



3b. Three compound layers: diffusion control

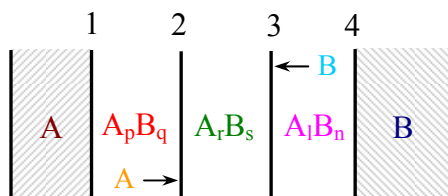


Fig. 3.17. Comparative schematic diagrams to illustrate the distinctions in the mechanism of growth of one, two and three compound layers. No restrictions on the growth of any layer under conditions of reaction control. No restrictions on the growth of one layer A_pB_q under conditions of diffusion control. Restricted diffusional growth of the layers A_pB_q and A_rB_s in the case of two compound layers. No growth (only the consumption) of the middle layer A_rB_s in the case of three compound layers, while the A_pB_q and A_lB_n layers grow.

4: Growth kinetics of the same chemical compound layer in various reaction couples of a multiphase binary system

If a binary system is multiphase, then the layer of the same chemical compound can obviously grow in different reaction couples consisting of elementary substances A and B and their other compounds. To show how its growth rate depends on the composition of initial phases, it suffices to consider a binary system with three compounds A_pB_q , A_rB_s and A_lB_n on the equilibrium phase diagram (see Fig. 3.1).

If the A_rB_s layer is the first to occur at the A – B interface, then in a certain range of temperature its growth can readily be observed between

- (i) elementary substances A and B (reaction couple A – B),
- (ii) one of the two other compounds and one of the elementary substances (reaction couples A_pB_q – B and A – A_lB_n),
- (iii) two other compounds (reaction couple A_pB_q – A_lB_n).

Note that in this chapter the A_rB_s layer will be assumed to be the only one in all possible reaction couples of the A – B multiphase binary system under given experimental conditions.

4.1. Growth of the A_rB_s layer in the A – B reaction couple

It is most convenient to compare the growth rates of the layer of the same chemical compound in various reaction couples with the rate of its growth at the interface of elementary substances. Therefore, let us first briefly analyse the case in which the A_rB_s compound layer is formed at the A – B interface (Fig. 4.1). To avoid considerable changes in the designations of the reaction-diffusion constants describing the layer-growth kinetics, the numeration of the interfaces of the A_rB_s layer, shown in Fig. 3.1, will be retained.

Solid-state growth of the A_rB_s layer at the interface between elementary substances A and B is due to two partial chemical reactions each of which occurs in two consecutive, alternate steps (see Chapter 1). Firstly, the B atoms diffuse across the layer bulk and then react at the A – A_rB_s interface (interface 2) with the surface A atoms in accordance with the equation

$$sB_{\text{dif}} + rA_{\text{surf}} = A_rB_s. \quad (4.1)$$

Secondly, the A atoms diffuse in the opposite direction and then react at the A_rB_s – B interface (interface 3) with the surface B atoms

$$rA_{\text{dif}} + sB_{\text{surf}} = A_rB_s. \quad (4.2)$$

During the time dt , the thickness of the A_rB_s layer increases by dy_{B2} at the $A-A_rB_s$ interface. As a result, this interface moves from position 2' into position 2. Simultaneously, it increases by dy_{A3} at the A_rB_s-B interface, so that this interface moves from position 3' into position 3. A kinetic equation describing the growth rate of the A_rB_s layer at the interface of mutually insoluble elementary substances A and B has the form (see Chapter 1)

$$\left(\frac{dy}{dt}\right)_{A-B} = \frac{k_{0B2}}{1 + \frac{k_{0B2}y}{k_{1B2}}} + \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}}. \quad (4.3)$$

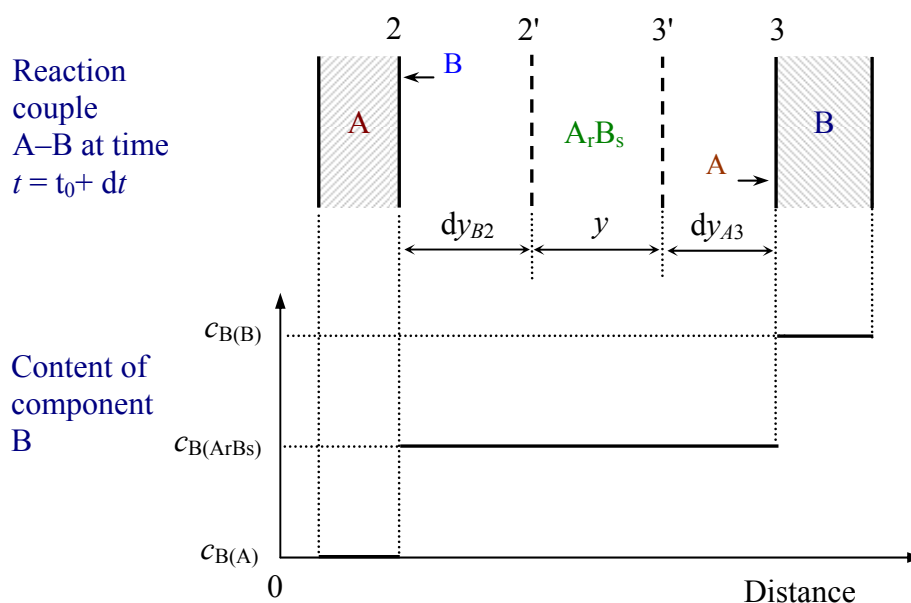


Fig. 4.1. Schematic diagram to illustrate the growth process of the A_rB_s layer between mutually insoluble elementary substances A and B at the expense of diffusion of both components.

When comparing the chemical constants in the systems $A-A_rB_s-B$ and $A-A_pB_q-A_rB_s-A_lB_n-B$ (see Chapter 3), it should be kept in mind that k_{0B2} is not equal to k'_{0B2} and k_{0A3} is not equal to k'_{0A3} since different partial chemical reactions take place in those systems at the interfaces of the A_rB_s layer with the adjacent phases. Though the rate of transport of any component across the bulk of the A_rB_s layer is an intrinsic property of this layer, not depending on the composition of the adjacent phases, the diffusional constants k_{1B2} and k'_{1B2} as well as k_{1A3} and k'_{1A3} are also not identical because in the systems $A-A_rB_s-B$ and $A-A_pB_q-A_rB_s-A_lB_n-B$ different numbers of the A_rB_s molecules are formed per one diffusing atom A or B . Therefore, the constants k_{1B2} and k'_{1B2} differ by a constant multiplier. The same applies to the constants k_{1A3} and k'_{1A3} .

4.2: Growth of the A_rB_s layer in the A_pB_q – B reaction couple

The mechanism of formation of the A_rB_s layer at the A_pB_q – B interface is essentially dependent upon which component (either A or B) has a higher mobility in the crystal lattice of the A_rB_s compound. Comparing the systems A – A_rB_s – B and A_pB_q – A_rB_s – B , it can easily be concluded that the same physico-chemical processes take place in both systems at the interface of the A_rB_s and B phases.

It does not mean, however, that if the diffusion of component A prevails in the A_rB_s layer, then the growth rates of this layer in the A_pB_q – B and A – B reaction couples will be identical. Consider this case in more detail.

4.2.1: Growth of the A_rB_s layer between A_pB_q and B at the expense of diffusion of only component A

Schematic diagram to illustrate the growth process of the A_rB_s layer at the interface between the A_pB_q and B phases at the expense of diffusion of component A is shown in Fig. 4.2. If the A_pB_q compound has a considerable range of homogeneity, then the content of component A in the initial phase A_pB_q will be assumed to be constant and equal to the lower limit of this range according to the equilibrium phase diagram of the A – B binary system.

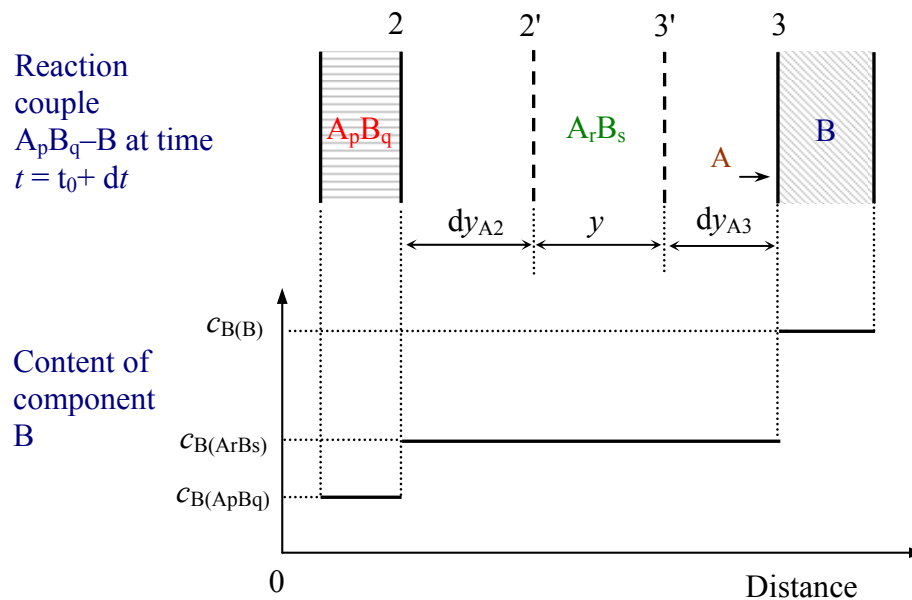


Fig. 4.2. Schematic diagram to illustrate the growth process of the A_rB_s layer in the A_pB_q – B reaction couple due to the diffusion of component A to interface 3 and the simultaneous partial decomposition of the A_pB_q phase at interface 2.

During the time dt , the thickness of the A_rB_s layer increases by dy_{A3} at interface 3 as a result of diffusion of the A atoms from interface 2 to interface 3 and their subsequent partial chemical reaction (4.2) with the surface B atoms. In the A_pB_q-B reaction couple, the A_pB_q phase serves as a source of diffusing A atoms. It must be clear, however, that the content of component A in this phase cannot be less than the lower limit of its homogeneity range. Hence, as reaction (4.2) proceeds, the A_pB_q compound becomes unstable and therefore should undergo a partial transformation into another compound of the $A-B$ multiphase binary system. To reveal the essence of this transformation, let us consider one of the simplest cases in which the layer of the chemical compound AB grows between the A_2B and B phases.

If a molecule A_2B loses one atom A which then diffuses across the AB layer and reacts with B to form a molecule AB at the $AB-B$ interface, it transforms into a molecule AB . Appropriate chemical reactions are



and



Thus, one molecule AB is formed at the $AB-B$ interface as a result of reaction (4.5). At the same time, an additional molecule AB is formed at the A_2B-AB interface as a result of the phase transformation inevitably following the reaction diffusion of component A . Consequently, enhanced growth of the AB layer must be observed in the $A_2B-AB-B$ system in comparison with its growth in the $A-AB-B$ system. The ratio of the growth rates of the AB layer in those systems is seen to be equal to 2.

This result can easily be generalised [146, 150-156]. It appears reasonable to assume that a most likely transformation is that in which an initial phase loses the minimum number of atoms and therefore transforms into an adjacent phase of the $A-B$ equilibrium phase diagram. Therefore, the phase transformation of A_pB_q into A_rB_s taking place at the $A_pB_q-A_rB_s$ interface under the influence of reaction diffusion of the A atoms to the A_rB_s-B interface can be represented as follows



Hence, during the same time dt , the thickness of the A_rB_s layer must also increase by dy_{A2} at interface 2 due to reaction (4.6). It is obvious that the values dy_{A2} and dy_{A3} are directly proportional

$$dy_{A2} = \alpha dy_{A3}. \quad (4.7)$$

The proportionality coefficient, α , can readily be found from equations (4.2) and (4.6). Indeed, according to reaction (4.2) an increase of the thickness of the A_rB_s layer at interface 3 is a result of diffusion of r A atoms. However, from reaction (4.6) it is seen that the loss of s A_pB_q molecules ($sp - qr$) A atoms is accompanied by the formation of q A_rB_s molecules at interface 2. Hence, from the proportion

$$\frac{\alpha}{q} = \frac{r}{sp - qr}, \quad (4.8)$$

it follows

$$\alpha = \frac{1}{\beta - 1}, \quad (4.9)$$

where $\beta = sp/qr$. Note that sp is always greater than qr because the A_pB_q compound is enriched in component A in comparison with the A_rB_s compound. Therefore, $\beta > 1$.

The total increase in thickness of the A_rB_s layer due to both the reaction diffusion of A atoms and the phase transformation of A_pB_q into A_rB_s under the influence of this reaction diffusion is

$$dy_A = dy_{A2} + dy_{A3} = \frac{\beta}{\beta - 1} dy_{A3}. \quad (4.10)$$

If only component A diffuses across the A_rB_s layer, then the rate of its growth in the $A-B$ reaction couple is (see equation (4.3))

$$\left(\frac{dy_A}{dt} \right)_{A-B} = \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}}, \quad (4.11)$$

because in this case $dy_A = dy_{A3}$.

From equation (4.10), it follows that the growth rate of the A_rB_s layer in the A_pB_q-B reaction couple is

$$\left(\frac{dy_A}{dt}\right)_{A_pB_q-B} = \frac{\beta}{\beta-1} \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}} \quad (4.12)$$

Therefore, the ratio of the rate of growth of the A_rB_s layer in the $A_pB_q-A_rB_s-B$ system to the rate of its growth in the $A-A_rB_s-B$ system is

$$\frac{\left(\frac{dy_A}{dt}\right)_{A_pB_q-B}}{\left(\frac{dy_A}{dt}\right)_{A-B}} = \frac{\beta}{\beta-1} \quad (4.13)$$

This ratio is seen to depend only upon the stoichiometry of the compounds A_pB_q and A_rB_s .

Equation (4.13) shows that the rate of growth of the A_rB_s layer in the $A_pB_q-A_rB_s-B$ system is greater than the rate of its growth in the $A-A_rB_s-B$ system because β always exceeds unity. The closer the composition of A_pB_q to that of A_rB_s (β tends to unity), the greater is the rate of growth of the A_rB_s layer in the A_pB_q-B reaction couple.

To illustrate the magnitude of this effect, consider a few numerical examples. If the growth rate of the AB_3 layer in the $A-AB_3-B$ system is taken as unity, then its growth rate in the $AB-AB_3-B$ system is equal to 3/2 and in the AB_2-AB_3-B system to 3. The rate of growth of the A_2B_3 layer in the $AB-A_2B_3-B$ system should be three times the rate of its growth in the $A-A_2B_3-B$ system.

If the A_pB_q compound has a considerable range of homogeneity, the growth rate of the A_rB_s layer in the A_pB_q-B reaction couple depends upon the composition of initial phase A_pB_q . The growth kinetics of the A_rB_s layer between the A_pB_q phase enriched in component A and elementary substance B is more complicated than the growth kinetics of this layer between the A_pB_q phase enriched in component B and substance B . In the former case, simultaneously with the consumption of the A_pB_q phase as a whole, a lowering of the content of component A in its bulk is likely (but not necessarily) to occur. If not, the ratio of the growth rates of the A_rB_s layer in the reaction couples consisting of substance B and the A_pB_q phase of different composition can readily be found from equation (4.13) simply by expressing its composition in atomic fractions or atomic percent. Note that equation (4.13) also holds if the initial phase is a solid solution that is consumed as a whole, *i.e.* without any change of composition, during growth of the A_rB_s layer.

Although in the case under consideration only component A diffuses across the bulk of the A_rB_s layer, the thickness of this layer nevertheless increases at its both interfaces. The final result is thus similar to that which would be observed if both components diffused simultaneously. This should be taken into account when interpreting the experimental data

on diffusional contributions of components A and B to the growth process of any chemical compound layer, obtained using inert markers. In the case of reaction couples of the A_pB_q-B type, their interpretation is not always unambiguous.

Indeed, if an inert marker is initially placed at the interface between A_2B and B and the movement of the A_2B-AB and $AB-B$ interfaces during growth of the AB layer is then observed, it will be found that the distances from the marker to those interfaces gradually increase with passing time and remain equal to one another. On the basis of these observations, the researcher might have concluded, from a diffusional viewpoint, that (i) both components A and B are diffusing across the AB layer in the opposite direction and (ii) the rates of their diffusion are equal. In fact, however, component B does not diffuse in the AB layer at all.

4.2.2: Growth of the A_rB_s layer between A_pB_q and B at the expense of diffusion of both components

Consider now the general case of growth of the A_rB_s layer between A_pB_q and B at the expense of diffusion of both components A and B (Fig. 4.3). Then, the additional increase, dy_{B2} , in thickness of the A_rB_s layer at interface 2 is caused by the diffusion to this interface of the B atoms and subsequent occurrence of partial chemical reaction (3.2₁). It is obvious that the values of this increase in the $A_pB_q-A_rB_s-B$ and $A-A_rB_s-B$ systems are different.

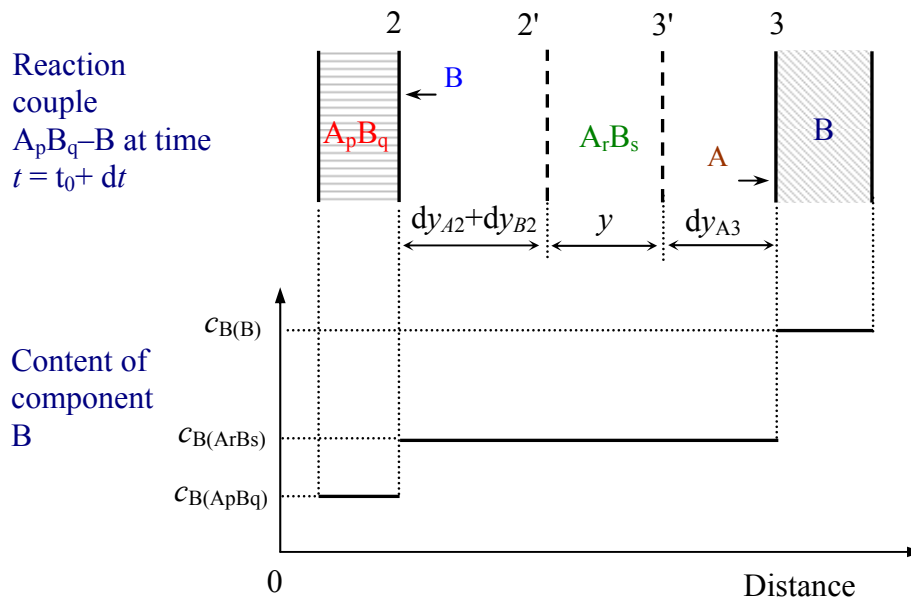


Fig. 4.3. Schematic diagram to illustrate the growth process of the A_rB_s layer in the A_pB_q-B reaction couple due to counter-diffusion of both components and partial decomposition of the A_pB_q phase at interface 2.

Clearly, the transport ability of the A_rB_s layer in regard to diffusing B atoms as well as in regard to diffusing A atoms does not depend upon with which phase this layer borders in each particular reaction couple and also upon which phase is a source of either B or A atoms. This ability only depends upon the number of diffusion paths in the A_rB_s lattice and upon the rate of travel of the atoms along those paths.

It should be taken into account, however, that the formation of one molecule of A_rB_s by reaction (4.1) requires s diffusing B atoms, whereas according to reaction (3.2₁) the interaction of $(sp-qr)$ diffusing B atoms with r A_pB_q molecules results in the occurrence of p A_rB_s molecules at interface 2. If the elementary acts of partial chemical reactions (4.1) and (3.2₁) had the same rate, the increase of the thickness of the A_rB_s layer in the $A_pB_q-A_rB_s-B$ system at this interface per unit time would be $sp/(sp-qr) = \beta/(\beta-1)$ times greater than that in the $A-A_rB_s-B$ system. In general, however, these rates appear to be different. If only component B diffuses in the A_rB_s layer, then from equations (3.11₁), (3.14₁) and (4.3) it can be found that the growth rate of this layer is

$$\left(\frac{dy_B}{dt} \right)_{A_pB_q-B} = \frac{\beta}{\beta-1} \frac{k''_{0B2}}{1 + \frac{k''_{0B2}y}{k_{1B2}}}, \quad (4.14)$$

where $k'_{0B2} = \frac{\beta}{\beta-1} k''_{0B2}$ and $k'_{1B2} = \frac{\beta}{\beta-1} k_{1B2}$.

Thus, in the case of diffusion of both components A and B , there are three velocities of movement of the interfaces of the A_rB_s layer with the adjacent phases of the $A_pB_q-A_rB_s-B$ system (see Fig. 4.3):

- (1) movement of interface 2 to the left as a result of partial chemical reaction (3.2₁);
- (2) movement of interface 3 to the right as a result of partial chemical reaction (4.2);
- (3) movement of interface 2 to the left as a result of the phase transformation of A_pB_q into A_rB_s according to reaction (4.6).

Summation of the right-hand parts of equations (4.12) and (4.14) yields a general kinetic equation describing the growth rate of the A_rB_s layer between the A_pB_q and B phases in the case where both components are diffusing in its bulk

$$\left(\frac{dy}{dt} \right)_{A_pB_q-B} = \frac{\beta}{\beta-1} \left(\frac{k''_{0B2}}{1 + \frac{k''_{0B2}y}{k_{1B2}}} + \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}} \right), \quad (4.15)$$

or in the form more convenient for subsequent comparisons

$$\left(\frac{dy}{dt}\right)_{A_pB_q-B} = \frac{sp}{sp-qr} \left(\frac{\frac{k''_{0B2}}{1 + \frac{k''_{0B2}y}{k_{1B2}}} + \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}}} \right). \quad (4.16)$$

Evidently, there is no significant difference between the growth kinetics of the A_rB_s layer in the A_pB_q-B reaction couple and its growth kinetics in the $A-A_lB_n$ reaction couple. The growth rate of this layer in the latter couple (Fig. 4.4) is in general described by the equation

$$\left(\frac{dy}{dt}\right)_{A-A_lB_n} = \frac{rn}{rn-ls} \left(\frac{\frac{k_{0B2}}{1 + \frac{k_{0B2}y}{k_{1B2}}} + \frac{k''_{0A3}}{1 + \frac{k''_{0A3}y}{k_{1A3}}}} \right). \quad (4.17)$$

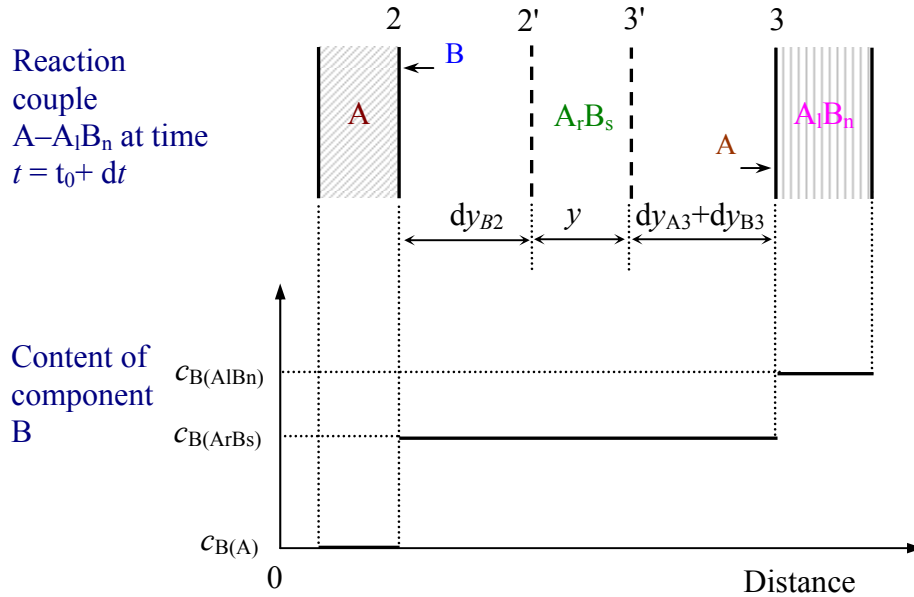


Fig. 4.4. Schematic diagram to illustrate the growth process of the A_rB_s layer in the $A-A_lB_n$ reaction couple due to the counter-diffusion of both components and the partial decomposition of the A_lB_n phase at interface 3.

Its derivation is similar to that of equation (4.16). Note that in the $A-A_lB_n$ reaction couple the phase transformation of A_lB_n into A_rB_s

$$rA_lB_n = lA_rB_s + (rn - ls)B_{\text{dif}} \quad (4.18)$$

takes place at interface 3 under the influence of reaction diffusion of the B atoms from interface 3 to interface 2. Hence, in this couple an increase in thickness of the A_rB_s layer at interface 3 is due to two reactions (3.2₂) and (4.18), while that at interface 2 only to one reaction (4.1). Appropriate changes of the A_rB_s layer thickness during the time dt are shown in Fig. 4.4.

4.3: Growth of the A_rB_s layer in the $A_pB_q-A_lB_n$ reaction couple

Schematic diagram illustrating the growth process of the A_rB_s layer between the A_pB_q and A_lB_n phases is shown in Fig. 4.5. As seen from equation (4.14), its thickness increases at interface 2 in the course of reaction (3.2₁) at a rate of

$$\left(\frac{dy_{B2}}{dt} \right)_{A_pB_q-A_lB_n} = \frac{sp}{sp - qr} \frac{k''_{0B2}}{1 + \frac{k''_{0B2}y}{k_{1B2}}} \quad (4.19)$$

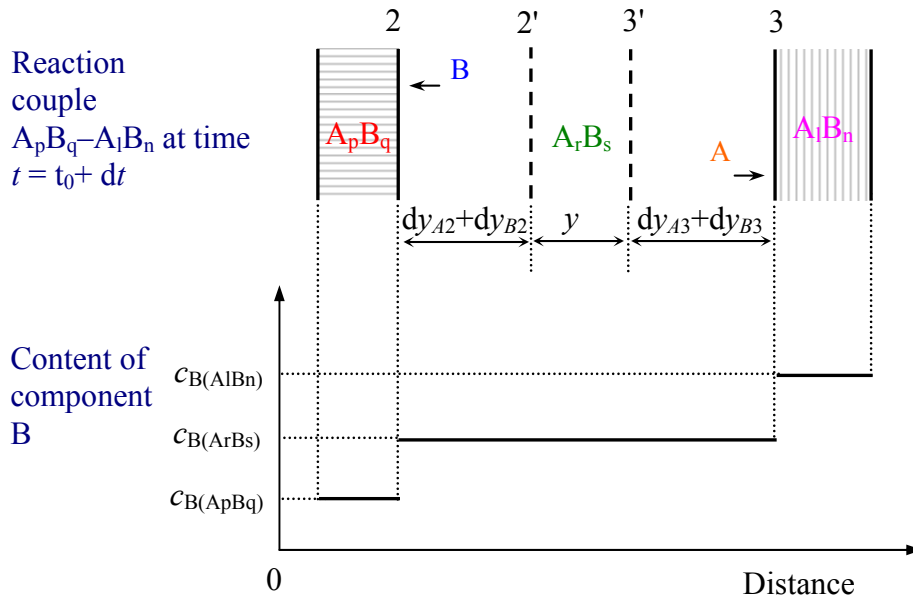


Fig. 4.5. Schematic diagram to illustrate the growth process of the A_rB_s layer in the $A_pB_q-A_lB_n$ reaction couple in the case of simultaneous diffusion of both components.

Simultaneously, the A_rB_s layer thickness increases at interface 3 as a result of the phase transformation of A_lB_n into A_rB_s by reaction (4.18). The diffusional constant k_{1B2} characterizes partial chemical reaction (4.1) in which s diffusing B atoms take part. Again, according to equation (4.18) the loss of r A_lB_n molecules ($rn-ls$) B atoms results in the formation of l A_rB_s molecules. Therefore, the growth rate of the A_rB_s layer at interface 3 is

$$\left(\frac{dy_{B3}}{dt} \right)_{A_pB_q-A_lB_n} = \frac{ls}{rn-ls} \frac{k_{0B2}''}{1 + \frac{k_{0B2}''}{k_{1B2}}}. \quad (4.20)$$

Hence, if only component B diffuses in the A_rB_s layer, then the rate of growth of this layer in the $A_pB_q-A_lB_n$ reaction couple is

$$\left(\frac{dy_B}{dt} \right)_{A_pB_q-A_lB_n} = \frac{rs(pn-ql)}{(sp-qr)(rn-ls)} \frac{k_{0B2}''}{1 + \frac{k_{0B2}''}{k_{1B2}}}. \quad (4.21)$$

This equation is a result of term-by-term summation of equations (4.19) and (4.20).

Partial chemical reaction (3.2₂) proceeds at interface 3 between the A atoms diffusing across the A_rB_s layer and the A_lB_n compound. Accordingly, the phase transformation of A_pB_q into A_rB_s takes place at interface 2 by reaction (4.6). The growth rate of the A_rB_s layer at interface 3 is

$$\left(\frac{dy_{A3}}{dt} \right)_{A_pB_q-A_lB_n} = \frac{rn}{rn-ls} \frac{k_{0A3}''}{1 + \frac{k_{0A3}''}{k_{1A3}}}. \quad (4.22)$$

Derivation of this equation is analogous to that of equation (4.14).

The growth rate of the A_rB_s layer at interface 2 can readily be found from equations (4.2) and (4.6). Indeed, the diffusional constant k_{1A3} characterises partial chemical reaction (4.2) in which r diffusing A atoms take part. On the other hand, $(sp-qr)$ diffusing A atoms occur per q A_rB_s molecules formed as a result of decomposition of the A_pB_q phase by reaction (4.6). Therefore,

$$\left(\frac{dy_{A2}}{dt}\right)_{A_pB_q-A_lB_n} = \frac{qr}{sp-qr} \frac{k''_{0A3}}{1 + \frac{k''_{0A3}y}{k_{1A3}}}. \quad (4.23)$$

Thus, if only component A diffuses across the A_rB_s layer, then the growth rate of this layer in the $A_pB_q-A_lB_n$ reaction couple is

$$\left(\frac{dy_A}{dt}\right)_{A_pB_q-A_lB_n} = \frac{rs(pn-ql)}{(sp-qr)(rn-ls)} \frac{k''_{0A3}}{1 + \frac{k''_{0A3}y}{k_{1A3}}}. \quad (4.24)$$

Term-by-term summation of equations (4.21) and (4.24) yields a general equation describing the growth kinetics of the A_rB_s layer between the A_pB_q and A_lB_n phases in the case of counter-diffusion of components A and B across its bulk at comparable rates

$$\left(\frac{dy}{dt}\right)_{A_pB_q-A_lB_n} = \frac{rs(pn-ql)}{(sp-qr)(rn-ls)} \left(\frac{k''_{0B2}}{1 + \frac{k''_{0B2}y}{k_{1B2}}} + \frac{k''_{0A3}}{1 + \frac{k''_{0A3}y}{k_{1A3}}} \right). \quad (4.25)$$

Consider the consequences following from equations (4.3), (4.16), (4.17) and (4.25). It is more convenient to do this separately for the linear and parabolic regions of growth of the A_rB_s layer.

4.4: Comparison of the growth rates of the A_rB_s layer in various reaction couples of the $A-B$ multiphase binary system

Initially, conditions of the type $k_0 \ll k_1/y$ are satisfied. The growth kinetics of the A_rB_s layer is therefore linear in all four reaction couples:

$$\left(\frac{dy}{dt}\right)_{A-B} = k_{0B2} + k_{0A3}, \quad (4.26)$$

$$\left(\frac{dy}{dt}\right)_{A_pB_q-B} = \frac{sp}{sp-qr} (k''_{0B2} + k_{0A3}), \quad (4.27)$$

$$\left(\frac{dy}{dt}\right)_{A-A_lB_n} = \frac{rn}{rn-ls} (k_{0B2} + k''_{0A3}), \quad (4.28)$$

$$\left(\frac{dy}{dt}\right)_{A_pB_q-A_lB_n} = \frac{rs(pn-ql)}{(sp-qr)(rn-ls)}(k''_{0B2} + k''_{0A3}). \quad (4.29)$$

If only the A atoms diffuse across the A_rB_s layer ($k_{0B2} = 0$ and $k''_{0B2} = 0$), then from equations (4.26) and (4.27) it follows that the ratio of the rate of linear growth of this layer in the A_pB_q-B reaction couple to the rate of its linear growth in the $A-B$ reaction couple is

$$\frac{sp}{sp-qr},$$

whereas according to equations (4.28) and (4.29) for the $A_pB_q-A_lB_n$ and $A-A_lB_n$ couples this ratio is

$$\frac{s(pn-ql)}{n(sp-qr)}.$$

If only the B atoms diffuse across the A_rB_s layer ($k_{0A3} = 0$ and $k''_{0A3} = 0$), then from equations (4.26) and (4.28) it follows that the ratio of the rate of linear growth of this layer in the $A-A_lB_n$ reaction couple to the rate of its linear growth in the $A-B$ reaction couple is

$$\frac{rn}{rn-ls},$$

whereas according to equations (4.27) and (4.29) for the $A_pB_q-A_lB_n$ and A_pB_q-B couples this ratio is

$$\frac{r(pn-ql)}{p(rn-ls)}.$$

It is clear that in the case of comparable mobility of components A and B in the A_rB_s lattice it is impossible to make any definite theoretical prediction because an exact relation between k_{0A3} and k''_{0A3} as well as between k_{0B2} and k''_{0B2} is not known *a priori*. It might be expected, however, that the constant k''_{0B2} characterising the rate of chemical interaction taking place in the $A_pB_q-A_rB_s-B$ system at the $A_pB_q-A_rB_s$ interface between the diffusing B atoms and the A_pB_q compound is at least not less than the constant k_{0B2} which characterises the rate of chemical interaction taking place in the $A-A_rB_s-B$ system at the $A-A_rB_s$ interface between the diffusing B atoms and the surface A atoms, since the A_rB_s phase is closer in composition to the A_pB_q than to A phase. In any case, therefore, the rate of linear growth of the A_rB_s layer in the $A_pB_q-A_lB_n$ and A_pB_q-B couples must be higher than the rate of its linear growth in the $A-B$ couple.

The same applies to a relation between k_{0A3} and k''_{0A3} . Moreover, it may happen that an increase in the rate of growth of the A_rB_s layer in a series of the reaction couples $A-B$, A_pB_q-B , $A-A_lB_n$, $A_pB_q-A_lB_n$ is even greater than that which would be expected merely putting $k_{0B2} = k''_{0B2}$ and $k_{0A3} = k''_{0A3}$ in equations (4.26)-(4.29). Undoubtedly, influence of the

structure of the crystal lattices of reacting phases is important. To find out an exact relationship between all the chemical constants and, accordingly, the ratio of the growth rates of the A_rB_s layer in various reaction couples of the $A-B$ multiphase binary system, it would be desirable to carry out thorough experimental investigations with thin films. In this respect, refined techniques elaborated by G. Blaise [328], K.D. Becker [348], R. Sinclair *et al.* [349], S.K. Verma *et al.* [350] and other researchers appear to be highly promising.

It can easily be seen that the ratio of the rates of parabolic (diffusional) growth of the A_rB_s layer in the reaction couples under consideration is unambiguously determined by the chemical composition of the interacting phases. Indeed, conditions of the type $k_0 \gg k_1/y$ are fulfilled in the diffusional stage of layer formation. Therefore, equations (4.3), (4.16), (4.17) and (4.25) become

$$\left(\frac{dy}{dt}\right)_{A-B} = \frac{k_{1B2} + k_{1A3}}{y}, \quad (4.30)$$

$$\left(\frac{dy}{dt}\right)_{A_pB_q-B} = \frac{sp}{sp-qr} \frac{k_{1B2} + k_{1A3}}{y}, \quad (4.31)$$

$$\left(\frac{dy}{dt}\right)_{A-A_lB_n} = \frac{rn}{rn-ls} \frac{k_{1B2} + k_{1A3}}{y}, \quad (4.32)$$

$$\left(\frac{dy}{dt}\right)_{A_pB_q-A_lB_n} = \frac{rs(pn-ql)}{(sp-qr)(rn-ls)} \frac{k_{1B2} + k_{1A3}}{y}. \quad (4.33)$$

From these equations, it follows that

- (i) the ratio of the growth rates of the A_rB_s layer in the $A-B$, A_pB_q-B , $A-A_lB_n$ and $A_pB_q-A_lB_n$ reaction couples only depends on the stoichiometry of the compounds;
- (ii) the growth rate of this layer is least in the $A-B$ couple and highest in the $A_pB_q-A_lB_n$ couple;
- (iii) if the rate of growth of the A_rB_s layer in any one of the reaction couples is known from the experimental data or assumed, then the rate of its growth in all other couples can be predicted exactly.

For example, if some binary system $A-B$ contains three chemical compounds A_2B , AB and AB_2 and the AB layer is the first to form in the $A-B$ reaction couple, then the ratio of the rate of diffusional (parabolic) growth of this layer in the A_2B-B couple to the rate of its diffusional growth in the $A-B$ couple must be equal to 2. For the A_2B-AB_2 and $A-B$ couples, this ratio is 3. For the A_2B-AB_2 and A_2B-B couples, it is $3/2$.

It should be noted that both Wagner's theory [50] and equations (4.30)-(4.33) yield the same ratio for the rates of diffusional growth of the A_rB_s layer in the $A-B$, A_pB_q-B , $A-A_lB_n$ and $A_pB_q-A_lB_n$ reaction couples. According to C. Wagner, the ratio of the rates of diffusional (parabolic) growth of the same layer in various reaction couples can be calculated using the concept of the integrated diffusion coefficient $D_{\text{int}}^{(i)}$

$$D_{\text{int}}^{(i)} = \int_{N^{(i)'}}^{N^{(i)'}} D dN, \quad (4.34)$$

where N is the mole fraction of one of the components in the i -th phase having the limits of the homogeneity range $N^{(i)'}$ and $N^{(i)''}$.

If the range of homogeneity is very narrow and there is no mutual solubility of the components in the solid state, then [50, 68]

$$D_{\text{int}}^{(i)} = \frac{(N^+ - N^{(i)})(N^{(i)} - N^-)}{N^+ - N^-} [k_1^{(i)}]_{N^+/N^-}, \quad (4.35)$$

where N^+ and N^- are the mole fractions of the same component in initial phases, $N^{(i)}$ is its mole fraction in the growing phase, $[k_1^{(i)}]_{N^+/N^-}$ is the parabolic growth-rate constant for the i -th phase of a given reaction couple, found from a plot of the squared layer thickness upon time.

Calculation of $D_{\text{int}}^{(i)}$, for example, for the AB phase ($N_A^+ = 1/2$) growing in the reaction couples $A-B$ ($N_A^+ = 1, N_A^- = 0$), A_2B-B ($N_A^+ = 2/3, N_A^- = 0$) and A_2B-AB_2 ($N_A^+ = 2/3, N_A^- = 1/3$) yields the following relations.

System	$D_{\text{int}}^{(i)}$
$A-AB-B$	$\frac{1}{4} [k_1^{(AB)}]_{A-B},$
$A_2B-AB-B$	$\frac{1}{8} [k_1^{(AB)}]_{A_2B-B},$
$A_2B-AB-AB_2$	$\frac{1}{12} [k_1^{(AB)}]_{A_2B-AB_2}.$

The quantity $D_{\text{int}}^{(i)}$ is an intrinsic characteristic of the i -th phase and must therefore be the same in all couples in which this phase occurs. Hence, the ratio of the parabolic growth-rate constants for the AB layer in the A_2B-AB_2 , A_2B-B and $A-B$ reaction couples is 3:2:1, in

agreement with the calculations on the basis of equations (4.30), (4.31) and (4.33). That this is not an occasional coincidence can readily be verified by carrying out calculations for other chemical compounds of different stoichiometry. Similar results follow, for example, from the data by F.J.J. van Loo on the integrated diffusion coefficients for the Ti–Al system [68].

It should be emphasised, however, that Wagner's theory is quite inapplicable to the region of linear growth of chemical compound layers. By contrast, the physico-chemical approach makes it possible not only to explain qualitatively the existence of linear growth region but in certain cases allows precise quantitative calculations of the ratio of the growth rates for the same layer in different reaction couples of the A – B multiphase system to be carried out.

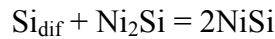
Note that the mechanism of formation of the A_rB_s layer in reaction couples of the A_pB_q – B type by the decomposition of the A_pB_q compound under the influence of reaction diffusion of the A atoms to the A_rB_s – B interface, described in this chapter, has numerous experimental verifications. When investigating the growth process of the NiSi layer between Ni₂Si and single crystals of silicon, T.G. Finstad [84] and also F.M. d'Heurle *et al.* [86] found it to proceed mainly by means of partial decomposition of Ni₂Si:



The nickel atoms released as a result of this reaction diffuse across the NiSi layer to the NiSi–Si interface and interact there with the surface silicon atoms to form additional molecules of NiSi



According to those authors, contribution of the reaction



to the process of formation of the NiSi layer is insignificant.

Similar growth mechanism is also typical of the NiSi₂ layer occurring between NiSi and Si [29, 351]. Its thickening at the NiSi–NiSi₂ interface is due to two partial chemical reactions



and



while that at the NiSi₂–Si interface is a result of one reaction



This kind of chemical reactions takes place in other systems, if one of the two constituents of a reaction couple is a chemical compound and another is an elementary substance. Since the diffusional stage of growth of the layers of transition-metal silicides has

been studied thoroughly, it becomes possible to compare theoretical predictions with available experimental data.

Consider the Co–Si binary system in which three compounds Co_2Si , CoSi and CoSi_2 exist at temperatures up to 1170°C as an example [157, 287, 330]. The Co_2Si layer is known to be the first to occur between cobalt and silicon. At 460°C , its growth follows a parabolic law [82]. Therefore, experimental data by K.N. Tu *et al.* [80] can be used to compare the growth rates of the Co_2Si layer in the Co–Si and Co–CoSi diffusion couples (Fig. 4.6).

Schematic diagrams illustrating the growth process of the Co_2Si layer in the Co–Si and Co–CoSi couples are shown in Figs 4.7 and 4.8, separately for the two hypothetical cases in which only one component is diffusing.

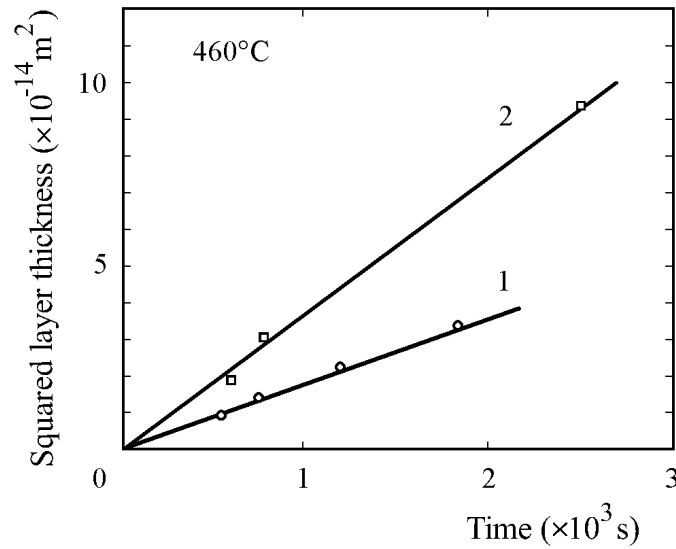


Fig. 4.6. Plots of the squared thickness of the Co_2Si layer in the Co–Si (1) and Co–CoSi (2) diffusion couples against annealing time at 460°C . According to the experimental data by K.N. Tu *et al.* [82]

If diffusion of cobalt is dominant, as in Fig. 4.7, then the growth of the Co_2Si layer in the Co–Si couple is due to partial chemical reaction between the diffusing cobalt atoms and the surface silicon atoms



taking place at the Co_2Si –Si interface. During the time dt , it causes the increase in thickness of the Co_2Si layer by $dy_{\text{Co}_2\text{Si}}$ at interface 3. Note that in the Co–Si couple one Co_2Si molecule is formed per two diffusing cobalt atoms.

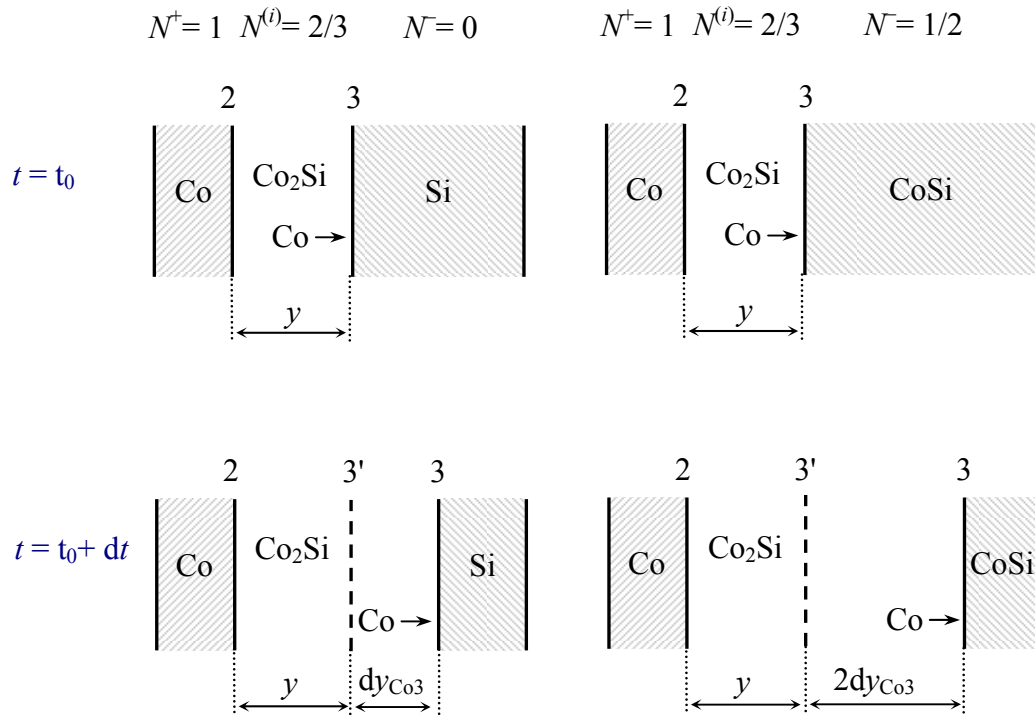


Fig. 4.7. Schematic diagram to illustrate the growth process of the Co₂Si layer in the Co–Si and Co–CoSi diffusion couples in the hypothetical case where only cobalt is the diffusing species.

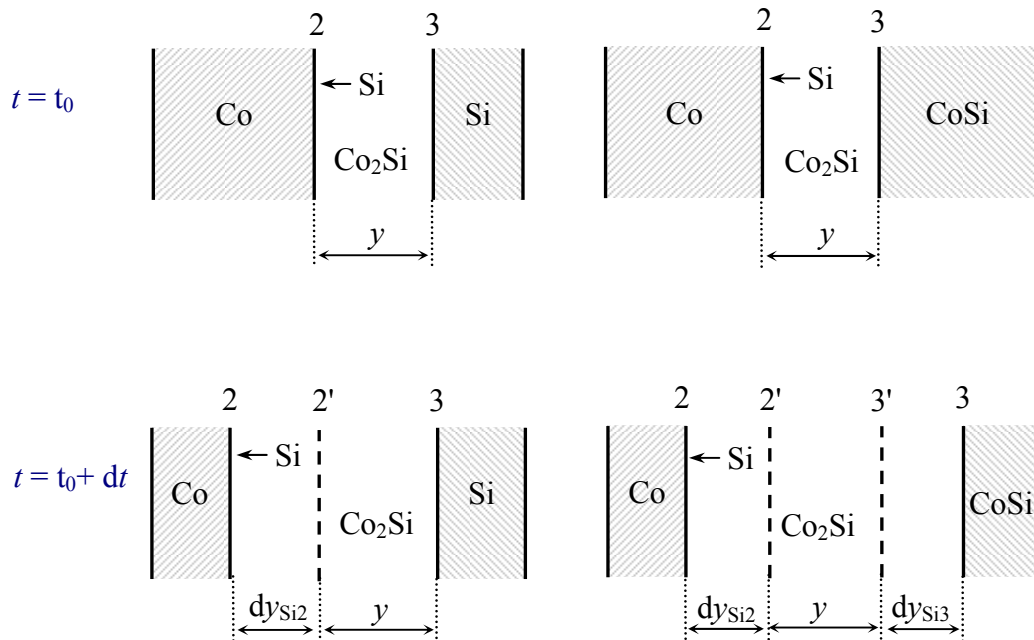


Fig. 4.8. Schematic diagram to illustrate the growth process of the Co₂Si layer in the Co–Si and Co–CoSi diffusion couples in the hypothetical case where only silicon is the diffusing species.

Partial chemical reaction



proceeds at interface 3 in the Co–CoSi diffusion couple. Hence, during the same time dt , the thickness of the Co_2Si layer must increase by $2dy_{\text{Co}_3}$ at interface 3 because in this couple one Co_2Si molecule is formed per one diffusing atom of cobalt. Therefore, the ratio of the rate of growth of the Co_2Si layer in the Co–CoSi diffusion couple to the rate of its growth in the Co–Si diffusion couple is equal to 2.

If diffusion of silicon prevails, as in Fig. 4.8, then partial chemical reaction at interface 2 is the same in both couples:



During the time dt , it causes the increase in thickness of the Co_2Si layer by dy_{Si_2} at this interface. Since in the Co–CoSi diffusion couple the CoSi compound is a source of silicon atoms, two CoSi molecules lose one silicon atom and thus one Co_2Si molecule is produced at interface 3



whereas this released silicon atom diffuses across the Co_2Si layer and reacts at interface 2 with two surface cobalt atoms to form one more Co_2Si molecule. Again, the growth rate of the Co_2Si layer in the Co–CoSi couple is seen to be twice that in the Co–Si couple.

Clearly, the same also applies to the general case of comparable mobility of the components in the Co_2Si layer. This result can readily be obtained merely by putting $r = 2$, $s = l = n = 1$ in equation (4.32) and then dividing this equation by equation (4.30).

As seen in Fig. 4.6, for the Co–CoSi couple the slope of a plot of the squared thickness of the Co_2Si layer against annealing time is in fact twice that of such a plot for the Co–Si couple. If the layer thickness is plotted against the square root of the time, $\sqrt{t}$, then the ratio of the slopes of straight lines for the couples of this type should be $\sqrt{2}$.

G. Ottaviani and M. Costato [76] established that during growth of the Pt_2Si layer the ratio of the slopes of the $y - \sqrt{t}$ dependences for the Pt–PtSi and Pt–Si couples was equal to about 1.5, in fairly good agreement with a theoretical value of 1.41. The activation energies for the process of growth of the Pt_2Si layer in both couples are equal to 145 kJ mol^{-1} (1.5 eV). It is interesting to note that the activation energies of formation of the Pd_2Ge layer in the Pd–Ge and Pd–PdGe couples are the same (for more detail, see Ref. [76]).

According to C. Wagner [50], in the case of parabolic growth of the Co_2Si layer in the Co–Si couple (see Fig. 4.7), $N^+ = 1$, $N^{(i)} = 2/3$ and $N^- = 0$, where N is the mole fraction of cobalt in appropriate phases. Hence,

$$D_{\text{int}}^{(\text{Co}_2\text{Si})} = \frac{2}{9} [k_1^{(\text{Co}_2\text{Si})}]_{\text{Co-Si}}. \quad (4.40)$$

For the Co–Co₂Si–CoSi system, $N^+ = 1$, $N^{(i)} = 2/3$ and $N^- = 1/2$. Therefore,

$$D_{\text{int}}^{(\text{Co}_2\text{Si})} = \frac{1}{9} [k_1^{(\text{Co}_2\text{Si})}]_{\text{Co-CoSi}} \quad (4.41)$$

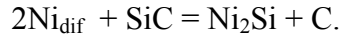
Thus,

$$[k_1^{(\text{Co}_2\text{Si})}]_{\text{Co-CoSi}} = 2[k_1^{(\text{Co}_2\text{Si})}]_{\text{Co-Si}} \quad (4.42)$$

if the constant $k_1^{(\text{Co}_2\text{Si})}$ is determined from the $y^2 - t$ plots for both reaction couples.

Note that the silicide layer can grow not only between silicon and a transition metal, but also between a silicon-containing phase and a transition metal or an intermetallic compound. Such layers are known to occur in the process of brazing the transition metals by their own melts with Si₃N₄-base ceramics [304] and also during the interaction of transition metals with silicon carbide [303, 305-310].

At temperatures above 700 °C, nickel reacts with silicon carbide to form Ni₂Si and C [303]. Nickel atoms are the dominant diffusing species in the Ni₂Si layer [29, 126]. Therefore, the thickness of this layer increases mainly at the Ni₂Si–SiC interface by the reaction



Since carbon is insoluble in the Ni₂Si phase, it forms fine-grained graphite inclusions in the bulk of the Ni₂Si layer. These inclusions are often seen in the microstructure as the regular bands parallel to the layer interfaces [307].

Formation of silicides in reaction couples, for example, of the Me₃Al–SiC type where Me is a transition metal, is more complicated. In this case, in addition to the Me₂Si layer, the MeAl layer (or some other aluminide layer) also occurs, *i.e.* the Me₃Al–MeAl–(Me₂Si+C)–SiC system is formed. Probably, the mechanism of its formation is as follows. The Me₃Al phase is decomposed at the Me₃Al–MeAl interface by the reaction



while two released transition metal atoms then diffuse across the layers of MeAl and (Me₂Si+C) to the (Me₂Si+C)–SiC interface where they enter into the reaction with SiC: $2\text{Me}_{\text{dif}} + \text{SiC} = \text{Me}_2\text{Si} + \text{C}$, causing an increase of the (Me₂Si+C) layer at this interface. Clearly, in such a case the ratio of the thicknesses of the MeAl and (Me₂Si+C) layers must remain unchanged with passing time. Unfortunately, available literature data are insufficient to make an unambiguous comparison of the growth rates of the Me₂Si layer in reaction couples of the type Me–Si, Me–SiC and Me₃Al–SiC.

It might seem that the A_rB_s layer could grow in the $A-A_pB_q-A_rB_s-A_lB_n-B$ system by the same mechanism as in the $A_pB_q-A_rB_s-B$ and $A_pB_q-A_rB_s-A_lB_n$ systems, *i.e.* at the expense of the phase transformation of A_pB_q into A_rB_s under the influence of reaction diffusion of the A atoms. However, this is not the case. If the growth regime of the A_pB_q layer in the $A-A_pB_q-$

$A_rB_s-A_lB_n-B$ system is reaction controlled with regard to component A ($x < x_{1/2}^{(A)}$), then there is an excess of A atoms in comparison with the reactivity of the A_rB_s surface towards these atoms and therefore no transformation will take place.

Assume that with time the growth regime of the A_pB_q layer with regard to component A became diffusion controlled ($x > x_{1/2}^{(A)}$), while the A_pB_q phase was partly transformed into the A_rB_s one by reaction (4.6). The A atoms released as a result of this transformation cannot, however, cross the $A_pB_q-A_rB_s$ interface in the $A-A_pB_q-A_rB_s-A_lB_n-B$ system in the same manner as in the $A_pB_q-A_rB_s-B$ or $A_pB_q-A_rB_s-A_lB_n$ system. Those A atoms will immediately be combined into the A_pB_q compound at this interface (onto the surface of the A_rB_s phase from the side of A_pB_q) by reaction (3.1₂) which is opposite to reaction (4.6). It is clear that the net result of these reactions is zero.

The behaviour of the same A_pB_q layer in relation to its neighbors in various reaction systems is thus seen to depend on whether it is growing or non-growing. In the $A-A_pB_q-A_rB_s-A_lB_n-B$ system, the A_pB_q layer is a *growing* one. Therefore, it tends to consume all diffusing A atoms for its own growth. By contrast, in the $A_pB_q-A_rB_s-B$ and $A_pB_q-A_rB_s-A_lB_n$ systems, this layer is a *non-growing* one. Therefore, it not only readily supplies the adjacent A_rB_s layer with diffusing A atoms but in addition partly transforms into the latter. This difference in the behavior of the A_pB_q layer is in turn due to the presence or absence of the A phase.

Obviously, the A_rB_s layer cannot grow in the $A-A_pB_q-A_rB_s-A_lB_n-B$ system by means of the phase transformation of A_lB_n into A_rB_s under the influence of reaction diffusion of the B atoms by reaction (4.18), as is the case in the $A-A_rB_s-A_lB_n$ and $A_pB_q-A_rB_s-A_lB_n$ systems. In the $A-A_pB_q-A_rB_s-A_lB_n-B$ system, the released B atoms are immediately combined onto the surface of the A_rB_s phase into the A_lB_n compound by reaction (3.2₂) opposite to reaction (4.18).

From these considerations, it becomes clear why, for example, the Mo_2B layer, missing from the Mo-B diffusion couple, readily occurs and grows under the same experimental conditions in the Mo-MoB diffusion couple. Though there are four stable molybdenum borides [352, 353], J. Brandstötter and W. Lengauer [354] found that only the MoB layer 450 μm thick is formed onto the surface of a molybdenum sheet during its boriding in a mixture of boron powder with 5 % KBF_4 (B-containing phase) at 1450 °C for 2.5 h (Fig. 4.9a).

However, if this same specimen is re-annealed at 1450 °C for 2 h in vacuum in the absence of the B-containing phase, the Mo_2B layer about 19 μm thick occurs between Mo and MoB (Fig. 4.9b). Its formation is due to the decomposition of MoB



and the subsequent reaction



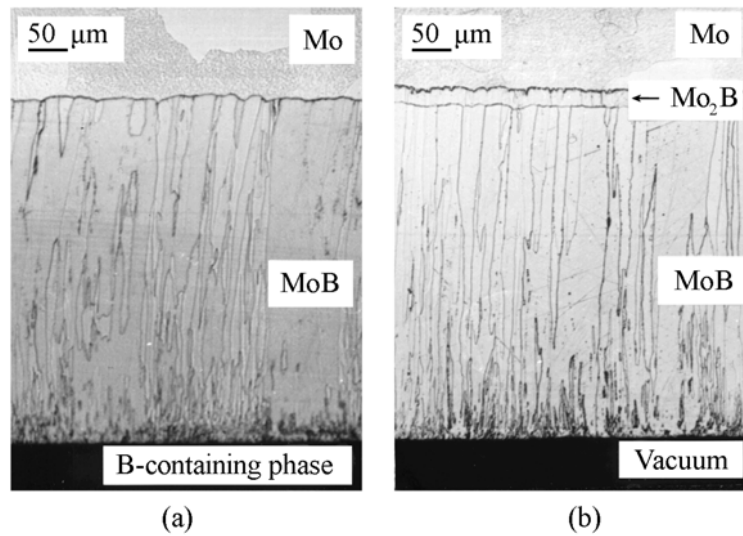


Fig. 4.9. Formation of molybdenum boride layers between (a) Mo and B-containing phase and (b) between Mo and MoB [289]. Annealing temperature 1450 °C. Time: (a), 9000 s (2.5 h); (b), 7200 s (2 h). Photographs kindly provided by Prof. W. Lengauer. Reprinted with permission from Elsevier Science.

It should be stressed that the processes of the phase transformation of A_pB_q into A_rB_s in the $A_pB_q-A_rB_s-B$ and $A_pB_q-A_rB_s-A_lB_n$ systems and the reaction diffusion of the A atoms across the A_rB_s layer from the $A_pB_q-A_rB_s$ interface to the A_rB_s-B or $A_rB_s-A_lB_n$ interface are inseparably linked with each other. Neither of them can occur without the other. It is clear, however, that their rates, when each is taken alone, are not identical.

The results presented in this chapter were obtained assuming that the rate of transformation of A_pB_q into A_rB_s is not less than the rate of diffusion of the A atoms across the A_rB_s layer. For thick layers, this appears to be rather substantiated. In thin layers of chemical compounds, especially if the structures of the A_pB_q and A_rB_s crystal lattices differ considerably, rearrangement of the A_pB_q into A_rB_s lattice may be the rate-determining step. Therefore, the growth kinetics of the A_rB_s layer will be dependent upon the rate of this transformation.

In such a case, the region of reaction control for the formation of the A_rB_s layer will merely be more extended in time. More essential differences between the kinetic dependences describing the growth rates of this layer in different reaction couples of the $A-B$ multiphase binary system can hardly be expected.

Note that the driving force for the reaction between initial phases, *i.e.* the difference of the chemical potentials of the components in those phases, decreases in the series $A-B$, A_pB_q-B , $A_pB_q-A_lB_n$. This can easily be seen from the distribution of the content of component B in interacting phases, shown in Figs 4.1, 4.2 and 4.5, the concentration

difference of component B being highest between A and B and least between A_pB_q and A_lB_n . Nevertheless, the growth rate of the A_rB_s layer increases in this series.

It seems therefore relevant to emphasise that great care is necessary in application of the usually unconditionally accepted thesis about a directly proportional relationship between the driving force for any physical or chemical process and its rate. This example clearly shows that without a detailed knowledge of the underlying mechanism of that process, starting only from “apparent general considerations”, so beloved by many theoreticians, it is hardly possible to accurately describe its peculiarities, even qualitatively. In the case under consideration, “general considerations” would definitely lead to the opposite, incorrect result because the highest growth rate of the A_rB_s layer is observed in the A_pB_q – A_lB_n reaction couple where the driving force for the reaction-diffusion process is least.

4.5: Duplex structure of the A_rB_s layer

Since in the A – A_lB_n , A_pB_q – B and A_pB_q – A_lB_n reaction couples the mechanisms of formation of the A_rB_s layer at its interfaces with adjacent phases are different, in many cases the duplex (dual) structure of this layer, shown schematically in Fig. 4.10, can readily be observed experimentally.

The term *duplex structure* means that in the microstructure of the transition zone between reacting phases the layer of the same chemical compound looks like the layers of two quite different chemical compounds. Its sublayers having a distinct common interface can differ by the shape, size or orientation of grains.

Using the results of the preceding section, it is easy to show that if only component A is diffusing, then the ratio, y_1/y_2 , of the thicknesses of these sublayers in the A_pB_q – B reaction couple is

$$\frac{y_1}{y_2} = \frac{1}{\beta - 1} = \frac{qr}{sp - qr}. \quad (4.43)$$

Note that although the mechanisms of formation of the A_rB_s layer by reactions (4.6) and (3.2₁) are different, the products of these reactions are hardly distinguishable in the microstructure because both reactions take place at the same interface A_pB_q – A_rB_s . Therefore, if the A_rB_s layer grows in the A_pB_q – A_rB_s – B system by means of diffusion of both components, then reaction (3.2₁) also contributes to the value of y_1 of the duplex structure (see Fig. 4.3), thereby causing an additional increase of the y_1/y_2 ratio compared to the case where only component A is diffusing.

Duplex structures often occur in metallic, oxide, salt and other binary and multi-component systems. W.J. Tomlinson and A. Easterlow [290] observed the duplex structure of the Co_3O_4 oxide layer in the CoO – Co_3O_4 – O_2 system, consisting of fine grains in the outer sublayer bordering the oxygen phase and coarse elongated grains in the inner sublayer

bordering CoO. At 700-800 °C, the thickness of the outer sublayer was 10.3 to 23.4% of the total thickness of the Co_3O_4 layer. The growth kinetics of this layer was found to be parabolic.

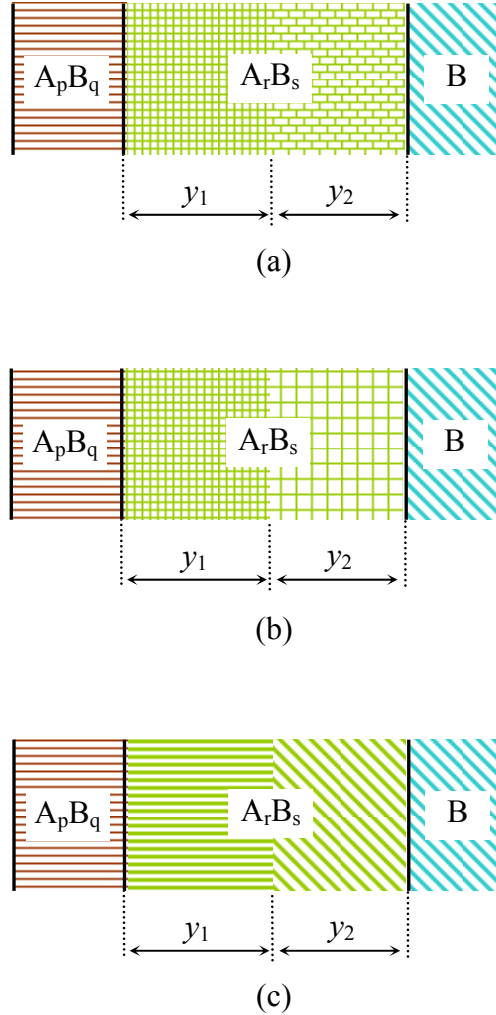
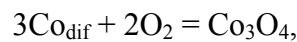
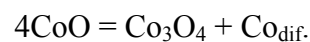


Fig. 4.10. Schematic representation of the duplex structure of the A_rB_s layer, in which its sublayers differ by (a) shape, (b) size or (c) crystallographic orientation of grains.

If only cobalt diffused, then an increase of the thickness of the Co_3O_4 layer at the Co_3O_4 – O_2 interface would be due to the partial chemical reaction



while that at the CoO – Co_3O_4 interface to the phase transformation of CoO into Co_3O_4 by the reaction



In the latter of these reactions, the number of CoO molecules formed per one diffusing Co atom is seen to be three times greater than in the former. Consequently, the ratio of the thicknesses of the outer and inner sublayers should be 1:3, *i.e.* the thickness of the outer sublayer must be equal to 25% of the total thickness of the Co₃O₄ layer. At 800 °C, this value is close to the experimental one (23.4%).

At other temperatures investigated, experimental values were much lower than the calculated value 25%. It means that the contribution of oxygen diffusion to the growth process of the Co₃O₄ layer through the reaction



was also considerable at those temperatures. This partial chemical reaction leads to additional thickening the Co₃O₄ layer at the CoO–Co₃O₄ interface, thereby affecting the ratio of sublayer thicknesses.

If only component *B* is diffusing in the *A_rB_s* layer, then in the *A–A_lB_n* reaction couple the ratio of the thickness of the sublayer bordering the *A_lB_n* phase to the thickness of the sublayer bordering the *A* phase is seen from equations (4.1) and (4.18) to be $ls/(rn-ls)$. Couples of this type are Fe–FeSn₂ [356] and Nb–Nb₆Sn₅ [357].

J.A. van Beek *et al.* [356] observed the duplex structure of the FeSn layer between Fe and FeSn₂. This layer consisted of two sublayers of equal thickness. The sublayer adjacent to iron consisted of fine-grained polyhedrons with approximately equal length of their sides. By contrast, the sublayer bordering the FeSn₂ phase consisted of elongated grains aligned at almost right angles to the FeSn–FeSn₂ interface.

The ratio of the thicknesses of the sublayers of the FeSn layer can readily be found immediately from the equations of chemical reactions



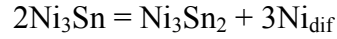
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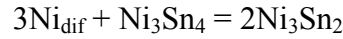
that occur in the Fe–FeSn–FeSn₂ system at the Fe–FeSn and FeSn–FeSn₂ interfaces, respectively. Since the same number (one at each) of the FeSn molecules is formed during these reactions at the interfaces of the FeSn layer, it is clear that the ratio of the thicknesses of the sublayers should be 1:1, provided that this layer grows entirely at the expense of diffusion of tin atoms.

W.L. Neijmeijer and B.H. Kolster [357] established the formation of the duplex structure of the Nb₃Sn layer between niobium and the Nb₆Sn₅ intermetallic compound. The sublayer adjacent to niobium had a fine-grained structure, while that bordering Nb₆Sn₅ had a coarse-grained one. The ratio of their thicknesses was found to be close to the theoretical value 2:3, resulting from the equations of chemical reactions under the assumption of dominant diffusion of tin atoms in the Nb₃Sn lattice ($r = 3, s = 1, l = 6, n = 5, ls/(rn-ls) = 2/3$).

Duplex structures are also formed in reaction couples of the type $A_pB_q-A_lB_n$. In the Ni–Sn binary system, such a structure is typical of the Ni_3Sn_2 layer occurring between the Ni_3Sn and Ni_3Sn_4 phases [356]. In the Ni_3Sn_2 lattice, the nickel atoms diffuse much faster than the tin atoms. Therefore, the Ni_3Sn_2 layer grows mainly by means of the reaction



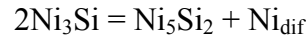
that takes place at the Ni_3Sn – Ni_3Sn_2 interface, and of the reaction



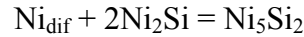
proceeding at the Ni_3Sn_2 – Ni_3Sn_4 interface.

The number of Ni_3Sn_2 molecules formed per unit time at the Ni_3Sn_2 – Ni_3Sn_4 interface is seen to be twice their number formed at the Ni_3Sn – Ni_3Sn_2 interface. Therefore, the ratio of the thicknesses of the sublayers in the duplex structure of the Ni_3Sn_2 layer must be 1:2. In this case, the shape of the grains was similar. However, their sizes were different. The sublayer adjacent to the Ni_3Sn_4 phase consisted of much larger grains than the sublayer bordering the Ni_3Sn phase [356].

Figure 4.11 shows the microstructure of the Ni_5Si_2 layer grown between the Ni_3Si and $\delta\text{-Ni}_2\text{Si}$ phases [307, 325]. The diffusion coefficient of nickel in the Ni_5Si_2 lattice is reported to be much higher than that of silicon [325]. Therefore, growth of the Ni_5Si_2 layer is due to the reactions



and



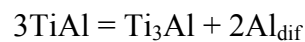
taking place at the Ni_3Si – Ni_5Si_2 and Ni_5Si_2 – Ni_2Si interfaces, respectively.

As seen in Fig. 4.11, the ratio of the thicknesses of the sublayers is about 1:1. The same value follows from the equations of chemical reactions because the numbers of Ni_5Si_2 molecules formed per unit time at the layer interfaces with the adjacent phases are equal.

It is now relevant to return to considering the formation of the Ti_3Al layer between Ti and TiAl (see Section 3.7.1 of Chapter 3). If only Ti were the diffusing species, then this layer would be homogeneous in appearance because its growth would be a result of the single reaction



In fact, however, it has a duplex structure, with the sublayer adjacent to titanium being about two times thicker than that adjacent to TiAl [68]. This means that the Ti_3Al layer grows mainly at the expense of diffusion of aluminium through the reactions



and



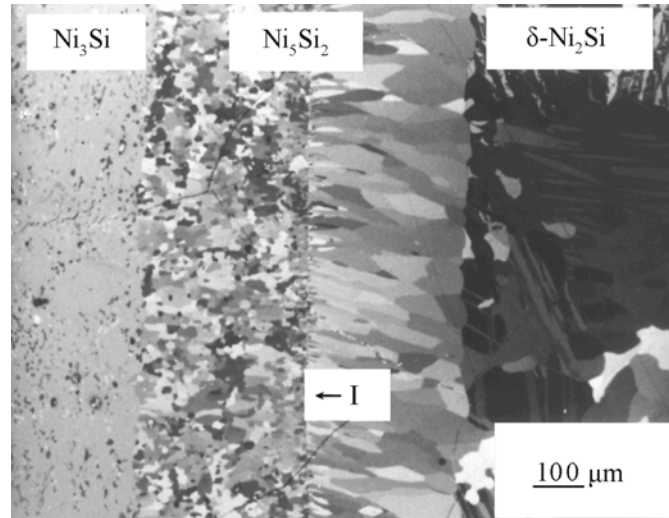


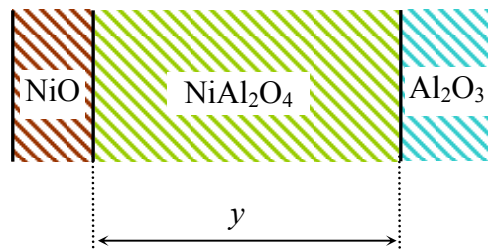
Fig. 4.11. Optical micrograph in the polarised light of the transition zone between Ni_3Si and $\delta\text{-Ni}_2\text{Si}$ phases [307, 325]. Diffusion couple was annealed at 900 °C for 176400 s (49 h). The Ni_5Si_2 layer formed has an easily distinguishable duplex structure. The thicknesses of its sublayers are almost equal. Their interface is denoted by I. Photograph kindly provided by Dr. J. Gülpen.

The former reaction yields one molecule of Ti_3Al at the Ti_3Al – TiAl interface and releases two aluminium atoms which then diffuse across the bulk of the Ti_3Al layer and enter into the latter reaction producing two molecules of Ti_3Al at the Ti – Ti_3Al interface.

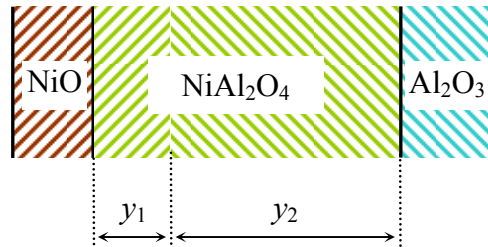
It is clear that in cases like this, there is even no need to do marker experiments to reveal the main diffusing species. Formation of duplex structures provides by itself evidence for the dominant diffusion of one of two components. If, in addition, the ratio of sublayer thicknesses coincides with a theoretically calculated value, then it can be concluded that the layer growth undoubtedly takes place exclusively at the expense of diffusion of that component.

Note that the duplex structure of the layer of a chemical compound, observed in the quasi-binary systems formed by the oxides or salts with a common ion, may be of somewhat different nature, frequently being simply a result of different crystallographic orientation of the grains of initial phases. A suitable example is the process of formation of the NiAl_2O_4 spinel between the NiO and Al_2O_3 oxide phases, studied in detail by D.W. Susnitzky *et al.* [358].

If the crystallographic orientations of the NiO and Al₂O₃ single crystals are identical, then the newly formed crystals of NiAl₂O₄ have the same orientation, and no duplex structure occurs, as shown schematically in Fig. 4.12a. If different, however, two sublayers of the same composition NiAl₂O₄ but of different crystallographic orientations of their crystals, readily distinguishable, for example by means of electron microscopy, are formed (Fig. 4.12b). The orientation of crystals of each sublayer is close to the orientation of crystals of the adjacent phase NiO or Al₂O₃.



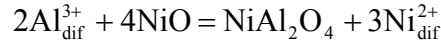
(a)



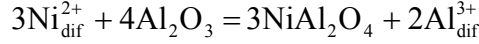
(b)

Fig. 4.12. Schematic representation of the growth process of the NiAl₂O₄ spinel layer between the oxides NiO and Al₂O₃. (a) All the phases have the same crystallographic orientation of their grains and therefore no duplex structure occurs. (b) The initial NiO and Al₂O₃ oxide phases have different crystallographic orientations of their grains. The NiAl₂O₄ layer assumes a duplex structure. Its sublayer adjacent to NiO retains the crystallographic orientation of this phase and is three times thinner than the sublayer bordering Al₂O₃, which retains the crystallographic orientation of the Al₂O₃ phase.

The ratio, $y_1 : y_2 = 1 : 3$, of the thicknesses of the sublayers follows immediately from the equations of chemical reactions



and



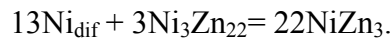
taking place at the NiO–NiAl₂O₄ and NiAl₂O₄–Al₂O₃ interfaces, respectively. Growth of the NiAl₂O₄ layer is thus due to the counter-diffusion of the aluminium and nickel ions, while its grains at different interfaces tend to retain the crystallographic orientation of the parent phase.

Let us now return to considering the physico-chemical processes taking place in the Ni–Zn diffusion couple (see Section 3.8) before and after its rupture. To understand their very essence, it suffices to analyse the simplified case where all the intermetallics NiZn, NiZn₃ and Ni₃Zn₂₂ are assumed to be the phases of constant composition.

At temperatures below the melting point of zinc, the NiZn phase is missing from the Ni–Zn diffusion couple, while the Ni₃Zn₂₂ layer grows at the expense of diffusion of the zinc atoms across its bulk and their subsequent chemical reaction with NiZn₃ (Fig. 4.13a)



Simultaneously, the NiZn₃ layer grows at the expense of diffusion of the nickel atoms across its bulk and their subsequent chemical reaction with Ni₃Zn₂₂



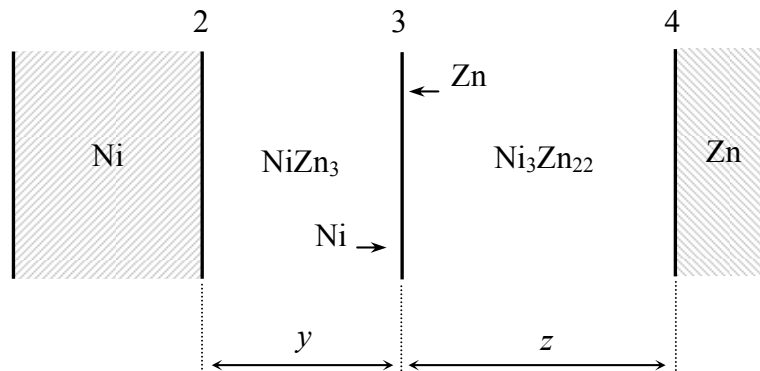
After separating the Zn phase from the main body of the Ni–Zn diffusion couple due to crack formation, the NiZn layer can readily grow in the Ni–Ni₃Zn₂₂ diffusion couple at the expense of diffusion of the nickel atoms across its bulk and their subsequent chemical reaction with NiZn₃ (Fig. 4.13b)



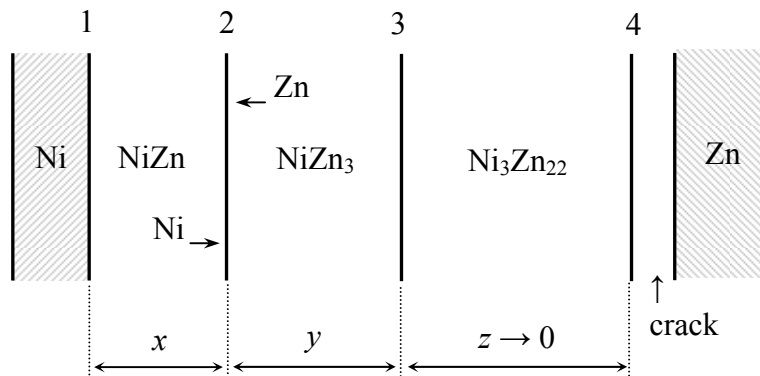
The NiZn₃ layer will clearly continue to grow but now already at the expense of (i) diffusion of the zinc atoms across its bulk and their subsequent chemical reaction with NiZn



and (ii) decomposition of $\text{Ni}_3\text{Zn}_{22}$



(a)



(b)

Fig. 4.13. Schematic diagram to illustrate the process of formation of intermetallic layers in the Ni–Zn diffusion couple (a) before and (b) after its rupture along interface 4.

With time, the $\text{Ni}_3\text{Zn}_{22}$ phase must entirely be consumed in the course of the latter reaction. However, if the experiment is interrupted before its full consumption, then the layers of all intermetallic compounds of the Ni–Zn binary system, stable at a given temperature, will be available at the interface between nickel and zinc. Moreover, metallographic examination of the cross-section surface after repeated anneals in the as-received condition may even reveal a greater number of distinguishable layers in the Ni–Zn transition zone than the number of those compounds on the Ni–Zn phase diagram because some of the layers will have duplex structures.

This applies, for example, to the NiZn_3 layer which is formed by two different partial chemical reactions. In total, the number of visible layers at 250–400 °C amounts to six [339]. Perhaps, cracks may also occur between the intermetallic layers, thereby producing a very complicated microstructure of the transition zone, not so easy to interpret unambiguously.

4.6: Growth kinetics of the same chemical compound layer in various reaction couples: short conclusions

1. The growth rate of the layer of any chemical compound in reaction couples consisting of one of elementary substances *A* or *B* and another compound of a multiphase binary system or of two other compounds, is higher than the rate of its growth between pure components, provided that this layer is the only one in all reaction couples under comparison.

2. The closer the chemical compositions of the initial phases of a given reaction couple, the greater is the layer-growth rate compared to that in the *A–B* reaction couple.

3. The ratio of the rates of diffusional (parabolic) growth of the same compound layer in different reaction couples can be predicted exactly knowing only the stoichiometry of all compounds of a multiphase binary system. In this case, the Wagner and physico-chemical approaches yield identical results which are in good agreement with available experimental data.

4. The physico-chemical approach allows also certain predictions regarding the layer-growth rate in the linear region to be made, whereas in the framework of the Wagner approach the linear growth cannot be explained, even qualitatively.

5. If diffusion of one of the two components prevails in the growing layer of a chemical compound, then in the reaction couples consisting of one of other compounds of a multiphase system and the non-diffusing component or of two other compounds this layer may be expected to have a duplex structure. Its sublayers will differ by the shape, size or orientation of their grains.

6. Due to the crack occurrence between interacting phases and because of the duplex structure of some compound layers, the number of distinguishable layers in the $A-B$ transition zone may happen to exceed the number of stable compounds on an appropriate equilibrium phase diagram of the $A-B$ binary system.

5: Reaction-diffusion kinetics in solid-liquid and solid-gas systems

The melting points of the components of a reaction couple are most frequently different. Therefore, there is a certain range of temperature in which one of the components is in the solid state, while the other in the liquid state. If soluble, the solid substance will dissolve in the liquid phase. The dissolution process should clearly affect the growth kinetics of a chemical compound layer at the solid-liquid interface.

If a solid interacts with a gas, the reaction product may happen to be appreciably volatile at a given temperature. Then, the rate of its evaporation must also be taken into account in kinetic equations.

The effect of dissolution in the solid-liquid system and of evaporation in the solid-gas system on the growth rate of a chemical compound layer will be established in this chapter. Substance A will be assumed to have a higher melting point than substance B . As before, substance B is considered to be insoluble in phase A .

5.1: Main relationships governing dissolution of solids in liquids

Let us briefly consider the main features of the process of dissolution of a solid substance in a liquid. Assume that the interaction of substances A and B takes place at temperature T_2 (see Fig. 1.1). The solubility of component A in liquid B at this temperature is c_s , kg m^{-3} or mol m^{-3} . If the instantaneous concentration, c , of A in B is below this value, then solid A will dissolve in liquid B .

Consider first the case where the chemical compound A_pB_q is not formed between initial substances A and B during dissolution. The rate of dissolution of any solid in the well-agitated liquid phase is described by an equation of the form

$$\frac{dc}{dt} = k \frac{S}{v} (c_s - c) \quad (5.1)$$

where c is the concentration of the dissolved substance in the bulk of the liquid phase at time t , c_s is the saturation concentration (solubility) of A in B at a given temperature, k is the dissolution-rate constant, S is the surface area of the solid in contact with the liquid, and v is the volume of the liquid.

Equation of this type was first proposed by A. Shchukarev in 1896 [359]. A year later, A.A. Noyes and W.R. Whitney have derived a similar equation [360]. Its validity was then verified experimentally by L. Bruner and St. Tolloczko [361] and E. Brunner [362].

According to W. Nernst [363], the dissolution-rate constant can be expressed as follows

$$k = \frac{D_A}{\delta} \quad (5.2)$$

where D_A is the coefficient of diffusion of the atoms of the dissolving substance A across the diffusion boundary layer adjacent to the surface of the solid into the liquid phase, and δ is the thickness of the diffusion boundary layer.

Note that equation (5.1) follows immediately from Fick's laws on the assumption of a quasi-stationary distribution of the concentration of components within the diffusion boundary layer. Indeed, if in this layer $\partial c_A / \partial t \approx 0$, then the second Fick law yields $\partial c_A / \partial x \approx \text{const}$. It means that the distribution of the concentration of component A within the diffusion boundary layer is close to linear (Fig. 5.1).

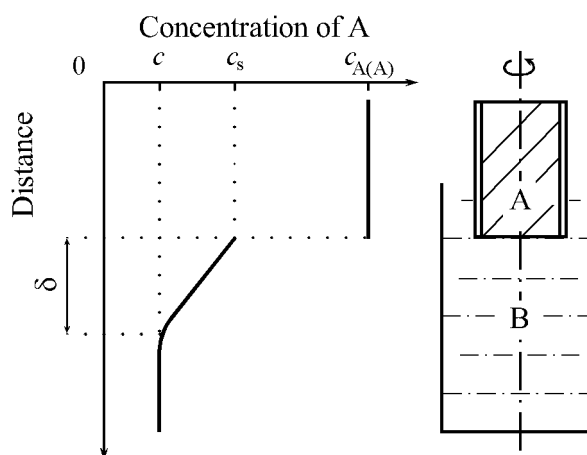


Fig. 5.1. Schematic diagram to illustrate the process of dissolution of a solid A in a liquid B in the case where no chemical compound layer is formed at their interface. Not to scale; in fact, the thickness, δ , of the diffusion boundary layer is very small in comparison with the height of the column of the liquid phase.

Anywhere outside, the concentration of A is assumed to be the same and equal to an instantaneous value, c . Clearly, this implies sufficiently intensive agitation of the liquid. In

such a case, the flow of A atoms across the diffusion boundary layer under the condition of constancy of the surface area of the dissolving solid is

$$j_A = -D_A \left(\frac{\partial c_A}{\partial x} \right)_s = -D_A \frac{c_s - c}{\delta}. \quad (5.3)$$

In terms of the concentration of substance A in the bulk of liquid B the flow, j_A , can be written as follows

$$j_A = \frac{v}{S} \frac{dc}{dt}. \quad (5.4)$$

Equation (5.1) is then obtained by combining equations (5.2)-(5.4).

Clearly, this derivation of equation (5.1) is valid only in the case of the diffusional regime of dissolution of substance A in liquid B when the overall rate of the process is limited by the rate of transition of the A atoms across the diffusion boundary layer. However, the equation itself is also applicable in the case of another, interface (decomposition) controlled regime of dissolution when the rate-determining step is the rate of separation of the A atoms from the solid surface due to their interaction with the B atoms at the solid-liquid interface.

Indeed, it appears obvious that a variation of the concentration of any dissolving solid substance in a liquid is directly proportional to both the area of its surface contacting with the liquid and the difference between the saturation concentration (solubility) at a given temperature and the instantaneous concentration of A in B , and is inversely proportional to the volume of the liquid phase. Therefore, the general form of equation (5.1) remains unchanged for either dissolution regime of any solid in any liquid. The difference lies in the character of the dependence of the dissolution-rate constant, k , upon the thickness, δ , of the diffusion boundary layer [364-368].

It is clear that under conditions of interfacial (decomposition) control the rate of dissolution of a solid in a liquid is independent of the thickness of the diffusion boundary layer and hence of the intensity of agitation of the liquid. By contrast, in the case of diffusional control the intensity of agitation of a liquid has a strong effect on the thickness of the diffusion boundary layer, thus influencing the value of the dissolution-rate constant, k .

Most frequently, the process of dissolution of solid substances in liquids is investigated using the rotating disc technique [364-374]. The main advantage of this method is an equal accessibility of the rotating disc surface, *i.e.* the dissolution of its surface (or the deposition of any reaction product on it) takes place uniformly [364].

According to V.G. Levich [364] (see also Refs [365, 367, 369]), the thickness of the diffusion boundary layer at the rotating disc surface is expressed by the equation

$$\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \quad (5.5)$$

where ν is the kinematic viscosity of the liquid phase, $\text{m}^2 \text{s}^{-1}$, ω is the angular speed of the disc rotation, rad s^{-1} . For simplicity, the subscript A at D_A was omitted.

From equations (5.2) and (5.5), it follows

$$k = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (5.6)$$

This equation allows the determination of the diffusion coefficient, D , of the atoms of the dissolving substance across the diffusion boundary layer, knowing the value of the dissolution-rate constant, k , and *vice versa*. It is essential to note, however, that equation (5.6) only holds for Schmidt's numbers, Sc , exceeding 1000.

The Schmidt number is a dimensionless parameter equal to the quotient of dividing the kinematic viscosity by the diffusion coefficient: $Sc = \nu/D$ (for more detail, see Refs [364, 365, 367]). Usually, for liquids Sc is less than 1000. In such a case, more accurate calculations can be carried out using the equation

$$k = 0.554 I^{-1} D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (5.7)$$

in which the factor I is a (slight) function of the Schmidt number: $I = f(Sc)$. The dependence of I upon Sc is provided in Table 5.1 [365, 371].

Equation (5.7) was proposed by T.F. Kassner [371]. It is valid for $Sc > 4$. In the range $10 < Sc < 10^3$ typical of liquid metals the difference in the results of calculations with the use of equations (5.6) and (5.7) varies from 3-17% [365].

In many cases, the solid disc indeed dissolves in a liquid uniformly over the entire surface, as in Fig. 5.2a [374]. Sometimes, however, spiral etch patterns reproducing the lines of laminar flow of the liquid [364, 365, 369] are seen on the disc surface after its dissolution in the liquid phase. An example is shown in Fig. 5.2b [374]. It takes place when the velocity of movement of the solid-liquid interface relative to its initial position exceeds a certain limiting value.

Table 5.1. Dependence of the correction factor, I , of the Kassner equation upon the Schmidt number, Sc [365, 371]

Sc^{-1}	I	Sc^{-1}	I	Sc^{-1}	I
0.001	0.9209	0.010	0.9564	0.100	1.0368
0.002	0.9286	0.020	0.9747	0.110	1.0412
0.003	0.9341	0.030	0.9877	0.120	1.0451
0.004	0.9385	0.040	0.9981	0.130	1.0488
0.005	0.9424	0.050	1.0068	0.140	1.0521
0.006	0.9457	0.060	1.0143	0.150	1.0552
0.007	0.9487	0.070	1.0209	0.160	1.0580
0.008	0.9515	0.080	1.0268	0.180	1.0631
0.009	0.9541	0.090	1.0321	0.200	1.0675

It is clear that the occurrence of visible etch patterns provides evidence for the violation of the condition of an equal accessibility of the rotating disc surface. Therefore, when investigating the dissolution process, the diameter of a disc is to be chosen in such a way as to ensure that, for the pre-determined volume of a liquid, the depth of dissolution of the disc should not exceed a critical value for that particular system.

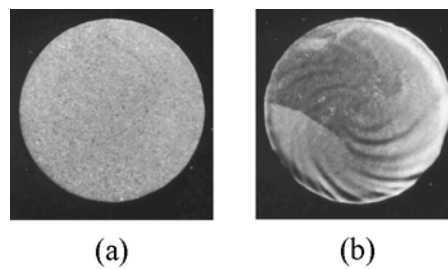


Fig. 5.2. (a) Niobium and (b) molybdenum discs (12 mm diameter) after their dissolution in liquid aluminum at 700 °C and an angular speed of the disc rotation of 25.0 rad s⁻¹. Dissolution time is 7200 s, while St/ν is 19440 s m⁻¹ [374].

Diameter values between 1 and 2 cm are practicable. With smaller discs, edge effects become significant [364, 365]. Greater discs are unsuitable from the point of view of experimental set-up.

The volume of the liquid phase usually varies between 10 and 50 cm³. The diameter of the column of the liquid phase is 2 to 3 times greater than that of the disc. The distance between the disc surface and the bottom of the liquid-phase column is on the order of the disc diameter or a little greater. The depth of immersion of the disc into the liquid is around half the disc diameter. Typical rotational speeds, ω , lie in the range 5-100 rad s⁻¹.

Note that both a small disc in the large volume of a liquid and a large disc in the small volume of a liquid will hardly produce reliable data on the dissolution kinetics of the solid in the liquid. In the former case, the small disc will not ensure sufficient convective agitation of the liquid phase. In the latter, the turbulence threshold may happen to be exceeded.

Turbulence is known to occur at Reynolds numbers in excess of 10⁵. Reynolds number, $Re = \omega r^2/\nu$, r being the disc radius, is a dimensionless parameter characterising the hydrodynamic regime of flow of liquids [364, 365]. Reproducible results are readily obtained if the flow is laminar.

It should be emphasised that the simplest way of avoiding the formation of deep etch patterns, namely, by reducing the time of the solid-with-liquid interaction, does not appear to be the best because it only masks the phenomenon, not eliminating its cause. Therefore, it appears to be much more reasonable to increase the disc diameter and to reduce the volume of the liquid phase (within acceptable limits and taking account of other restrictions [22, 364, 365, 370]), so that during dissolution from the zero up to saturation concentration (solubility) of A in B no etch patterns will occur onto the disc surface.

Integration of equation (5.1) with the initial condition $c = 0$ at $t = 0$ yields

$$c = c_s \left[1 - \exp\left(-\frac{kSt}{\nu}\right) \right] \quad (5.8)$$

or in another form

$$\ln \frac{c_s}{c_s - c} = k \frac{St}{\nu}. \quad (5.9)$$

If the initial concentration of the dissolving substance in the liquid is equal to c_0 , then

$$\ln \frac{c_s - c_0}{c_s - c} = k \frac{St}{\nu}. \quad (5.10)$$

Equations (5.1), (5.8)-(5.10) indicate that the process of dissolution of a solid in a liquid is characterised by two quantities, namely, the saturation concentration or solubility, c_s , and the dissolution-rate constant, k . At constant pressure, the former only depends upon temperature. The latter is in addition dependent upon the hydrodynamic conditions of flow of the liquid. Experimental determination of these quantities will be considered in detail in next sections.

5.2: Experimental investigation of the dissolution process of a solid in a liquid

The process of dissolution of a solid in a liquid can readily be investigated using a rapid-quenching device like that shown in Fig. 5.3. Depending on the nature of substances to be studied, this may be carried out either in vacuum, or in a protective atmosphere (inert gases, hydrogen, nitrogen, *etc.*), or under a flux [221, 368, 374].

To heat the materials under investigation to the required temperature and to maintain it, the electric-resistance furnace 1 is employed. The specimen 2 of a solid substance is connected, by means of the protective tube 3, with the shaft 5, being rotated by the electric motor 4. The shaft is free to move in the vertical direction and can be fixed in the required position by the stopper 6. The temperature is measured with the help of the thermocouple 7. The flux 8 is used both to pre-heat the solid specimen to the experimental temperature and to protect the liquid 9 from oxidation by atmospheric air.

Consider the main features of the process of dissolution of some transition metals in liquid aluminium as an typical example [195, 368, 369-373]. Cylindrical specimens of a transition metal, 11.28 ± 0.01 mm in diameter and 5-6 mm high, were machined from 12-13 mm diameter rods prepared by arc melting the metal under investigation. The disc surface was then ground flat and polished mechanically.

Immediately before the experiment, the solid specimen was rinsed with ethanol and dried. Then, it was pressed into a high-purity graphite tube, 16 mm diameter, to protect its lateral surface from contact with the metallic melt. Therefore, only the disc surface, 1 cm^2 area, dissolved in liquid aluminium during the run. If a larger surface area was desirable (for example, when determining the solubility values), while its instantaneous value was unimportant, the specimens with unprotected lateral surfaces were used. In such cases, graphite tubes served only as holders for transition-metal specimens.

A special flux consisting of the halides of alkali metals with the addition of sodium and aluminium fluorides was employed both to protect the aluminium melt from oxidation and to pre-heat the solid specimen to the required temperature. First, the flux was melted in a 26 mm inner diameter alumina crucible. Melting started at about 350°C . The height of the flux column was around 15 mm. Aluminium pieces were then melted under the flux layer. The amount of aluminium taken was equivalent to a volume of the liquid metal of 10 cm^3 . At $700\text{-}900^\circ\text{C}$, it is approximately 24 g.

For pre-heating, the disc specimen rotating at a low angular speed ($6.45.0 \text{ rad s}^{-1}$ or less) was lowered into the flux bulk, so that the distance between its surface and the top surface of the liquid-aluminium column was around 10 mm. When the temperature had equilibrated (typically after 500 s), the specimen rotating at the required speed was lowered into the bulk of molten aluminium, so that the distance from the disc surface to the bottom of the crucible was $15.0 \pm 0.5 \text{ mm}$. This was the start of the run. The rotating disc was held in the melt for a pre-determined period of time. The run was then completed in one of two following ways.

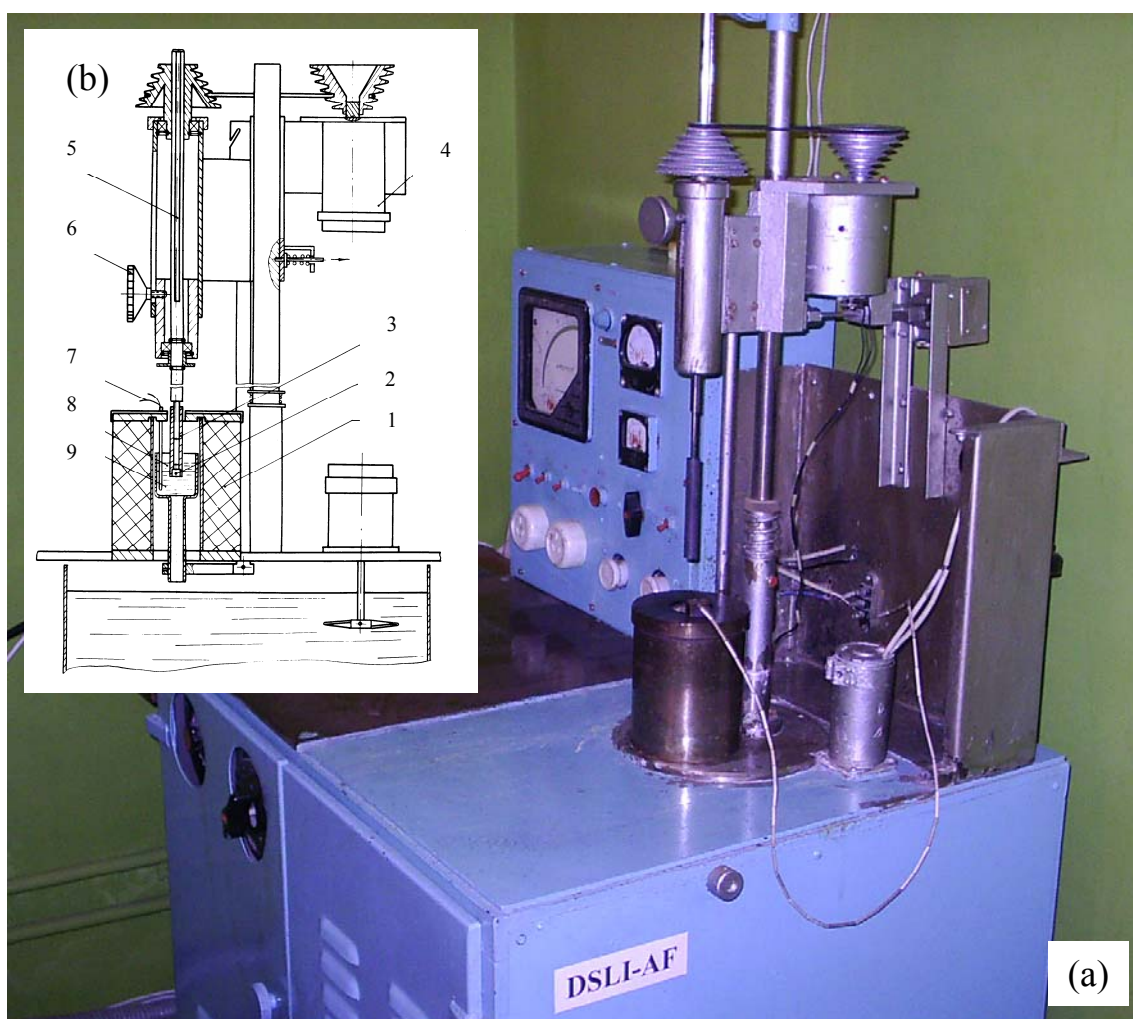


Fig. 5.3. (a) General view and (b) schematic diagram of the rapid-quenching device for investigating the process of dissolution of a solid in a liquid by the rotating disc technique [374]. Temperature up to $850 \text{ }^{\circ}\text{C}$; rotational speeds 6.45, 9.00, 15.3, 24.0, 32.7, 54.0 and 82.4 rad s^{-1} . 1, electric-resistance furnace; 2, solid specimen; 3, protective tube; 4, electric motor; 5, rotating shaft; 6, stopper; 7, thermocouple; 8, flux; 9, liquid.

1. When studying the dissolution process, the solid transition-metal specimen was lifted from the aluminium melt into the middle of the flux column, and then the crucible, together with the melt, the flux and the specimen, was rapidly cooled down in a water bath located below the electric furnace. After cooling down to room temperature, the major portion of the aluminium alloy adhering to the surface of the transition-metal specimen was removed mechanically. The remainder was dissolved in a 20% aqueous solution of NaOH at a slow heating. The specimen, free of both aluminium and intermetallic layers, was then washed with water and alcohol, dried and weighed. Because the specimen had also been weighed before the run, its mass loss during dissolution in liquid aluminium could readily be determined.

Samples of the aluminium alloys obtained were analysed chemically to determine their transition-metal contents. Use was usually made of photometric methods. The results were then compared with those found from mass loss measurements.

2. When studying the growth kinetics of intermetallic layers, after the run the crucible, together with the flux, the melt and the solid specimen, was “shot” into cold water to arrest the reactions at the transition metal-aluminium interface. Note that the solid specimen continued to rotate until melt solidified. It is especially essential in examining the formation of the intermetallic layers under conditions of their simultaneous dissolution in the liquid phase (with undersaturated aluminium melts). The time of cooling the experimental cell from the experimental temperature down to room temperature did not exceed 2 s.

After cooling, the bimetallic specimen obtained was cut along the cylindrical axis, ground flat and polished electrolytically [139]. The cross-sections prepared were examined by metallography, X-ray diffraction techniques and electron probe microanalysis. Microhardness measurements in the transition zone between initial phases were also carried out.

5.2.1: Determination of the saturation concentration

The saturation concentration is equal to the solubility of a solid in a liquid at a given temperature. Therefore, its value can in principle be extracted from the liquidus curve of the equilibrium phase diagram of the $A-B$ binary system (see Fig. 1.1).

However, in the great majority of cases the accuracy of determining the position of this curve on the phase diagrams is too far from being satisfactory. The data obtained by various authors may differ very considerably, especially in the case of low solubility values ($< 1\%$). Meanwhile, to obtain reasonable results in calculating the dissolution parameters from equations (5.1) and (5.8)-(5.10), the solubility (saturation concentration) should be known with a relative error not exceeding 5 %. For this reason, it is advisable to begin studying the dissolution process with its experimental determination by saturating a liquid with a solid using, for example, the same rotating disc technique.

Figure 5.4 shows a plot of the tungsten concentration in the aluminium melt against St/ν (often called the reduced dissolution time, even though it is measured in s m^{-1}) at 700-850 °C. It is seen that at a constant temperature the tungsten content in aluminium gradually increases up to some limiting value and then remains unchanged. This is just the quantity c_s entering into equations (5.1) and (5.8)-(5.10). The solubility values of some transition metals in liquid aluminium are presented in Table 5.2 [368].

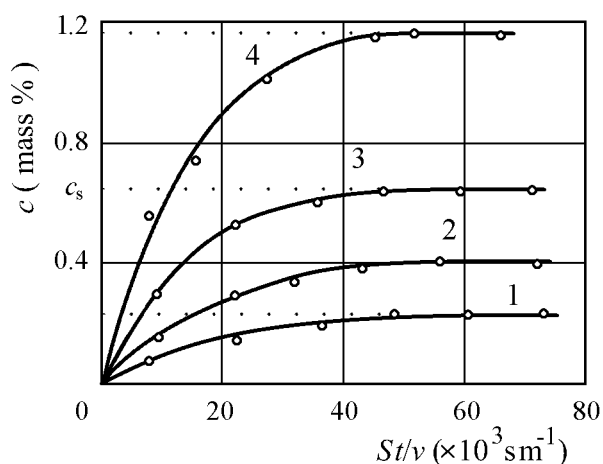


Fig. 5.4. Concentration of tungsten in liquid aluminium plotted against St/ν to determine its solubility (saturation concentration) [368]. Angular speed of disc rotation, $\omega = 25.0 \text{ rad s}^{-1}$. Temperature: 1, 700 °C; 2, 750; 3, 800; 4, 850.

Table 5.2. Solubility values (%) of transition metals in liquid aluminium [368]

Metal	700 °C	750°C	800°C	850 °C	900°C
Ti	0.214	0.33	0.51	0.73	1.06
V	0.28	0.46	0.73	0.96	1.4
Cr	0.72	1.29	2.5	4.1	6.7
Fe	2.5	3.4	5.3	7.9	9.9
Co	1.6	2.4	4.2	6.9	11.3
Ni	10.0	13.5	19.5	27.0	31.0
Zr	0.156	0.276	0.46	0.66	1.11
Nb	0.0197	0.0337	0.057	0.101	-
Mo	0.215	0.44	0.71	1.14	-
Ta	0.105	0.17	0.25	0.37	-
W	0.23	0.40	0.84	1.16	-
Re	0.24	0.61	1.21	1.8	2.8

The solubility of various metals is seen to differ considerably. For example, at 700 °C the solubility of nickel in the aluminium melt is 10 %, while that of niobium is only about 0.02 %. For other transition metals, appropriate values are more closer, although iron and cobalt also stand apart in this respect. To reveal the causes of such differences, detailed investigations of the structure of liquid alloys are badly needed.

If a binary or multicomponent alloy is undergoing the liquid-metal attack, then its dissolution can be either selective or non-selective. In the former case, the more soluble component dissolves at a higher rate. Hence, the solid phase becomes depleted, while the liquid enriched in this component. In the latter case, the ratio of the alloy components in both phases remains unchanged during dissolution.

On the one hand, selective dissolution of transition-metal alloys in liquid aluminium might be expected in view of considerable differences in their solubility in respective binary systems. On the other, however, in these alloys the atoms of different elements are connected together by metallic bonds of nearly equal strength. Any of the elements can therefore scarcely be expected to leave the alloy lattice at a rate that significantly exceeds the rates of transition of other elements into liquid aluminium.

Iron-nickel alloys are known to dissolve in the aluminium melts non-selectively [375-377]. As seen from Table 5.3, during dissolution of a 50 % Fe–50 % Ni alloy the ratio, $c_{\text{Fe}} : c_{\text{Ni}}$, of iron to nickel concentrations in the melt is 1.00 ± 0.05 , *i.e.* it is equal to that in the initial solid material. The same applies to other Fe–Ni alloys over the whole range of compositions. Appropriate saturation concentrations are presented in Table 5.4.

The data obtained display a strong mutual influence of the elements on their solubility in liquid aluminium because in its absence at constant temperature the solubility diagram would be like that shown by the dotted lines in Fig. 5.5, with the eutonic point, E, at 2.5 % Fe and 10.0 % Ni. The effect of iron on the nickel solubility is seen to be more profound than that of nickel on the iron solubility.

Dependence of the total concentration, $c_{\text{total}} = c_{\text{Fe}} + c_{\text{Ni}}$, of iron and nickel from Fe–Ni alloys in the saturated aluminium melt at 700 °C upon the iron content, C_{Fe} , of the initial Fe–Ni alloy can formally be described by two straight-line equations [375]

$$c_{\text{total}} = 7.51 - 0.054C_{\text{Fe}} \quad \text{at } 90 \% < C_{\text{Fe}} < 28 \%$$

and

$$c_{\text{total}} = 11.0 - 0.19C_{\text{Fe}} \quad \text{at } 28 \% < C_{\text{Fe}} < 5 \%$$

obtained by the least-squares-fit method. The correlation factor is 0.992 for the first line and 0.995 for the second. These equations can readily be used to find the saturation concentrations of iron and nickel from any commercial Fe–Ni alloy of known composition in liquid aluminium.

Dissolution of iron-chromium alloys in molten aluminium bears a similar character, at least at chromium contents up to 25 %. The ratio, $c_{\text{Fe}} : c_{\text{Cr}}$, of iron to chromium

concentrations in the melts corresponds to that in initial alloys (Table 5.5). At 700 °C, the solubility values (saturation concentrations) are 2.5 ± 0.2 % Fe and 0.28 ± 0.03 % Cr for a 90 % Fe–10 % Cr alloy and 2.2 ± 0.2 % Fe and 0.72 ± 0.06 % Cr for a 75 % Fe–25 % Cr alloy.

Table 5.3. Concentrations of iron and nickel undergoing dissolution from a 50 % Fe–50 % Ni alloy into liquid aluminium [375]. Temperature 700 °C, rotational speed $\omega = 24.0 \text{ rad s}^{-1}$, $S/\nu = 10 \text{ m}^{-1}$

Time (s)	Concentration of elements in aluminium (%)				$c_{\text{Fe}} : c_{\text{Ni}}^{\text{a}}$ in aluminium
	Fe		Ni		
	ML ^b	CA ^c	ML ^b	CA ^c	
300	0.41	0.40	0.41	0.39	1.03
600	0.69	0.67	0.69	0.70	0.96
1500	1.28	1.23	1.28	1.17	1.05
4500	2.07	1.9	2.07	2.1	0.90
8100	2.28	2.4	2.28	2.2	1.09
11700	2.43	2.4	2.43	2.3	1.04
13500	2.54	2.4	2.54	2.4	1.00
15000	2.50	2.4	2.50	2.5	0.96

^a Calculated using the results of chemical analysis of Al–Fe–Ni alloys.

^b Calculated from mass loss measurements.

^c Found by chemical analysis of Al–Fe–Ni alloys after the runs.

As seen from Fig.5.6 and Table 5.6, even such a complicated material as an 18Cr-10Ni stainless steel (70.0 % Fe, 18.0 % Cr, 10.5 % Ni) also dissolves in aluminium non-selectively [221]. During dissolution, the ratio of the elements in the melt is practically equal to that in the steel. Appropriate values of saturation concentrations of its main constituents in liquid aluminium are presented in Table 5.7.

Note that the attainment of saturation concentrations does not necessarily mean that the equilibrium has established because the reaction of formation of intermetallic or other compounds continues to proceed at the solid-liquid interface. However, the solubility values found coincide with equilibrium ones which are obtained as an intersection of the lines of constant ratio of dissolving elements, for example Fe and Ni, drawn from the corner of the solvent (Al), with an appropriate isotherm on the liquidus surface of the isothermal section of the ternary phase diagram.

Table 5.4. Values of solubility (saturation concentration) of iron and nickel from Fe–Ni alloys in liquid aluminium at 700 °C [375]

Content of Fe in alloy (%)	Solubility (%)		$c_{\text{Fe}} + c_{\text{Ni}}$ in saturated aluminium
	Fe	Ni	
100	2.5±0.1	-	2.5
90	2.5±0.2	0.28±0.02	2.78
80	2.5±0.2	0.63±0.05	3.13
75	2.5±0.2	0.86±0.07	3.36
65	2.5±0.2	1.35±0.08	3.85
60	2.5±0.2	1.67±0.09	4.17
50	2.5±0.2	2.5±0.2	5.0
40	2.2±0.1	3.3±0.1	5.5
30	1.76±0.07	4.0±0.2	5.76
25	1.61±0.05	4.8±0.3	6.41
20	1.44±0.09	5.8±0.4	7.24
15	1.25±0.04	7.1±0.5	8.35
10	0.90±0.04	8.1±0.3	9.0
5	0.51±0.03	9.8±0.2	10.3
0	-	10.0±0.5	10.0

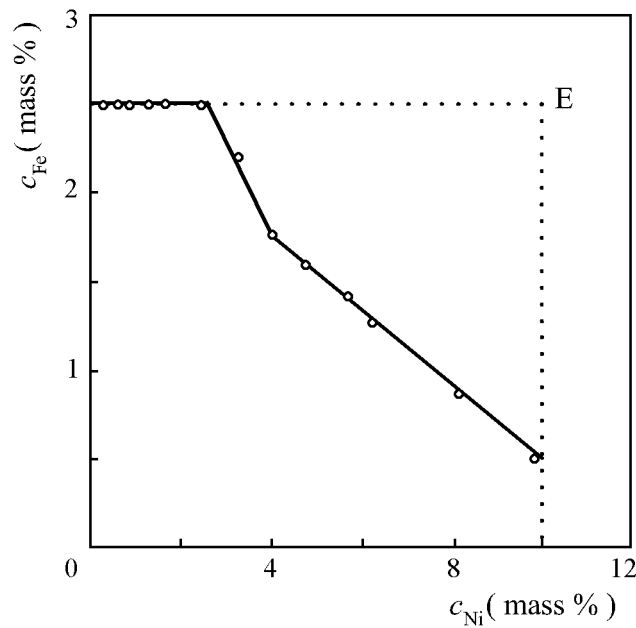


Fig. 5.5. Solubility diagram of iron and nickel from Fe–Ni alloys in liquid aluminium at 700 °C [375].

Table 5.5. Concentrations of iron and chromium undergoing dissolution from Fe–Cr alloys into liquid aluminium. Temperature 700 °C; rotational speed $\omega = 54.0 \text{ rad s}^{-1}$; $S/\nu = 27.5 \text{ m}^{-1}$

Content of Fe in alloy (%)	Time (s)	Concentration of elements in aluminium (%)				$c_{\text{Fe}} : c_{\text{Cr}}^{\text{a}}$ in aluminium
		Fe		Cr		
		ML ^b	CA ^c	ML ^b	CA ^c	
90	3600	2.48	2.51	0.27	0.28	8.96
	3700	2.49	2.45	0.28	0.27	9.07
	4500	2.31	2.50	0.26	0.29	8.62
75	3600	2.35	2.25	0.78	0.72	3.12
	3700	2.10	2.13	0.70	0.65	3.27
	4500	2.20	2.09	0.74	0.72	2.90

a Calculated using the results of chemical analysis of Al–Fe–Cr alloys.

b Calculated from mass loss measurements.

c Found by chemical analysis of Al–Fe–Cr alloys after the runs.

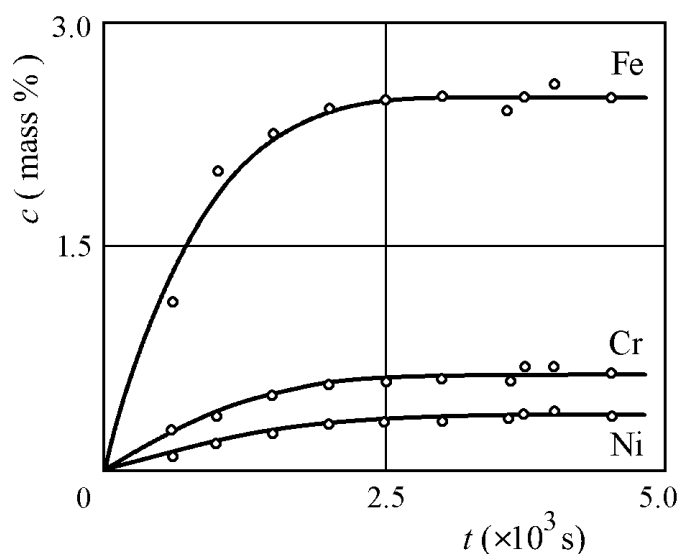


Fig. 5.6. Concentration-time plots for iron, chromium and nickel undergoing dissolution from an 18Cr–10Ni stainless steel into liquid aluminium at 700 °C ($\omega = 54.0 \text{ rad s}^{-1}$) [221].

Table 5.6. Results of determination of saturation concentrations of iron, chromium and nickel from an 18Cr–10Ni stainless steel in liquid aluminium at 700 and 850 °C [221]

Temperature (°C)	Angular speed of rotation (rad s ⁻¹)	Time (s)	Concentration of elements in aluminium (%)					
			Fe		Cr		Ni	
			ML ^a	CA ^b	ML ^a	CA ^b	ML ^a	CA ^b
700	32.7	4000	2.5	2.5	0.63	0.59	0.37	0.33
	32.7	4500	2.5	2.5	0.63	0.61	0.37	0.33
	54.0	3600	2.4	2.2	0.61	0.58	0.36	0.48
	54.0	3700	2.5	2.3	0.63	0.63	0.37	0.32
	54.0	4000	2.6	2.4	0.67	0.66	0.39	0.45
	54.0	4500	2.4	2.5	0.61	0.60	0.36	0.48
850	54.0	2500	7.1	7.8	1.8	1.4	1.07	1.2
	54.0	3700	7.4	7.1	1.9	1.4	1.11	1.05
	54.0	4500	7.2	7.4	1.9	1.6	1.8	1.1

^a Calculated from mass loss measurements.

^b Found by chemical analysis of aluminium alloys after the runs.

Table 5.7. Saturation concentrations of iron, chromium and nickel undergoing dissolution from an 18Cr–10Ni stainless steel into liquid aluminium at 700-850 °C [221]

Temperature (°C)	Saturation concentrations of elements in aluminium (%)		
	Fe	Cr	Ni
700	2.5±0.2	0.64±0.03	0.37±0.02
725	3.0±0.2	0.78±0.03	0.45±0.02
750	3.4±0.2	0.88±0.04	0.52±0.03
800	5.0±0.2	1.3±0.1	0.76±0.05
850	7.2±0.3	1.9±0.1	1.10±0.06

5.2.2: Evaluation of the dissolution-rate constant

To determine accurate values of the dissolution-rate constant, thorough investigations of initial portions of the $c - St/v$ curves like those shown in Figs 5.4 and 5.6 are to be carried out. Figure 5.7 shows the experimental data for tungsten single crystals of different orientation as an example.

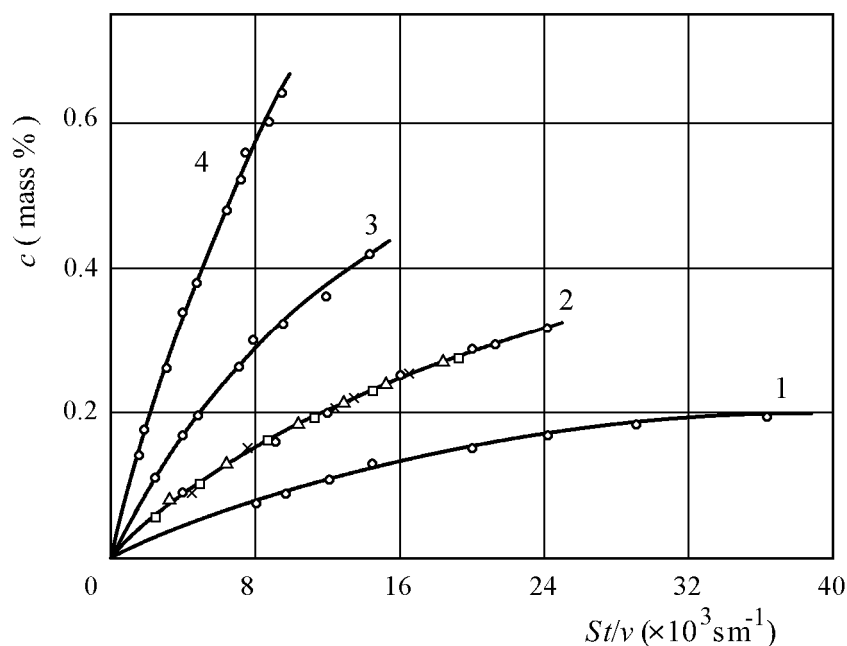


Fig. 5.7. Tungsten concentration in liquid aluminium plotted against St/v at $\omega = 25.0 \text{ rad s}^{-1}$. Temperature: 1, 700 °C; 2, 750; 3, 800; 4, 850. Crystallographic orientation of single crystals: $\square$, (001); $\times$, (101); $\circ$, (111); Δ , (112) [374].

Clearly, under conditions of diffusion control the rate of dissolution expressed in terms of the concentration of dissolving elements in the melt does not depend upon the atomic packing density of the crystallographic faces of any substance under investigation. Therefore, dissolution of single crystals of different orientation (line 2 in Fig. 5.7) is characterised by the same value of the dissolution-rate constant found from equation (5.9) or (5.10). Note, however, that if the dissolution process is followed by measuring the decrease in the disc height, then the faces of looser package will have a higher decrease compared to those of denser package.

Strictly speaking, when using equations (5.1) and (5.8)-(5.10), both the instantaneous and the saturation concentration (solubility) should be expressed in kilograms or moles per cubic metre. However, in this particular case the content of tungsten in aluminium is relatively

small (on the order of 1 % or less). Therefore, it can be expressed in any units because a directly proportional relationship is retained between them with sufficient accuracy.

From equations (5.9) and (5.10), it follows that the experimental points plotted in the coordinates

$$\ln \frac{c_s}{c_s - c} - \frac{St}{v} \text{ or } \ln \frac{c_s - c_0}{c_s - c} - \frac{St}{v},$$

if the initial concentration is $c_0 \neq 0$, should produce a straight line of the slope equal to the dissolution-rate constant of a solid substance in a liquid at a given temperature and hydrodynamic conditions of flow of the liquid phase. As seen in Fig. 5.8, for tungsten this relationship is indeed linear. The same applies to other transition metals and alloys hitherto investigated [368, 369, 372-375, 377]. For some of them, values of the dissolution-rate constant in liquid aluminium at a disc rotational speed of 25.0 rad s^{-1} are presented in Table 5.8.

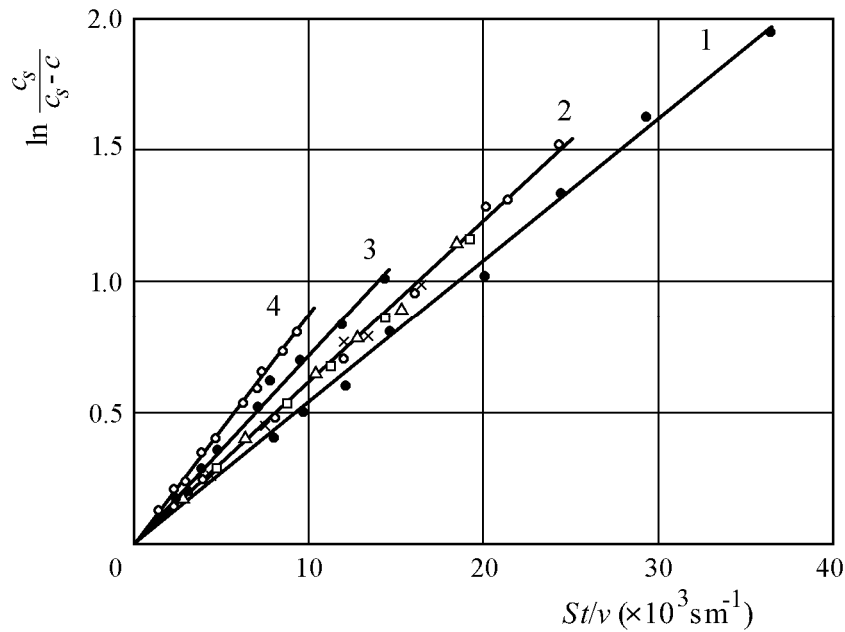


Fig. 5.8. A plot of $\ln[c_s/(c_s - c)]$ against St/v for the data of Fig. 5.7 [374].

In contrast to the solubility, the values of the dissolution-rate constants of different metals and alloys in liquid aluminium are very close. At least, they are of the same order of magnitude, namely 10^{-5} m s^{-1} , although the solubility values may differ by two orders of magnitude or more (see Table 5.2). This is also typical of dissolution of other solid substances in liquids [364-366].

Table 5.8. Values of the dissolution-rate constant, k ($\times 10^{-5} \text{ m s}^{-1}$), of transition metals in liquid aluminium at an angular speed of the disc rotation of 25 rad s^{-1} . The mean relative error of their determination is around 5 %

Metal	700°C	750°C	800°C	850°C	900°C
Ti	5.8	6.9	8.2	9.3	10.5
V	3.0	3.6	4.5	5.0	5.5
Cr	5.5	6.5	7.5	8.5	9.2
Co	6.1	7.0	7.5	8.1	8.5
Ni	6.5	9.1	10.0	10.7	13.1
Zr	5.4	6.1	7.1	7.7	8.2
Nb	4.6	5.1	6.2	6.8	-
Mo	5.4	6.0	7.4	8.0	-
Ta	4.6	5.5	6.4	7.3	-
W	5.4	6.1	7.6	8.5	-
Re	5.3	6.0	7.0	7.5	9.0

Values of the dissolution-rate constant rarely reveal any regular change over the compositional range of a binary alloy, indicative of the complicated nature of interaction in the liquid state. For example, at 700°C and $\omega = 24.0 \text{ rad s}^{-1}$ $k = 3.8 \times 10^{-5} \text{ m s}^{-1}$ for iron, $6.5 \times 10^{-5} \text{ m s}^{-1}$ for nickel and $5.5 \times 10^{-5} \text{ m s}^{-1}$ for chromium [368, 374]. Under the same conditions, $k = 5.9 \times 10^{-5} \text{ m s}^{-1}$ for a 90 % Fe–10 % Ni alloy and $6.0 \times 10^{-5} \text{ m s}^{-1}$ for a 75 % Fe–25 % Ni alloy. For 90 % Fe–10 % Cr and 75 % Fe–25 % Cr alloys, appropriate values are $4.2 \times 10^{-5} \text{ m s}^{-1}$ and $3.0 \times 10^{-5} \text{ m s}^{-1}$. The dissolution-rate constant of any Fe–Ni alloy in liquid aluminium tends to slightly decrease with increasing time [375, 377], while that of Fe–Cr alloys and a stainless steel is indeed constant, being $4.8 \times 10^{-5} \text{ m s}^{-1}$ for the latter [221].

It should be emphasised that accurate calculations of the dissolution-rate constant, k , can only be carried out if the difference between c and c_s is sufficiently large. The error in computing this constant rapidly increases as $c \rightarrow c_s$ due to the low value of the denominator ($c_s - c$) in equations (5.9) and (5.10). In such a case, even a small inaccuracy in determining the instantaneous concentration, c , which is clearly practically unavoidable, yields a very large error in calculating the value of k .

At the real accuracy of determining the concentration, c , with a relative error of 2-5%, its upper limit should not exceed $(0.6-0.7)c_s$. The lower limit depends on the sensitivity and accuracy of experimental methods employed to investigate the process of dissolution of a solid in a liquid.

Although the assumption of a quasi-stationary distribution of the concentration of component A within the diffusion boundary layer seems to be very rough, nevertheless under

conditions of sufficiently intensive convection the dissolution kinetics of solids in liquids is well described by equations (5.1) and (5.8)-(5.10) (see Refs [366, 368, 369, 371-373]). Clearly, these equations are only applicable at a low solubility of the solid in the liquid phase, typically about 10-100 kg m⁻³ or up to 5 %. Note that in some cases they may also describe fairly well the dissolution process in systems of much higher solubility. An example is the Al-Ni binary system in which the solubility of nickel in aluminium amounts to 10 % even at a relatively low temperature of 700 °C (in comparison with the melting point of aluminium, 660 °C) [373].

At a high solubility of the solid in the liquid phase, account must be taken of a variation of the volume of their solution with passing time, due to the transition of the dissolving substance into the bulk of the liquid. For most systems, an exact dependence of the volume of the solution upon its concentration is not known. In such cases, use is made of various approximate methods of determining this dependence. Usually, satisfactory results may be obtained by assuming a linear relation between the solution volume and the concentration of the dissolved substance

$$v = v_0(1 + \gamma c), \quad \gamma = (v_s - v_0)/v_s c_s, \quad (5.11)$$

where v_0 is the initial volume of the liquid and v_s is the volume of the liquid after its saturation with the dissolving substance.

Substitution of this expression for the volume into equation (5.1) and subsequent integration with the initial condition $c = 0$ at $t = 0$ yield an equation for calculating the dissolution-rate constant [378]

$$k_v = \frac{v_s}{St} \left[\ln \frac{c_s}{c_s - c} - \frac{v_s - v_0}{v_s c_s} \right]. \quad (5.12)$$

It is easy to estimate the error associated with neglecting a variation of the volume of the liquid phase due to the dissolution of a solid substance. Indeed, term-by-term dividing of equation (5.12) by (5.9) shows that

$$\frac{k_v}{k} \rightarrow 1, \quad \text{as } c \rightarrow 0, \quad (5.13_1)$$

and

$$\frac{k_v}{k} \rightarrow 1 + \frac{v_s - v_0}{v_0}, \quad \text{as } c \rightarrow c_s. \quad (5.13_2)$$

Hence, this error does not exceed a value,

$$\frac{v_s - v_0}{v_0} \times 100\%,$$

of the relative change in volume of the liquid phase during dissolution of the solid from the zero concentration up to the saturation of the solvent.

The result obtained makes it possible to decide whether it is necessary to take account of a variation of the volume of any liquid due to the dissolution of a solid substance or it can be neglected in comparison with other possible uncertainties. To do this, one must know an experimental value of the density of the saturated solution. If not available, it may readily be estimated using the rule of additivity of the reciprocals: $1/\rho_{\text{solution}} = 1/\rho_A + 1/\rho_B$.

From equations (5.6) and (5.7), it follows that under conditions of diffusion control the dissolution-rate constant should depend linearly on the square root of the angular speed of the disc rotation. As seen in Fig. 5.9, this is indeed the case (see also Refs [221, 365, 366, 368, 369, 372, 373]).

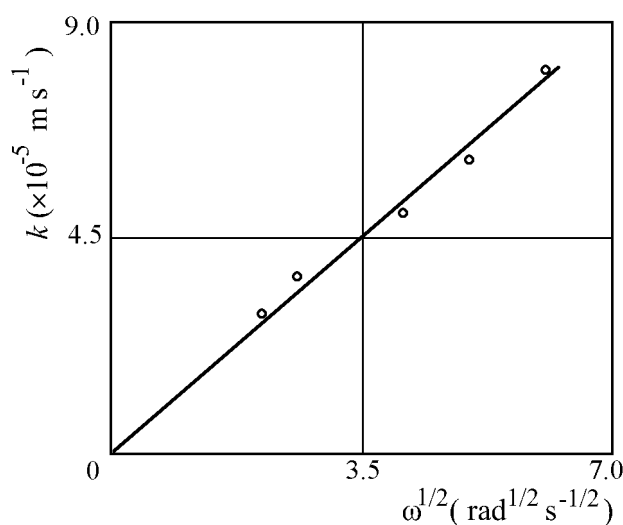


Fig. 5.9. A plot of the dissolution-rate constant of tungsten in liquid aluminium against the square root of the disc angular rotational speed at 750 °C [374].

5.2.3: Estimation of the diffusion coefficient

Knowing an experimental value of k , it is possible to evaluate the diffusion coefficient of the atoms of a dissolving solid substance across the diffusion boundary layer at the solid-liquid interface into the bulk of the liquid phase by using equations (5.6) and (5.7). Its calculation includes two steps.

First, an approximate value of D is calculated from equation (5.6). Then, the Schmidt number, Sc , and the correction factor, I , is found (see Table 5.1). The final, more accurate value is evaluated from equation (5.7). In most cases, the results of these calculations do not differ by more than 10 %. Values of the diffusion coefficient of some transition metals in liquid aluminium thus found are presented in Table 5.9 [368].

Since even at the zero initial concentration of component A in the solution its average concentration in the diffusion boundary layer at the solid-liquid interface varies during dissolution from $c_s/2$ to c_s , the values in Table 5.9 characterise the diffusion in saturated solutions rather than in the pure solvent. It must therefore be quite clear that the rotating disc method cannot be employed to establish the concentration dependence of the diffusion coefficient of A in B .

As illustrated in Fig. 5.10, the temperature dependence of the diffusion coefficient of transition metals into liquid aluminium is well described by the Arrhenius equation, $D = D_0 \exp(-E/RT)$, giving a linear plot of $\ln D$ against T^{-1} . Values of the pre-exponential factor, D_0 , and the activation energy, E , for some of them are given in Table 5.10.

Table 5.9. Diffusion coefficients of transition metals, D ($\times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), across the diffusion boundary layer at the solid-liquid interface into liquid aluminium [368]. The mean relative error of their determination is around 10 %

Metal	700 °C	750 °C	800 °C	850 °C	900 °C
Ti	2.3	3.0	3.8	4.6	5.5
V	0.83	1.1	1.4	1.8	2.2
Cr	2.0	2.7	3.5	4.0	4.4
Co	2.5	3.0	3.5	3.7	4.1
Ni	2.7	4.3	4.8	5.4	7.3
Zr	2.1	2.5	3.1	3.5	3.7
Nb	1.6	1.9	2.5	2.9	-
Mo	2.0	2.5	3.3	3.8	-
Ta	1.6	2.1	2.6	3.2	-
W	2.1	2.5	3.4	4.0	-
Re	2.0	2.4	2.9	3.5	4.5

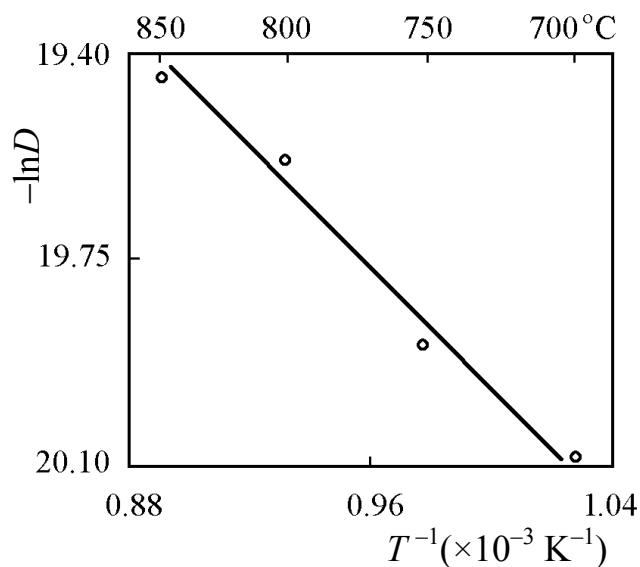


Fig. 5.10. Temperature dependence of the diffusion coefficient of the tungsten atoms across the diffusion boundary layer at the solid-liquid interface into the bulk of liquid aluminium.

Table 5.10. Parameters of the Arrhenius equation, $D = D_0 \exp(-E/RT)$, describing the temperature dependence of the diffusion coefficient of some transition metals into liquid aluminium [368]

Metal	Temperature range (K)	$D_0 (\times 10^{-7} \text{ m}^2 \text{ s}^{-1})$	$E (\text{kJ mol}^{-1})$
Ti	973–1173	4.5 ± 0.7	42.8 ± 1.5
V	973–1173	2.8 ± 0.3	47.4 ± 0.8
Cr	973–1173	2.6 ± 1.3	39.1 ± 3.8
Co	973–1173	0.43 ± 0.13	22.8 ± 2.4
Ni	973–1173	6.2 ± 3.5	43.5 ± 5.8
Zr	973–1173	0.80 ± 0.22	29.5 ± 2.1
Nb	973–1123	1.50 ± 0.89	36.9 ± 4.0
Mo	973–1123	2.82 ± 0.90	40.2 ± 2.7
Ta	973–1123	2.62 ± 0.55	41.2 ± 1.7
W	973–1123	3.54 ± 1.80	41.9 ± 5.0
Re	973–1173	2.1 ± 0.6	37.8 ± 2.3

Note that both Stokes-Einstein's and Swalin's relations usually produce a less satisfactory fit to the experimental data on the solute diffusion. The former predicts D to be roughly proportional to T , while the latter to T^2 (for more detail, see for example Refs [379-387]). Hence, according to these relations, in the 700-900 °C (973-1173 K) temperature range the ratio of diffusion coefficients would be expected to increase either by $1173/973 = 1.21$ or by $1173^2/973^2 = 1.45$. However, as seen in Table 5.9, in most cases it increases twice or more, in accordance with the Arrhenius relation. The same applies to experimental results of V.I. Itin *et al.* [388], A.N. Tabachenko *et al.* [389], G.A. Pribytkov *et al.* [390], T.V. Kasparova *et al.* [391] and others (see Refs [368, 392]), though exceptions are also rather numerous.

It should be emphasised that the diffusion data for liquid metals, obtained by different authors, especially with the use of the capillary-reservoir technique, differ very considerably. If desired, therefore, examples may easily be found in the literature, providing evidence for the validity of either of those three relations and many others. Generally, however, much wider applicability of the Arrhenius relation can hardly be doubted. It appears to hold in the greater number of cases than all other known dependences taken together.

5.3: Growth kinetics of the chemical compound layer under conditions of its simultaneous dissolution in the liquid phase

The processes of growth of a chemical compound layer at the solid-liquid interface and its dissolution into the liquid phase take place simultaneously. Depending on the sign of the difference of the growth and dissolution rates, the layer is formed (at a positive value of this difference) or is not formed (at a negative value) between interacting substances.

Equations (5.1) and (5.8) describe the dissolution process in terms of the concentration of component A in liquid B . Let us now describe it in terms of a variation of linear dimensions of a solid disc specimen. Since the concentration is the mass divided by the volume, then

$$c = \frac{\rho_A S x_d}{v}, \quad (5.14)$$

where ρ_A is the density of substance A , kg m^{-3} , and x_d is the thickness of the dissolved part of the solid specimen, m. Substituting this expression into equations (5.1) and (5.8) yields

$$\frac{dx_d}{dt} = \frac{c_s k}{\rho_A} \exp\left(-\frac{kSt}{v}\right) \quad (5.15)$$

and

$$x_d = \frac{c_s v}{\rho_A S} \left[1 - \exp\left(-\frac{kSt}{v}\right) \right]. \quad (5.16)$$

It is assumed that the volume of the liquid phase does not change significantly during dissolution, so that $v_0 \approx v \approx v_s$.

If the chemical compound A_pB_q and not substance A is dissolving in the liquid (Fig. 5.11), two alternatives are possible.

(i) The A_pB_q compound does not decompose during dissolution in the liquid phase. In such a case, equations (5.15) and (5.16) retain their form, but the density of A should be replaced by that of A_pB_q (kg m^{-3}), while the saturation concentration (solubility), c_s , should be expressed in kilograms of A_pB_q , not A , per cubic metre of the solution.

(ii) During dissolution, the A_pB_q compound entirely decomposes to atoms or ions. Then, equations (5.15) and (5.16) become

$$\frac{dx_d}{dt} = \frac{c_s k}{\rho_{A_pB_q} \varphi} \exp\left(-\frac{kSt}{v}\right) \quad (5.17)$$

and

$$x_d = \frac{c_s v}{\rho_{A_pB_q} \varphi S} \left[1 - \exp\left(-\frac{kSt}{v}\right) \right], \quad (5.18)$$

where φ is the content of A in A_pB_q in mass fractions. In these equations, c_s is the amount of A , not A_pB_q , per unit volume of the liquid phase. Note that in the case of a linear dependence of the volume of the liquid solution upon the content of component A equations (5.15)-(5.18) are also valid, but v should be replaced with v_s [378].

To derive an equation describing the growth kinetics of the A_pB_q layer under conditions of its simultaneous dissolution in liquid B , use will again be made of the principle of independency of the rates of all elementary physical or chemical processes taking place simultaneously. In the case under consideration, these are

(i) increase in thickness of the A_pB_q layer as a result of diffusion of component B across its bulk to the A - A_pB_q interface and subsequent occurrence of partial chemical reaction (1.1) (see Chapter 1 and Fig. 5.11),

(ii) increase in thickness of the A_pB_q layer as a result of diffusion of component A across its bulk to the A_pB_q - B interface and subsequent occurrence of partial chemical reaction (1.2),

(iii) decrease in thickness of the A_pB_q layer at the A_pB_q - B interface due to its dissolution in the liquid phase B undersaturated with component A .

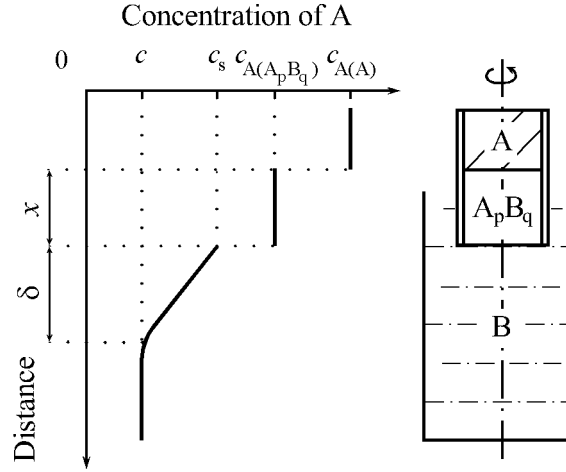


Fig. 5.11. Schematic diagram to illustrate the growth process of the A_pB_q layer under conditions of its simultaneous dissolution in the liquid phase. Not to scale.

The growth rate of the A_pB_q layer is described by equation (1.24), while its dissolution rate by equation (5.17). Term-by-term subtracting of the latter equation from the former yields the required equation describing the rate of formation of this layer at the interface between solid A and liquid B

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} - b \exp(-at), \quad (5.19)$$

where $a = kS/v$ and $b = c_s k / \rho_{A_pB_q} \varphi$.

Consider most important practical consequences following from equation (5.19). First of all, a criterion for the absence of the A_pB_q layer between the A and B phases will be established.

It is evident that the third term of equation (5.19) has the highest possible value equal to b if $at \rightarrow 0$. This condition is satisfied in the following cases.

(1) At $t \rightarrow 0$, *i.e.* in the very initial period of dissolution that is a trivial case. To evaluate the time during which the dissolution rate can be regarded as almost constant and maximal, it is

necessary to take into account that its variation can only be revealed if the value of this variation becomes comparable with the accuracy of measurements.

Upon expanding the exponential function of equation (5.17) into a power sign-alternate series [393] and retaining only its first two terms, one obtains

$$\frac{dx_d}{dt} = b(1 - at). \quad (5.20)$$

It is known that in this case the error does not exceed the value of the first rejected term, *i.e.* $a^2 t^2 / 2$ [394]. In percentage to at , it is $(at/2) \times 100\%$.

Let the relative error of determining the dissolution-rate constant be equal to $\Delta\%$. Consequently, a decrease in the dissolution rate will be noticeable, if $\Delta \approx 100at$. During dissolution of solid metals in liquid ones, $\Delta \approx 5\%$. The dissolution-rate constant is known to vary in the range $(2-10) \times 10^{-5} \text{ m s}^{-1}$ at angular speeds of the disc rotation of $5-80 \text{ rad s}^{-1}$ [368, 369, 372, 373]. The value of S/ν is usually of the order of 10 m^{-1} . Then, assuming that on the average $k = 5 \times 10^{-5} \text{ m s}^{-1}$, one obtains $a = 5 \times 10^{-4} \text{ s}^{-1}$. Consequently, $t \approx 100 \text{ s}$.

Hence, at least during the first two minutes since the start of the interaction of solid A with liquid B , the dissolution rate of the $A_p B_q$ layer can with sufficient accuracy be considered to be constant and equal to b . It should be noted that in this case the error resulting from replacing $\exp(-at)$ with $(1 - at)$ is about $2.5 \times 10^{-2}\%$. Hence, such a substitution is quite justified.

(2) At $S/\nu \rightarrow 0$. This condition is evidently satisfied for systems of forced circulation, in which the surface of a solid is continuously washed with a pure solvent. Note that if the concentration of A in B is $c_0 \neq 0$, then the dissolution rate of the $A_p B_q$ layer will be constant, but less than b :

$$\frac{dx_d}{dt} = \frac{(c_s - c_0)k}{\rho_{A_p B_q} \varphi}. \quad (5.21)$$

If the dissolution rate remains constant and equal to b , equation (5.19) is simplified to

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} - b. \quad (5.22)$$

From this equation, a condition for the absence of the A_pB_q layer at the interface between solid A and liquid B can readily be derived. Indeed, the highest value of the first two terms of the right-hand side of equation (5.22) is equal to the sum $k_{0B1} + k_{0A2}$. Therefore, at

$$k_{0B1} + k_{0A2} < b \quad (5.23)$$

the A_pB_q layer cannot occur between A and B since $dx/dt < 0$, *i.e.* the rate of growth of this layer is less than the rate of its dissolution in the liquid phase.

This result is of importance for practice because too rapid formation of compound layers at the interface of reacting substances is often undesirable. An example is the occurrence of thick layers of intermetallic compounds during welding or brazing dissimilar metals, whose presence is known to strongly deteriorate the mechanical strength of the joint (see, for example, Refs [395, 396]).

To simplify further analysis of equations (5.19) and (5.22), instead of the sum of two terms

$$\frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}}$$

only one term with constants k_0 and k_1 will be retained. Then, equation (5.22) takes the form [397]

$$\frac{dx}{dt} = \frac{k_0}{1 + \frac{k_0x}{k_1}} - b. \quad (5.24)$$

Its solution at the initial condition $x = 0$ at $t = 0$ is

$$-\frac{k_1}{b^2} \ln \left[1 - \frac{k_0bx}{k_1(k_0 - b)} \right] - \frac{x}{b} = t. \quad (5.25)$$

By setting $dx/dt = 0$ in equation (5.24), the largest value of the thickness of the A_pB_q layer possible under conditions of its simultaneous dissolution in the liquid phase at a rate b is found:

$$x_{\max} = \frac{k_1(k_0 - b)}{k_0 b}. \quad (5.26)$$

At a constant dissolution rate, the time dependence of the A_pB_q layer thickness is seen to be similar that shown in Fig. 2.7b (line 1). After a certain period of time, the thickness of the layer reaches the value $x_{\max}$ and then it grows no longer because the stationary state is established when an increase in layer thickness is just equal to a decrease due to its dissolution in the liquid phase [397]. The process of an asymptotic approach of the thickness of the A_pB_q layer with passing time to its maximal value possible under given dissolution conditions is described by equation (5.25).

If the growth rate of the A_pB_q layer is restricted by the rate of diffusion of components A and B across its bulk, so that $k_0 \gg k_1/x$, while the rate of chemical transformations (partial chemical reactions) far exceeds the dissolution rate ($k_0 \gg b$), equations (5.19), (5.22), (5.25) and (5.26) take a simpler form:

$$\frac{dx}{dt} = \frac{k_1}{x} - b \exp(-at), \quad (5.27)$$

$$\frac{dx}{dt} = \frac{k_1}{x} - b, \quad (5.28)$$

$$-\frac{k_1}{b^2} \ln \left(1 - \frac{bx}{k_1} \right) - \frac{x}{b} = t, \quad (5.29)$$

$$x_{\max} = \frac{k_1}{b}. \quad (5.30)$$

Using these equations, the thickness of the layer of any chemical compound under conditions of dissolution of a solid in a liquid can readily be estimated. It should be remembered, however, that at very low t and x equations (5.27), (5.28) and (5.29) become inapplicable in view of the assumptions on which their derivation rests.

Since equation (5.27) can hardly be integrated precisely [398], calculations are carried out with the use of different approximate methods. For example, the piecemeal-analytical method may successfully be employed [397]. It is based on dividing the examined time range into a finite number of sufficiently short intervals and the subsequent application of equation (5.29) to each of them. Also, equation (5.27) can be transformed into a transcendental equation [399] that is then solved by numerical methods.

To carry out any calculations, it is clearly necessary to know the values of the chemical and physical (diffusional) constants and also of the parameters characterising the dissolution

rate of a solid in a liquid. At present, all these quantities can only be determined experimentally or evaluated from other experimental data.

The chemical and physical constants can be found when investigating the growth kinetics of the A_pB_q layer between solid A and liquid B saturated with component A , *i.e.* experiments should be carried out under conditions excluding the process of dissolution of the solid phase in the liquid one. Other steps of the determination of these quantities are identical to those described in Chapter 1.

It should be noted that in many works the degree of saturation of liquid B with the dissolving component A is not taken into account, and even in cases where a pure solvent is used, the experimental data are treated using a linear, parabolic, logarithmic or some other dependence in order to establish the so-called growth law of a chemical compound layer. It is clear, however, that both the academic and practical value of such “laws” is not too high because each of them holds only under particular experimental or technological dissolution conditions which most frequently remain unspecified. It is therefore sufficient to change, for example, the dimensions of a solid specimen or the volume of the liquid or its agitation conditions, and the parameters of the “layer-growth law” thus found will at best assume other numerical values or at worst even the shape of the layer thickness-time dependence will change considerably, in spite of the lack of any essential changes in the mechanism of formation of the layer of that chemical compound.

It should be emphasised that in following the rate of dissolution of solid A in liquid B by the mass loss of a solid specimen of substance A , measured by weighing the specimen before and after the experiment, errors may arise due to the formation of a chemical compound layer at the solid-liquid interface. On the one hand, dissolution of the solid phase A in the liquid phase B reduces the mass of the solid specimen. On the other, however, formation of the A_pB_q compound layer adhering to the surface of the solid specimen results in an increase of its mass (at $k_0 > b$). Hence, the experimentally determined change in mass of the solid specimen is a consequence of the two simultaneously occurring processes, namely, growth and dissolution of the A_pB_q layer.

If the thickness of the dissolved part of the solid specimen far exceeds the thickness of the A_pB_q layer formed at the solid-liquid interface in the course of dissolution, the error of determination of the mass loss by weighing the specimen before and after the experiment will be negligibly small. However, at low t and $k_0 > b$ the increase in the specimen mass due to the formation of the A_pB_q layer may prove greater than its decrease caused by dissolution. In such a case, instead of decreasing, the mass of the specimen will increase, as was observed, for example, by V.I. Zhalybin *et al.* [400] during dissolution of titanium in the stainless-steel melt.

From these considerations, it follows that in the case of formation of the layer of a chemical compound under conditions of simultaneous dissolution of a solid in a liquid, the shape of the layer thickness-time dependence may be rather complicated. Evolution of this dependence in the course of interaction of initial substances from the moment of their

contact to the establishment of equilibrium in the $A-B$ system will now be analysed. The time of wetting the solid surface by the liquid phase will not be taken into account, *i.e.* this process is assumed to be instantaneous.

After solid A and liquid B undersaturated with component A are brought into contact with each other, two somewhat different ways of their interaction are possible.

(1) The layer of the A_pB_q chemical compound immediately occurs and then grows between the A and B phases. It happens if

$$k_{0B1} + k_{0A2} > b, \quad (5.31)$$

i.e. when the sum of the rates of chemical reactions at layer interfaces with initial substances exceeds the dissolution rate. Since in the initial period of time (in the region of small layer thicknesses) $k_{0B1} \ll k_{1B1}/x$ and $k_{0A2} \ll k_{1A2}/x$, while the dissolution rate does not yet change appreciably, equation (5.19) shows that in this stage of the growth process the time dependence of the layer thickness is close to linear

$$x = (k_{0B1} + k_{0A2} - b)t. \quad (5.32)$$

As the thickness of the A_pB_q layer increases with passing time, its growth rate must gradually decrease. If $k_{0B1} + k_{0A2} \gg b$, $k_{0B1} \gg k_{1B1}/x$, $k_{0A2} \gg k_{1A2}/x$ and $(k_{1B1} + k_{1A2})/x \gg b$, then the growth kinetics of the A_pB_q layer will be almost parabolic. The abundance of necessary conditions to be satisfied indicates that this is a rather rare case. Strictly speaking, the initial portion of the layer thickness-time dependence can in general hardly be expected to be either linear or parabolic.

If the dissolution rate is maintained constant, after reaching its maximal thickness (see equation (5.26)), the A_pB_q layer simply moves as a whole into the bulk of solid phase A until its full consumption (if liquid B is in excess). Most frequently, however, the dissolution rate decreases from b to 0 with increasing time. Therefore, the effect of dissolution on the process of formation of the A_pB_q layer gradually weakens, and the layer thickness-time dependence steadily approaches the parabola $x^2 = 2(k_{1B1} + k_{1A2})/t$.

(2) If $k_{0B1} + k_{0A2} < b$, then the A_pB_q layer is not formed at the interface of substances A and B during a certain initial period of their interaction. Since the dissolution rate steadily decreases, a time t_0 is always reached when the dissolution and layer-growth rates become equal, *i.e.*

$$k_{0B1} + k_{0A2} = b \exp(-at_0). \quad (5.33)$$

This corresponds to the start of formation of the A_pB_q layer at the $A-B$ interface. Subsequently,

$$k_{0B1} + k_{0A2} > b \exp(-at)_{t > t_0}. \quad (5.34)$$

Therefore, after a time delay, often referred to as the incubation or latent period, the A_pB_q layer occurs and grows between the solid and liquid phases. Note that knowing both the time, t_0 , of occurrence of the compound layer at the $A-B$ interface and the dissolution rate, b , the sum, $k_{0B1} + k_{0A2}$, of the chemical constants can readily be estimated from equation (5.33). It is another method of its determination, in addition to that described in Chapter 1.

Thus, the reason for the absence of the layer of a chemical compound between reacting substances follows in a natural way from the proposed physico-chemical equations. Note that according to diffusional views the A_pB_q layer should grow at the interface between A and B at *any* finite dissolution rate. It is easily seen from equations (5.27)-(5.30). Indeed, whatever the dissolution rate, the thickness of the layer will never be less than $x_{\max} = k_1/b$. Clearly, this value is always positive.

Hence, the diffusional theory does not “allow” any existing compound layer to disappear during dissolution. Intuitively, this conclusion appears to be quite evident because an increase in the dissolution rate, resulting in a decrease of the layer thickness, automatically leads to an increase in its growth rate (see equations (5.27) and (5.28) in which x is in the denominator of the term k_1/x responsible for the layer-growth rate). Due to such a compensation effect, the thickness of the A_pB_q layer exceeds zero at any real values of the diffusion coefficients of the components across its bulk.

In the framework of the diffusional approach the absence of the layer of a chemical compound in the course of interaction of a solid with a liquid is thus unexplainable. The reason for this is therefore sought outside of this approach. In most cases, it is assumed to be the difficulty with the formation of nuclei of a new phase (see, for example, Ref. [22]). Perhaps, in some (very limited) number of systems the rate of nucleation indeed plays a significant role. However, such an explanation can hardly be expected to be valid in all cases of absence of the layers of chemical compounds.

Note that in practice the actual role of nucleation in each particular system can be revealed very simply. It suffices to carry out experiments, preferably at a constant dissolution rate, on specimens where a chemical compound layer is already present. If the compound layer disappears during interaction of those specimens with the liquid phase, then it becomes quite clear that its absence between the A and B phases is due to the effect of dissolution and not to the difficulties of nucleation.

It is worth noting that the condition of constancy of the dissolution rate is rather essential. If the dissolution rate decreases during the experiment, as is often the case, it may happen that the conditions under which inequality (5.34) is satisfied are established even before the

full disappearance of the A_pB_q layer due to its dissolution in the liquid. Therefore, after some temporary reduction, the layer thickness will again start to increase. Both equations (5.19) and (5.27) allow such a form of the layer thickness-time dependence. Hence, under varying dissolution conditions it is not so easy to unambiguously decide whether the absence of the A_pB_q layer is due to the difficulties of phase nucleation or to its too high dissolution rate exceeding the rate of interfacial chemical reactions.

With passing time, liquid B becomes more and more saturated with component A . Therefore, dissolution of the A_pB_q layer in the liquid phase eventually ceases, while its growth between A and B continues until at least one of the initial substances is consumed completely. Depending on the amounts of substances A and B taken, phases A and A_pB_q , or A_pB_q and B , or only one phase A_pB_q remain in the equilibrium state.

Analysis of the effect of dissolution on the growth kinetics of the layers of two or more chemical compounds is carried out in a similar way. To take account of this effect, it is necessary to subtract the dissolution rate $b \exp(-at)$ from the right-hand side of a differential equation describing the growth rate of a compound layer bordering liquid B (see equation (2.27₂) in Chapter 2 and (3.26₃) in Chapter 3).

5.4: Kinetics of growth of intermetallic layers at the transition metal-liquid aluminium interface

Consider a few examples of formation of intermetallic layers between a transition metal or an alloy of transition metals and molten aluminium. Let us begin with iron, a metal most widely used in practice.

The main aim of this section is to illustrate the influence of dissolution on layer-growth kinetics. Therefore, for each pair of initial substances, experiments with saturated and non-saturated melts will be described.

5.4.1: Formation of the Fe_2Al_5 layer between Fe and Al

At 700 °C, a single-phase layer (see Fig. 1.6 of Chapter 1) of the Fe_2Al_5 intermetallic compound, having a readily distinguishable structure consisting of elongated grains oriented in the direction of growth [170, 195, 374, 401], is formed at the solid iron-liquid aluminium interface. According to T. Heumann and S. Dittrich [170], growth kinetics of the Fe_2Al_5 layer between iron and the iron-saturated aluminium melt follows the parabolic law $x^2 = 2k_1t$, with $k_1 = 1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

To reveal the effect of dissolution on the rate of layer growth, experiments were carried out with the melts of pure aluminium at an angular speed of the disc rotation of 24.0 rad s^{-1} , as described in Section 5.2. The first experiment was a check-up one. After pre-heating under a flux, the rotating iron specimen was immersed into the aluminium melt at 700 °C, and immediately the crucible, together with the specimen and the melt, was “shot” into a water bath (see Fig. 5.3). Examination of the bimetallic specimen obtained showed a

continuous Fe_2Al_5 intermetallic layer around $1\text{ }\mu\text{m}$ thick to form at the Fe–Al interface. Since the time of cooling from $700\text{ }^\circ\text{C}$ down to room temperature was at most 2 s , it is evident that wetting and nucleation were relatively fast processes that could hardly be expected to have any significant influence on the layer-growth kinetics. This time, 2 s , was a small portion of the total experiment duration ($50\text{--}300\text{ s}$), and the thickness, $1\text{ }\mu\text{m}$, of the intermetallic layer formed during cooling was a small portion of the measured layer thicknesses, $40\text{--}90\text{ }\mu\text{m}$. It will become clear later how essential it is to count all these seconds and micrometres in order to avoid incorrect conclusions regarding the actual time of layer formation.

The average value of the maximum height of the Fe_2Al_5 crystallites was used as a measure of the intermetallic layer thickness. The experimental points are shown in Fig. 5.12 by open circles [195]. The relative error of determining the layer thickness was around 15% .

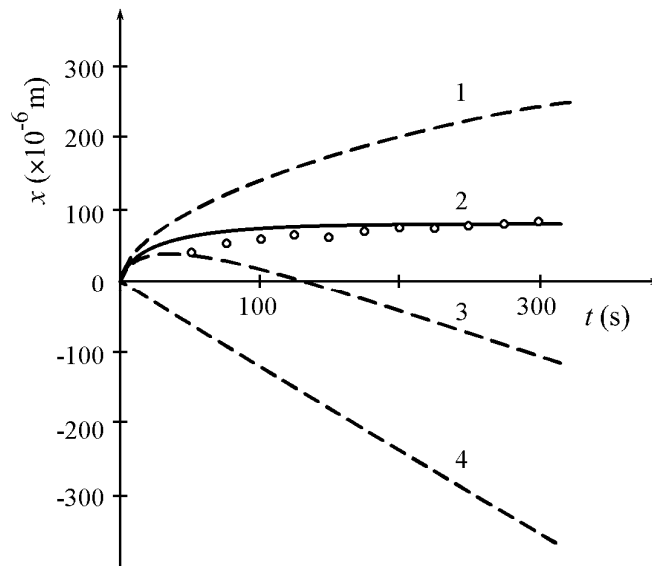


Fig. 5.12. Thickness–time relationships for the Fe_2Al_5 layer at $700\text{ }^\circ\text{C}$ [195]: 1, parabolic growth kinetics of the layer in the case of the Fe-saturated aluminium melt; 2, theoretical dependence of the thickness of the layer upon time under conditions of its simultaneous dissolution in the aluminium melt ($c_0 = 0$), calculated from equation (5.29); 3, difference between the dependences represented by lines 1 and 4; 4, thickness of the dissolved portion of the layer plotted against dipping time. Open circles are experimental values of the thickness of the Fe_2Al_5 layer formed at the Fe–Al interface under conditions of its simultaneous dissolution in the aluminium melt at an angular speed of the disc rotation of 24.0 rad s^{-1} .

The theoretical thickness-time dependence (solid line 2) was calculated from equation (5.29), using the following quantities:

- (1) $c_s = 60 \pm 3 \text{ kg m}^{-3}$ [373];
- (2) $s = 1 \text{ cm}^2$, $v = 10 \text{ cm}^3$, $s/v = 10.0 \pm 0.2 \text{ m}^{-1}$;
- (3) $k = (3.8 \pm 0.1) \times 10^{-5} \text{ m s}^{-1}$;
- (4) $\rho_{\text{int}} = (4.1 \pm 0.1) \times 10^3 \text{ kg m}^{-3}$ (density of Fe_2Al_5) [159];
- (5) $\varphi = 0.453$ (mass fraction of Fe in Fe_2Al_5).

The dissolution rate of the Fe_2Al_5 layer was assumed to be constant and equal to its average value in the 0–300 s range. Expressed in terms of the thickness of the Fe_2Al_5 layer dissolved, it is

$$b = \frac{c_s k}{\rho_{\text{int}} \varphi} = 1.23 \times 10^{-6} \text{ m s}^{-1} \text{ at } t = 0$$

and

$$b \exp(-at)_{t=300} = 1.10 \times 10^{-6} \text{ m s}^{-1} \text{ at } t = 300 \text{ s.}$$

Deviations from the average value, $1.16 \times 10^{-6} \text{ m s}^{-1}$, are seen not to exceed $\pm 6 \%$. Therefore, equation (5.29) may reasonably be expected to describe the growth kinetics of the Fe_2Al_5 layer with a sufficient degree of accuracy.

To make further discussion more illustrative, shown in Fig. 5.12 also are

- (i) kinetic dependence for the case of growth of the Fe_2Al_5 layer at the interface of iron with iron-saturated liquid aluminium (line 1);
- (ii) kinetic dependence expressing the thickness of the dissolved portion of the Fe_2Al_5 layer (line 4);
- (iii) difference of the first two dependences (line 3).

The agreement between the calculated theoretical dependence (line 2) and the experimental points is seen to be fairly good. A certain disagreement is only observed near the initial, abruptly ascending part of the curve 2. The reasons for this appear to be the following.

- (1) The rate of dissolution of the Fe_2Al_5 layer was assumed to be constant, whereas in fact it decreases almost linearly from $1.23 \times 10^{-6} \text{ m s}^{-1}$ to $1.10 \times 10^{-6} \text{ m s}^{-1}$. As a result, the theoretical curve overestimates the thickness of the intermetallic layer for the first half (0–150 s) and underestimates it for the second half (150–300 s) of the examined time range. Clearly, this reason alone cannot lead to the observed disagreement because the error arising from such an assumption is small compared to the experimental error of measuring the layer thickness.
- (2) Growth of the Fe_2Al_5 crystallites is known to be anisotropic. Each elongated crystallite (see Fig. 1.6) is a single crystal whose axis coincides with the c -axis of the orthorhombic unit cell of the Fe_2Al_5 intermetallic compound [170]. The highest value of the growth rate of

the crystallites is just observed in the direction of the *c*-axis. This is due to the peculiarities of the Fe₂Al₅ lattice structure (for more detail, see Ref. [170]).

However, the maximum values of the growth rates of the crystallites are only observed if the angle between the *c*-axis and the initial Fe–Al interface is 90°. If this angle considerably differs from 90°, then neighboring crystallites hinder each other's growth. The early stage of interaction of solid iron with liquid aluminium is characterised by the formation of a number of randomly orientated nuclei of the Fe₂Al₅ phase. Therefore, in this stage the growth-rate constant, k_1 , of the layer is probably somewhat less than the accepted value of $1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Hence, the experimental points might be expected to lie below the calculated curve 2 in its initial portion. This was indeed observed experimentally.

During dissolution, the unfavorably orientated Fe₂Al₅ crystallites gradually disappear, while the favorably orientated ones continue to grow. As a result, the morphology of the Fe₂Al₅ layer becomes more and more regular, with its crystallites being almost parallel to each other, and eventually the growth-rate constant, k_1 , attains its maximum value which then changes no longer. Therefore, the agreement between the calculated and experimental dependences for the second half of the 0–300 s time range is much better than for the first half. This is another (masked) aspect of the influence of dissolution on the growth kinetics of the Fe₂Al₅ layer. Clearly, its precise quantitative evaluation is hardly possible.

Comparison of the curves 1 and 2 in Fig. 5.12 demonstrates how significant the effect of dissolution on the layer-growth kinetics is. It should be noted that of all intermetallic compounds formed by transition metals with aluminium under similar conditions, the Fe₂Al₅ layer has the highest growth rate [368, 369, 374, 402–404]. This causes serious difficulties in welding aluminium and its alloys with iron and steels, in hot-dip protective coating, and in producing composite materials [315, 395, 405–408]. By increasing the rate of dissolution, it is possible to significantly reduce the thickness of the Fe₂Al₅ layer, but its formation can scarcely be fully prevented at any real dissolution rate.

Note that, when taking account of the effect of dissolution on the growth kinetics of a chemical compound layer, in some works the integrated quantities are simply subtracted from each other. This yields a dependence shown schematically in Fig. 5.12 by line 3 which is the difference between the parabola $x = (2k_1t)^{1/2}$ giving the layer thickness in the absence of dissolution and equation (5.18) giving the dissolved portion of its thickness. Such an approach is clearly misleading. It is not surprising, therefore, that the dependence thus obtained has nothing in common with the experimentally determined curve 2, excepting a narrow region near the origin of co-ordinates, where $k_1/x \gg b$.

5.4.2: Occurrence of the MoAl₄ layer between Mo and Al

Figure 5.13 shows a micrograph of the transition zone between solid molybdenum and liquid aluminium saturated with molybdenum. As established by X-ray diffraction, electron probe microanalysis and chemical analysis, the intermetallic layer formed consists of the MoAl₄ compound [374].

In contrast to the Fe_2Al_5 layer with its ragged Fe_2Al_5 -Fe interface (see Fig. 1.6), the MoAl_4 intermetallic layer is seen to have relatively even interfaces with both initial phases. In the case of the Mo-saturated aluminium melt, its growth kinetics follows the parabolic law $x^2 = 2k_1t$ (Fig. 5.14).

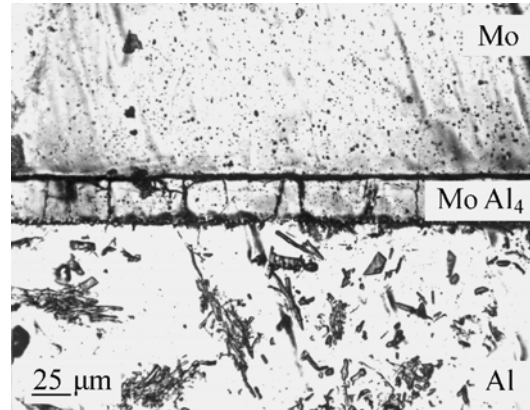


Fig. 5.13. A micrograph of the transition zone between molybdenum and Mo-saturated liquid aluminium [374]. Temperature 750 °C, dipping time 1800 s. Inclusions in the aluminium matrix are crystals of MoAl_4 formed during cooling the aluminium melt.

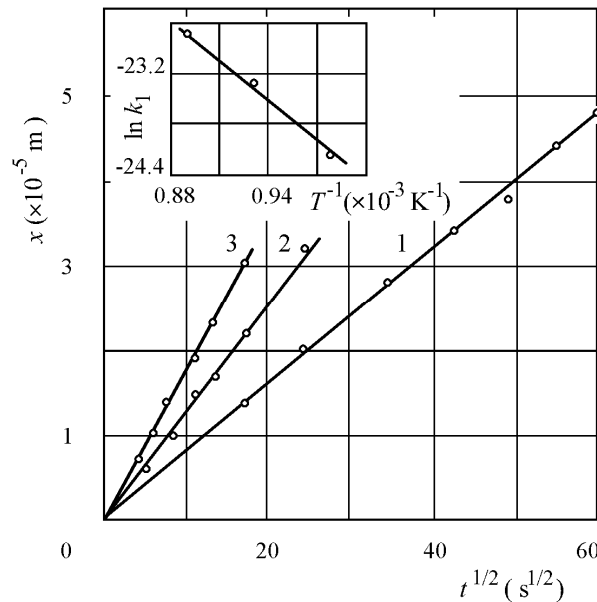


Fig. 5.14. Thickness of the MoAl_4 layer formed at the interface of molybdenum with Mo-saturated liquid aluminium plotted against the square root of the time, and the temperature dependence of layer growth-rate constant [374]. Temperature: 1, 750°C; 2, 800; 3, 850.

In the 750-850 °C range the temperature dependence of the layer growth-rate constant, k_1 , is described by the equation [374, 402]

$$k_1 = (9.2 \pm 1.2) \times 10^{-6} \exp \left[-\frac{(145 \pm 1) \times 10^3}{RT} \right] \text{ m}^2 \text{ s}^{-1}$$

where the pre-exponential factor is expressed in $\text{m}^2 \text{ s}^{-1}$ and the activation energy in J mol^{-1} .

The effect of dissolution on the growth rate of the MoAl_4 layer will be estimated at a temperature of 750°C, using the following quantities:

- (1) $k_1 = 3.2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ [374];
- (2) $c_s = 10.6 \text{ kg m}^{-3}$ [374];
- (3) $s = 1 \text{ cm}^2$, $v = 10 \text{ cm}^3$, $s/v = 10.0 \text{ m}^{-1}$;
- (3) $k = 3.8 \times 10^{-5} \text{ m s}^{-1}$ [374];
- (4) $\rho_{\text{int}} = 4.35 \times 10^3 \text{ kg m}^{-3}$ [234];
- (5) $\varphi = 0.47$.

The initial dissolution rate of molybdenum discs in liquid aluminum is seen from equation (5.17) to be $1.97 \times 10^{-7} \text{ m s}^{-1}$. After 300 s, it drops to $1.77 \times 10^{-7} \text{ m s}^{-1}$. Assume that in the 0–300 s time range the dissolution rate is constant and equal to the latter value. Then, according to equation (5.30), after 300 s holding the thickness of the MoAl_4 layer at the Mo–Al interface cannot exceed

$$x_{\text{max}} = \frac{3.2 \times 10^{-13}}{1.77 \times 10^{-7}} = 1.8 \times 10^{-6} \text{ m}.$$

Note that in the case of the aluminum melt saturated with molybdenum the thickness of the MoAl_4 layer at $t = 300 \text{ s}$ is $14 \times 10^{-6} \text{ m}$. In welding dissimilar metals, the maximal permissible thickness of an intermetallic layer is known to be 2–5 μm . Thus, the dissolution conditions in question ensure the formation of the Mo–Al transition zone with a MoAl_4 layer thickness not exceeding this value.

It should be remembered that equation (5.30) greatly overestimates the layer thickness. Its experimental value is less than half the value obtained from this equation. In the case of the Mo-saturated aluminum melt, it takes only 5 s for the MoAl_4 layer to reach a thickness of $1.8 \times 10^{-6} \text{ m}$. For this reason, when investigating the effect of dissolution on the growth rate of any chemical compound layer it is so important to ensure sufficiently rapid cooling-down the melt. This example clearly shows that a few seconds of layer formation during cooling, when the process of dissolution has already ceased but the temperature of the experimental cell has not yet dropped considerably and therefore the layer growth-rate constant still retains its former value, may happen to exert the same effect on thickening the compound layer as do a few minutes of its growth under conditions of simultaneous dissolution in the melt.

5.4.3: Formation of intermetallics at the interface of Fe–Ni and Fe–Cr alloys with liquid aluminium

Aluminium is known to form a number of binary [157, 159, 241] and ternary [231, 409, 410] intermetallic compounds with iron and nickel or chromium. In this section, results on the intermetallic-layer formation and dissolution at the interface between a solid iron-nickel or iron-chromium alloy and aluminium melts will be considered [411–415]. Also, the effect of dissolution in the liquid phase on the process of layer growth will be illustrated.

Note that in contrast to binary systems where only one-phase compound layers can occur at the interface between two elementary substances, in ternary systems, when a two-component alloy or a binary compound reacts with a third metal or non-metal (either solid or liquid), the formation of both compact one-phase layers and two-phase reaction zones is observed. These may have a different morphology, possible types of which were considered, for example, in works by F.J.J. van Loo [37] and J.E. Morrel *et al.* [416].

Chemical compositions of the Fe–Ni specimens containing 90, 75, 50, 25, 20, 15 and 10 mass% Fe corresponded to nominal values within ± 0.5 mass%. At room temperature, the alloy specimens consisted of the α -phase (ferrite) at nickel contents less than or equal to 25 mass% or the γ -phase (austenite) at higher Ni contents, while at a temperature of 700 °C the specimens of all compositions had the austenitic structure. Ferrite constituted the microstructure of the Fe–Cr alloy specimens (10 and 25 mass% Cr) over this range of temperature.

Consider first the Al–Fe–Ni system. Generally, the equilibrium phase diagram is known to be helpful in analysing the process of intermetallic layer formation. Projection of the liquidus surface on the concentration triangle and distribution of the phase fields in the solid state for Al-rich Al–Fe–Ni alloys are shown in Fig. 5.15.

The Al-richest Al–Fe binary phase is designated FeAl_3 (25.0 at.% Fe, 75.0 at.% Al) or Fe_2Al_7 (22.2 at.% Fe, 77.8 at.% Al) [157, 411]. Yet, it is debatable whether these intermetallic compounds are two different phases or the same phase with a wide range of homogeneity. The FeAl_3 compound is reported to have a homogeneity range of 74.5 to 75.5 at.% Al [412]. The range of homogeneity of the Fe_2Al_7 compound is indicated as 77.5 to 78.6 at.% Al [157].

The X-ray powder pattern of FeAl_3 was found to be only slightly different from that of Fe_2Al_7 [157]. Up to 11 at.% Ni can be dissolved in FeAl_3 [412].

In the Al–Ni binary system, the homogeneity range of Ni_2Al_3 (ideal chemical composition 40 at.% Ni and 60 at.% Al) is given as 59.2 to 63.7 [142] or 58.5 to 63.0 at.% Al [412], whereas that of NiAl_3 (25.0 at.% Ni, 75.0 at.% Al) is considered to be very narrow, if any [157, 231, 412]. In the ternary Al–Fe–Ni system, the solubility of Fe in the Al-richest phase NiAl_3 is 4 at.%, while that in Ni_2Al_3 is 2 at.% [412].

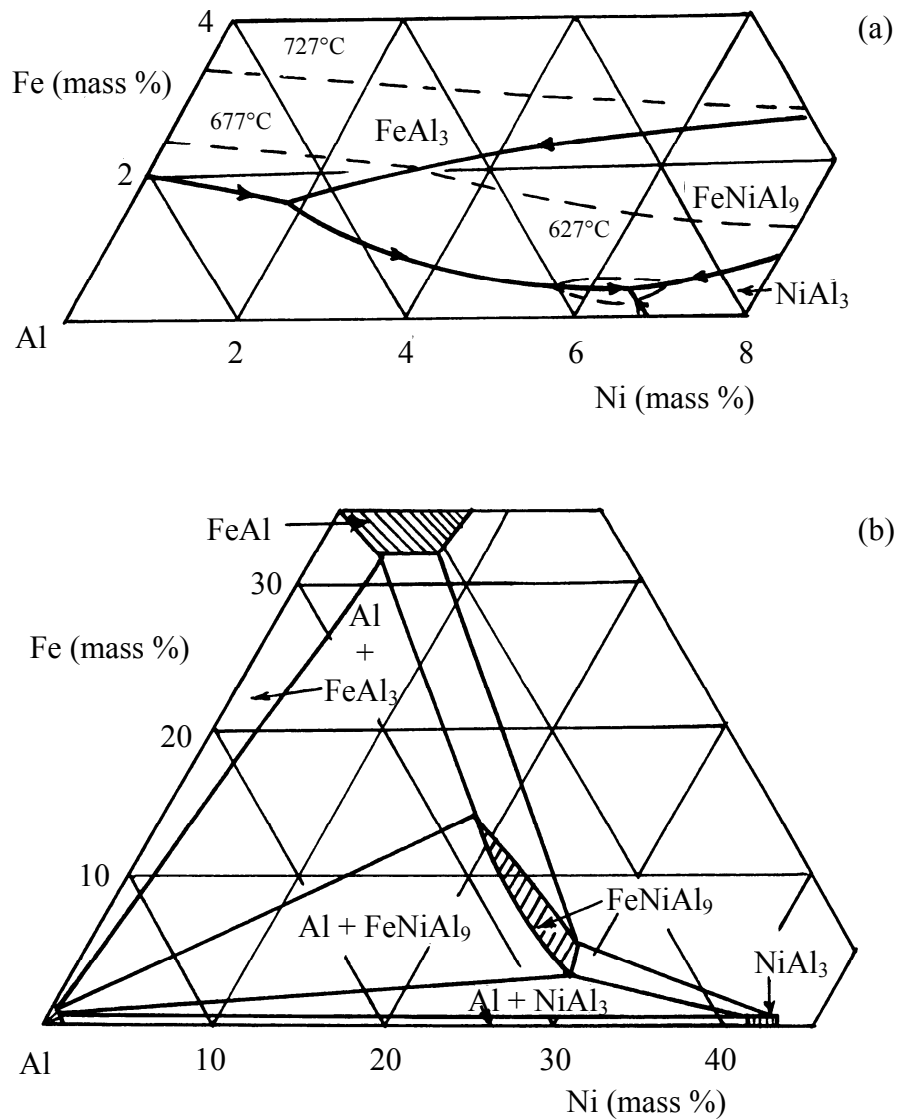


Fig. 5.15. (a) Projection of the liquidus surface on the concentration triangle and (b) distribution of the phase fields in the solid state for Al-rich Al–Fe–Ni alloys [231].

The ternary intermetallic compound FeNiAl₉ (9.1 at.% Fe, 9.1 at.% Ni, 81.8 at.% Al) is formed at 809 °C according to the peritectic reaction between the liquid phase L_1 (87.06 at.% Al, 2.11 at.% Fe, 10.83 at.% Ni), FeAl₃ and NiAl₃ [347]:



Its range of homogeneity extends from about 3 to 11 at.% Fe and from 7 to 17 at.% Ni.

At 638 °C, the eutectic reaction



takes place (see Fig. 5.15a). On cooling down the liquid L_2 (96.72 at.% Al, 0.105 at.% Fe, 3.174 at.% Ni), the eutectic consisting of the aluminium solid solution $\langle\text{Al}\rangle$, NiAl_3 and FeNiAl_9 is formed.

Typical microstructures of the alloy-aluminium transition zone of the Al-(Fe+Ni) samples obtained under similar conditions (temperature 700 °C, dipping time 3600 sec, saturated aluminium melts) are shown in Fig. 5.16. The intermetallic layer, $80 \pm 10 \mu\text{m}$ thick, grown between a 90 % Fe–10 % Ni alloy and the aluminium melt saturated with the alloy constituents, seems to be one-phase (Fig. 5.16a).

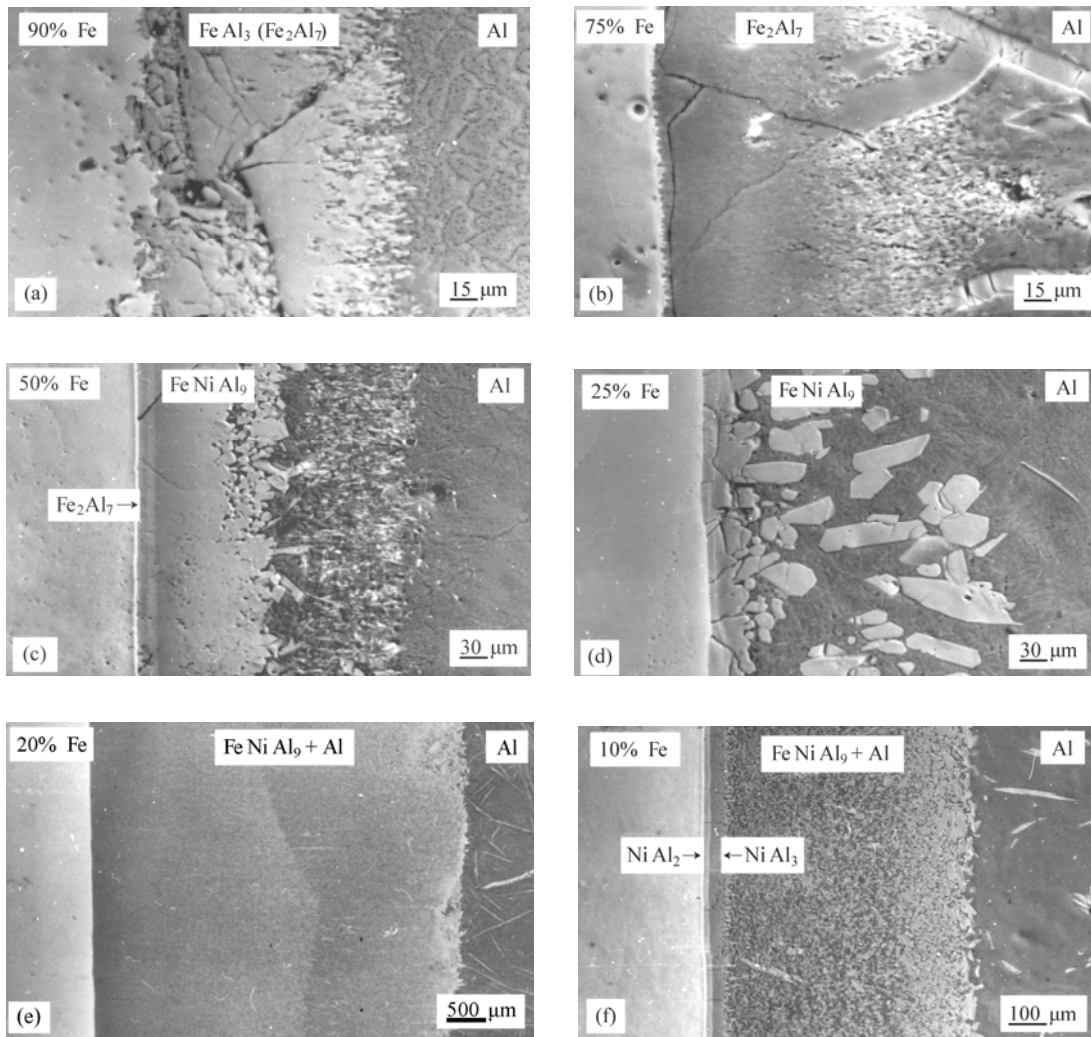


Fig. 5.16. Backscattered electron image (BEI) of the transition zone between a Fe–Ni alloy and the aluminium melt saturated with the alloy constituents. Temperature 700 °C, dipping time 3600 s.

Upon closer examination, however, it could be noticed that its crystals were not uniform in colour, some of them being a little darker than the others. Wherever the cracks were not too numerous, two separate sublayers could be distinguished. The sublayer adjacent to the alloy base was a little lighter in colour than that bordering the aluminium matrix. The chemical composition of the former sublayer, found by electron probe microanalysis, well corresponded to the composition of the FeAl_3 compound in which 5.5 ± 0.5 at.% Ni was dissolved. The chemical composition of the latter sublayer was close to the upper Al limit of the homogeneity range of the Fe_2Al_7 compound in which much less Ni (0.7 to 1.4 at.%) was dissolved. The content of iron was found to be approximately the same in both sublayers. Hence, FeAl_3 and Fe_2Al_7 appear to be two different, though very closely related, phases.

Of 2.5 % Fe and 0.28 % Ni added initially to aluminium in order to obtain the saturated melt at 700 °C, only 0.41 % (0.20 at.%) Fe and 0.05 % (0.03 at.%) Ni is retained in an aluminium solid solution during cooling down the aluminium melt. The remaining iron and nickel react with aluminium to form a eutectic and intermetallic grains distributed at random in the aluminium matrix. Microhardness, HV_{50} , was found to be 2.0 GPa for the Fe–Ni alloy base, 9.3 GPa for the intermetallic layer and 0.5 GPa for the aluminium matrix. The relative error of its measurement was around 10 %.

The intermetallic layer, 90 ± 10 μm thick, at the interface between a 75 % Fe–25 % Ni alloy and the aluminium melt saturated with the alloy constituents, is one-phase (Fig. 5.16b). Elongated crystals of another phase, seen in the microstructure, were evidently formed from the melt during cooling. Microhardness value is 2.5 GPa for the alloy base, 7.6 GPa for the intermetallic layer and 0.7 GPa for the aluminium matrix. In this case, no formation of FeAl_3 was observed at dipping times 900 and 3600 sec. The intermetallic layer consisted entirely of the Fe_2Al_7 compound. Its composition ranged from 76.2 to 79.8 at.% Al, the content of Ni being 2.5 to 4.8 at.%.

The contents of iron and nickel in the aluminium solid solution were around 1.30 % (0.63 at.%) Fe and 0.47 % (0.22 at.%) Ni. Note that initially 2.5 % Fe and 0.86 % Ni were added to aluminium to obtain the saturated melt. Thus, about half of these quantities could be retained in the supersaturated Al solid solution during cooling down the aluminium melt. Some of the elongated crystals, seen in the aluminium matrix (see Fig. 5.16b), were found to be the FeAl_3 phase, while the others the Fe_2Al_7 phase.

Two intermetallic layers are observed in the transition zone between a 50 % Fe–50 % Ni alloy and the aluminium melt saturated with the alloy constituents (Fig. 5.16c). The layer adjacent to the alloy base is only about 8 μm thick and consists of the Fe_2Al_7 compound. The much thicker layer bordering the aluminium matrix tends to destroy under the influence of the liquid phase. The ternary FeNiAl_9 compound is dominant in this layer. Its microhardness is 6.2 GPa. The microhardness of the alloy base is 2.1 GPa and that of the aluminium matrix is 0.7 GPa.

The chemical composition of FeNiAl_9 ranged across the layer thickness from 81.5 at.% (67.9 %) Al, 14.5 at.% (24.9 %) Fe and 4.0 at.% (7.2 %) Ni to 83.6 at.% (70.5 %) Al, 8.7

at.% (16.0 %) Fe and 7.7 at.% (13.5 %) Ni. These values agree fairly well with those known from the Al–Fe–Ni ternary phase diagram. Chemical composition of the Fe₂Al₇ layer was 77.7 at.% (62.3 %) Al, 14.7 at.% (24.4 %) Fe and 7.6 at.% (13.3 %) Ni at a distance of 2 µm away from the alloy–Fe₂Al₇ interface and 79.7 at.% (65.1 %) Al, 13.6 at.% (22.9 %) Fe and 6.7 at.% (12.0 %) Ni at a distance of 2 µm away from the Fe₂Al₇–FeNiAl₉ interface.

A tendency to destroying proved more profound in the case of an intermetallic layer between a 25 % Fe–75 % Ni alloy and the aluminium melt saturated with the alloy constituents (Fig. 5.16d). As seen in Fig. 5.16d, relatively large intermetallic grains have separated from the alloy base and passed into the liquid phase. Microhardness values are 2.3 GPa for the alloy base, 5.3 GPa for the intermetallic grains and 0.7 GPa for the aluminium matrix.

Besides the FeNiAl₉ compound layer, two more phases were revealed at the interface between a 25 % Fe–75 % Ni alloy and the saturated aluminium melt. At a smaller dipping time of 900 sec, cracking was not so severe as at 3600 sec, and the layers adjacent to the alloy base could readily be investigated by electron probe microanalysis. The first measurement was carried out at a distance of 2 µm away from the alloy–intermetallic interface, while subsequent measurements were made at a step of 2.5 µm towards the aluminium matrix. The following set of aluminium, iron and nickel contents (at.%) was obtained (Camebax SX50):

Al	66.4	67.5	67.7	70.4	75.6	75.6	81.3	82.0	82.9
Fe	7.5	8.1	9.5	9.2	6.9	6.6	5.4	6.0	7.1
Ni	26.1	24.4	22.8	20.4	17.5	17.8	13.3	12.0	10.0

First four points are seen to be close to the composition of a ternary solid solution based on the NiAl₂ compound (33.3 at.% Ni, 66.7 at.% Al). However, such a phase does not exist according to the Al–Ni and Al–Fe–Ni equilibrium phase diagrams, the Ni-enriched phase next to NiAl₃ being Ni₂Al₃ [231, 411, 412]. As the Al content of the intermetallic layer under consideration far exceeds the upper limit of the homogeneity range of the Ni₂Al₃ phase (63.7 at.% Al [157] or 63.0 at.% Al [412]), the phase grown can hardly be regarded as Ni₂Al₃. The next two points clearly belong to the NiAl₃ phase in which about 7 at.% Fe is dissolved. The last three are in accordance with the composition of the FeNiAl₉ intermetallic compound.

This specimen was re-measured with the help of another microanalyser (Superprobe 733). Similar results were again obtained. For example, five measurements in the NiAl₂ layer at a step of 1.5 µm gave the following contents of the elements (at.%):

Al	63.5	66.8	67.0	67.6	67.7
Fe	7.3	8.9	9.0	8.1	8.8
Ni	29.2	24.3	24.0	24.3	23.5

Therefore, no systematic instrumental error was possible. Thus, nine measurements carried out in the NiAl_2 layer yield an average Al content of 67.2 at.%, with the limiting values being 63.5 to 70.4 at.%.

Unlike preceding cases, the broad fine-grained two-phase zone, 2 mm thick, is formed at the interface between a 20 % Fe–80 % Ni alloy and the saturated aluminium melt (Fig. 5.16e). The same applies to a 15 % Fe–85 % Ni alloy, the thickness of the two-phase zone being 1.7 mm. The FeNiAl_9 compound is dominant in the two-phase zone. Its fine crystals form a framework whose pores are filled with an aluminium solid solution. The NiAl_3 inclusions are relatively seldom.

The composition of FeNiAl_9 grains was found to vary from 80.6 at.% (65.7 %) Al, 2.2 at.% (3.7 %) Fe and 17.2 at.% (30.6 %) Ni to 84.0 at.% (70.9 %) Al, 3.5 at.% (6.0 %) Fe and 12.5 at.% (23.1 %) Ni. The content of nickel in the aluminium solid solution was up to 3 at.% (6.5 %), while that of iron did not exceed 0.2 at.% (0.4 %). No microhardness measurements could be carried out in two-phase zones due to the irregular shape of indentations. Microhardness was 2.4 GPa for the 20 % Fe–80 % Ni alloy base and 0.57 GPa for the aluminium matrix. In the case of a 15 % Fe–85 % Ni alloy, appropriate values are 2.1 GPa and 0.74 GPa.

As seen in Fig. 5.16f, the most complicated microstructure is formed between a 10 % Fe–90 % Ni alloy and the aluminium melt saturated with the alloy constituents. The compact one-phase intermetallic layer adjacent to the alloy base is about 8 μm thick. The next layer, 20 ± 5 μm thick, is also compact. Then, the broad (around 300 μm) two-phase zone is observed. Microhardness value is 1.9 GPa for the alloy base and 0.88 GPa for the aluminium matrix. Intermetallic layers were too thin to measure their microhardness.

The phase of composition close to NiAl_2 rather than Ni_2Al_3 has also been found at the interface between a 10 % Fe–90 % Ni alloy and the aluminium melt saturated with the alloy constituents. This phase formed a thin compact layer with even interfaces, adjacent to the Fe–Ni alloy base (see Fig. 5.16f). In this connection, it seems relevant to remind that, in investigating the Al–Ni binary phase diagram, the formula NiAl_2 , not Ni_2Al_3 , was first ascribed to a phase enriched in nickel compared to NiAl_3 [157, 159]. That might probably be due to insufficiently pure materials used.

The impurities could definitely cause a shift of the intermetallic phase composition to higher Al content ($\text{Ni}_2\text{Al}_3 \rightarrow \text{NiAl}_2$), as is readily seen from the presented data. Indeed, if the Fe content in the NiAl_2 layer is around 8 ± 1 at.%, then the Al content varies across its width from 63.5 to 70.4 at.%. However, if the Fe content lowers down to 3 or 4 at.%, the Al content is 63.6 to 64.6 at.%. The latter values are already close to the upper Al limit of the homogeneity range of the Ni_2Al_3 phase. The other elements might perhaps produce a more pronounced effect.

Clearly, this explanation is purely speculative. Due to small layer thicknesses, no structural studies could be carried out to establish whether the crystal structures of NiAl_2 and

Ni_2Al_3 were the same or different. Most likely, under non-equilibrium conditions the NiAl_2 phase forms first, especially if a third component is present. As the system tends to equilibrium, it may transform into the Ni_2Al_3 phase. Clearly, in reaction couples investigated the intermetallic layer growth conditions were far from the equilibrium state.

In contrast to the pure NiAl_3 phase, the ternary solid solution based on this phase exhibits a considerable range of homogeneity. Its composition was found to change in growing intermetallic layers from 73.4 at.% (56.3 %) Al, 7.5 at.% (11.9 %) Fe and 19.1 at.% (31.8 %) Ni to 79.7 at.% (64.5 %) Al, 2.6 at.% (4.4 %) Fe and 17.7 at.% (31.1 %) Ni.

The composition of the FeNiAl_9 grains present at the interface of a 10 % Fe–90 % Ni alloy and aluminium varied within the homogeneity range of the FeNiAl_9 phase from 81.2 at.% (66.8 %) Al, 5.4 at.% (9.3 %) Fe and 13.4 at.% (23.9 %) Ni to 84.6 at.% (72.0 %) Al, 3.9 at.% (6.8 %) Fe and 11.5 at.% (21.2 %) Ni. Of 8.1 % Ni and 0.51 % Fe added initially to aluminium in order to obtain the saturated melt at 700 °C, up to 7.2 % (3.4 at.%) Ni and 0.2 % (0.1 at.%) Fe are retained in an aluminium solid solution formed during cooling of this melt to room temperature.

To show the influence of dissolution of the Fe-Ni alloy base into liquid aluminium on the process of layer formation, two sets of experiments were carried out at 700 °C and a dipping time of 900 s. In the first set, the saturated aluminium melts were used, so that the dissolution of the solid in the liquid phase did not occur. In the second, pure liquid aluminium was employed. In this case, the solid alloy specimen was rotated at an angular speed of 24.0 rad sec⁻¹ to ensure its relatively rapid dissolution in liquid aluminium [411, 412]. In the first set of experiments the thickness of intermetallic layers formed at interfaces was a few times greater than that in the second, as is illustrated in Fig. 5.17. Moreover, with some Fe-Ni alloys even the number of the layers was different.

Similar experiments have also been carried out with Fe-Cr alloys [413-415]. The results obtained are shown in Fig. 5.18 [413, 414].

As seen in Fig. 5.17a, three layers (NiAl_2 , NiAl_3 and FeNiAl_9) are present at the interface between a 25 % Fe–75 % Ni alloy and the saturated aluminium melt, whereas only two of them (NiAl_3 and FeNiAl_9) survive under conditions of simultaneous dissolution in liquid aluminium (Fig. 5.17b), the total thickness of the layers being around 30 and 10 µm, respectively.

Whenever pure liquid aluminium was employed, the content of aluminium in the NiAl_3 layer was close to the lower Al limit of the homogeneity range of the ternary solid solution based on the NiAl_3 phase (73.4 at.% or 56.3 %). The FeNiAl_9 layer contained 87.7 at.% (77.0 %) Al, 4.6 at.% (8.3 %) Fe and 7.7 at.% (14.7 %) Ni. The value 87.7 at.% (77.0 %) is the upper Al limit of the homogeneity range of the FeNiAl_9 phase present as a separate layer in reaction couples.

The total thickness of the Fe_2Al_7 and FeNiAl_9 intermetallic layers at the interface between a 50 % Fe–50 % Ni alloy and aluminium was 25 to 30 µm in the case of the saturated melt

and 10 to 12 μm under conditions of simultaneous dissolution in pure liquid aluminium. In the latter case the Al content (76.7 at.%) in the Fe_2Al_7 layer was close to the lower Al limit of the homogeneity range of the Fe_2Al_7 phase, while that in the FeNiAl_9 layer varied from 82.3 to 87.7 at.%.

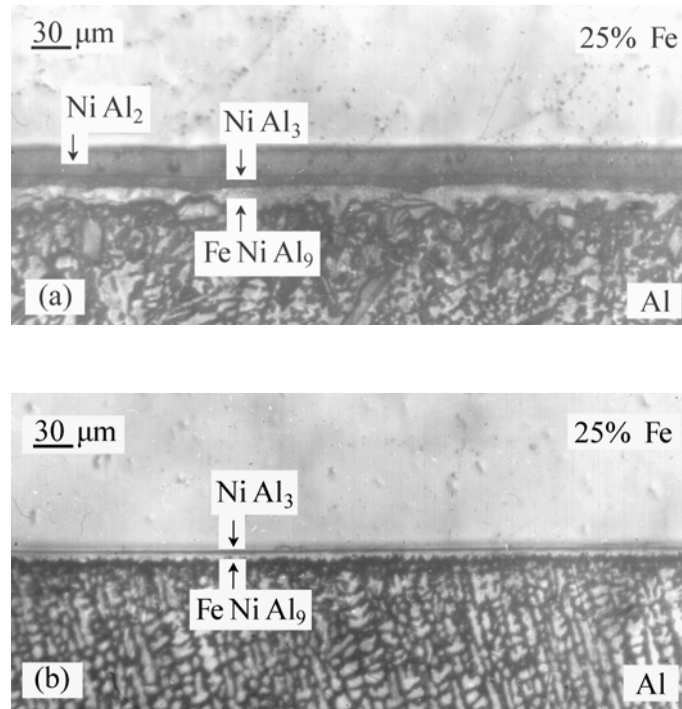


Fig. 5.17. Optical micrographs of the transition zone between a 25 % Fe–75 % Ni alloy and aluminium. Temperature 700 °C, dipping time 900 s. Initial liquid phase: (a) aluminium melt saturated with the alloy constituents, (b) pure aluminium ($\omega = 24.0 \text{ rad s}^{-1}$).

It is noteworthy that the intermetallic layer formed at the interface between a 75 % Fe–25 % Ni alloy and pure aluminium exhibited a composition range covering the ranges of homogeneity of both the FeAl_3 and Fe_2Al_7 phases. Three EPMA measurements across its width (10 to 12 μm) at a step of 3 μm gave the following contents (at.%):

Al	73.7	78.3	80.2
Fe	19.3	19.2	17.3
Ni	7.0	2.5	2.5

In the case of the saturated melt (in the absence of dissolution), the intermetallic layer thickness was $55 \pm 5 \mu\text{m}$, while its composition varied from 76.2 at.% (60.3 %) Al, 17.5 at.% (28.8 %) Fe and 6.3 at.% (10.9 %) Ni to 78.4 at.% (63.5 %) Al, 19.1 at.%(32.0 %) Fe and 2.6 at.% (4.5 %) Ni. This composition corresponds to the Fe_2Al_7 phase.

It may thus be concluded that the FeAl_3 and Fe_2Al_7 phases are formed at 700 °C at the interface between a Fe–Ni alloy and the aluminium melt saturated with the alloy constituents, if the Ni content of initial Fe–Ni alloys is less than or equal to 50 %. If this content is 50 % or more, the layers of the FeNiAl_9 , NiAl_2 and NiAl_3 phases are formed, with FeNiAl_9 being the dominant phase.

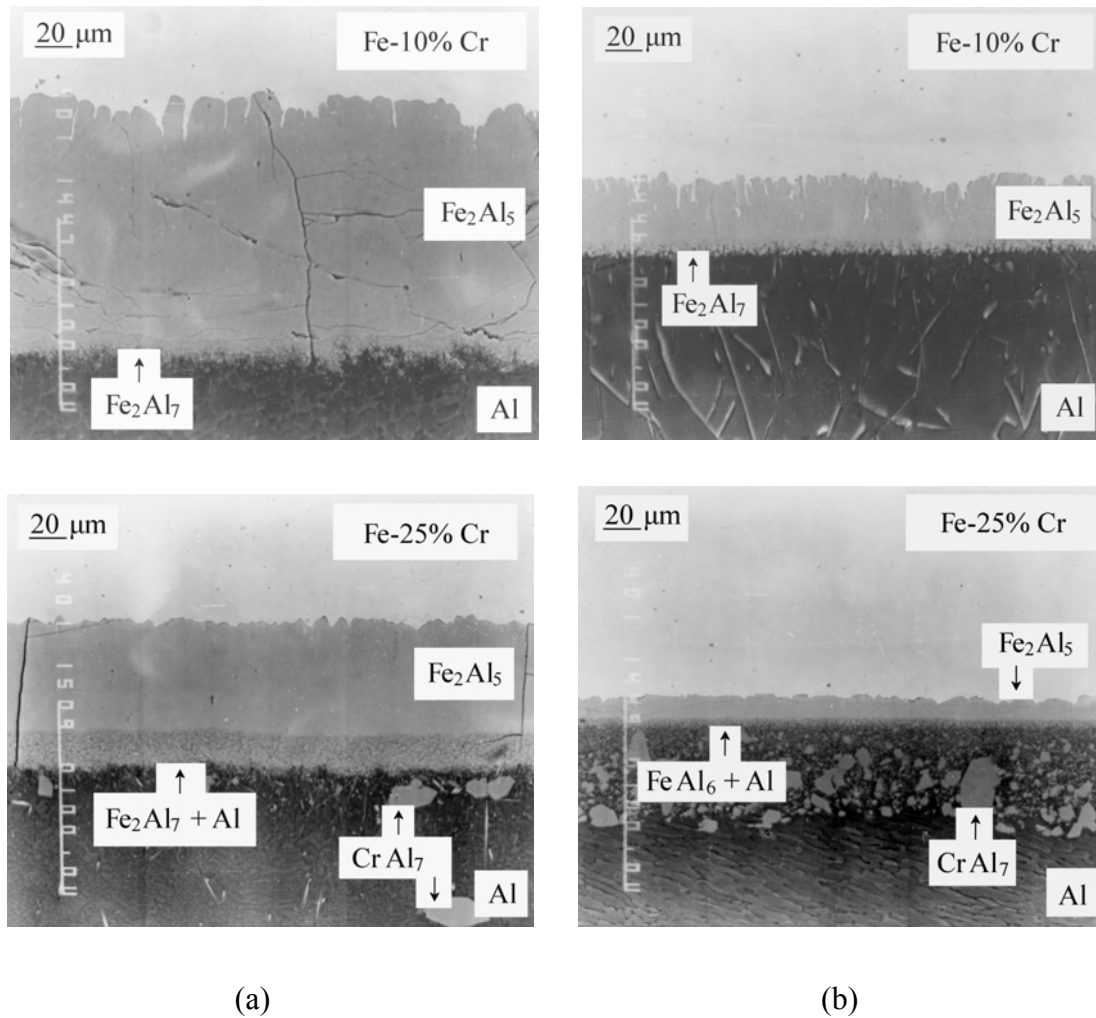


Fig. 5.18. Secondary electron image (SEI) of the transition zone between Fe–Cr alloys and aluminium. Temperature 700 °C, dipping time 3600 s. Initial liquid phase: (a) aluminium melt saturated with the alloy constituents, (b) pure aluminium ($\omega = 24.0 \text{ rad s}^{-1}$).

The FeAl_3 , Fe_2Al_7 , NiAl_2 and NiAl_3 phases form one-phase layers, whereas the FeNiAl_9 phase can form either a one-phase layer or a two-phase zone with an aluminium solid solution. The formation of broad two-phase zones is only typical of Fe–Ni alloys containing 10 to 20 % Fe. The Al content of the ternary solid solutions based on these intermetallic phases varies in growing layers in the following ranges:

FeAl₃: 73.7 to 75.5 at.%,
Fe₂Al₇: 76.2 to 79.8 at.%,
FeNiAl₉: 80.6 to 87.7 at.%,
NiAl₂: 63.5 to 70.4 at.%,
NiAl₃: 73.4 to 79.7 at.%.

The Fe:Ni ratio of the intermetallic phases present in growing layers is strongly dependent upon the composition of initial Fe-Ni alloys. In some cases, this ratio somewhat exceeds the limits predicted by the Al-Fe-Ni equilibrium diagram.

Generally, two intermetallic layers were found to form at the interface between Fe-Cr alloys and aluminium, namely, a compact uniform layer adherent to the alloy base and a porous non-uniform layer bordering the aluminium matrix (see Fig. 5.18). In many cases, the latter actually consisted of separate grains weakly linked or not linked at all with each other. This means that, whenever present, its formation might be partly a result of a solid-state chemical reaction and partly a consequence of crystallisation from the melt. On the contrary, the layer adjacent to the alloy base was formed exclusively in the course of another solid-state chemical reaction.

To identify the intermetallic phases, X-ray patterns were taken from different sections of the intermetallic layers. Experimental values of the interplanar distances were compared with those available in the literature for the intermetallics of the Al-Fe and Al-Cr systems [229, 230]. Two main constituent phases were Fe₂Al₅ and FeAl₃, with the compact layer being the Fe₂Al₅ phase and the porous layer the FeAl₃ (Fe₂Al₇) phase. It should be noted that X-ray patterns of the porous layer also contained a number of unidentifiable, very weak diffraction peaks, indicative of the presence of small amounts of other intermetallic compounds.

To reveal the chemical composition of the phases formed, EPMA measurements were carried out across the transition zone up to a depth of 100 µm into the alloy bulk and 100 µm into the aluminium bulk. The composition of the compact layer was found to correspond to that of the Fe₂Al₅ phase (28.6 at.% Fe, 71.4 at.% Al). A change of elemental content across its thickness (69.0-72.9 at.% Al) agrees fairly well with the width (70.0-72.5 at.% Al) of the homogeneity range of this intermetallic compound.

Somewhat lower aluminium contents obtained at some places near the Fe₂Al₅-alloy interface are easily explainable. When carrying out the EPMA measurements, it was noticed that, wherever cracks stretching along the intermetallic layer were present (see Fig. 5.18a), the aluminium content dropped very considerably, even down to the composition of the adjacent phase FeAl₂. This may be illustrated by the following two sets of aluminium percentage (at.%) obtained on a “75 % Fe–25 % Cr alloy + saturated aluminium” sample (700 °C, 3600 s):

without a crack	69.11	69.12	69.35	69.47	70.08	70.99	71.68	71.99	72.23	72.50
with a crack	<u>65.04</u>	<u>65.05</u>	<u>65.26</u>	<u>65.85</u>	<u>66.18</u>	69.07	70.27	70.51	71.06	71.36

In both cases, the measurements were made at a step of 2 μm , starting from the alloy-intermetallic layer interface. Underlined values evidently represent the aluminium content of FeAl_2 , though this phase does not form a continuous layer. The mechanism of its formation is as follows. The crack separates some part of the Fe_2Al_5 layer from its main body. As a result, a new reaction couple consisting of an iron-chromium alloy and the Fe_2Al_5 phase is formed. The formation of the FeAl_2 intermetallic compound in this couple is due to two chemical reactions: $\text{Fe}_2\text{Al}_5 = 2\text{FeAl}_2 + \text{Al}_{\text{dif}}$ and $2\text{Al}_{\text{dif}} + \text{Fe} = \text{FeAl}_2$.

EPMA measurements showed the porous layer to consist of grains of Fe_2Al_7 or FeAl_6 , with an aluminium solid solution between them. The layer also contained inclusions of FeAl_3 and occasionally Fe_2Al_5 .

The coarse grains in the vicinity of the Fe-Cr alloy-aluminium interface are the CrAl_7 phase, also designated $\text{Cr}_2\text{Al}_{13}$ or $\text{Cr}_7\text{Al}_{45}$, with the homogeneity range 86.3-87.6 at.% Al [417] or 87.3-88.5 at.% Al [410]. It is worth mentioning that, when formed under non-equilibrium conditions, this phase has a composition closer to CrAl_6 than to CrAl_7 . In the presence of a third metal (Fe, Mn, etc.), the CrAl_6 phase is known to give rise to a few metastable phases of five-fold symmetry [418] whose composition corresponds to the chemical formula $\text{Cr}_{0.7}\text{Fe}_{0.3}\text{Al}_6$.

Fine grains near the Fe_2Al_5 layer had an approximate composition of $\text{Cr}_{0.67}\text{Fe}_{0.33}\text{Al}_{13}$. Their size increased with increasing distance from this layer towards aluminium, while the composition approached CrAl_7 . The phase sequence observed and composition profile are probably a result of a series of transformations, namely $\text{Cr}_{0.67}\text{Fe}_{0.33}\text{Al}_{13} \rightarrow \text{Cr}_{0.7}\text{Fe}_{0.3}\text{Al}_6 \rightarrow \text{CrAl}_6 \rightarrow \text{CrAl}_7$. Iron solubility in the latter phase reaches 4 at.%.

The effect of dissolution on the process of intermetallic-layer formation is visualised in Fig. 5.18 where two sets of micrographs with the (a) saturated and (b) undersaturated melt are presented and also in Fig. 5.19 where the layer thickness-time dependence for a 90 % Fe–10 % Cr alloy and the saturated (1) and undersaturated (2) melt is shown [414]. Dissolution is seen to cause about a three-fold decrease in layer thickness. Moreover, under conditions of simultaneous dissolution in the undersaturated melt only the compact Fe_2Al_5 layer survives, whereas other intermetallic phases (FeAl_6 , Fe_2Al_7 , FeAl_3) exist as separate inclusions in the aluminium matrix.

Equation (5.30) was again employed to evaluate the thickness of the Fe_2Al_5 layer at the interface of a Fe–Cr alloy and aluminium during dissolution of the alloy base in the undersaturated melt. When employing this equation, the main difficulty to overcome is evaluating the layer growth-rate constant, k_1 . It can be done as follows.

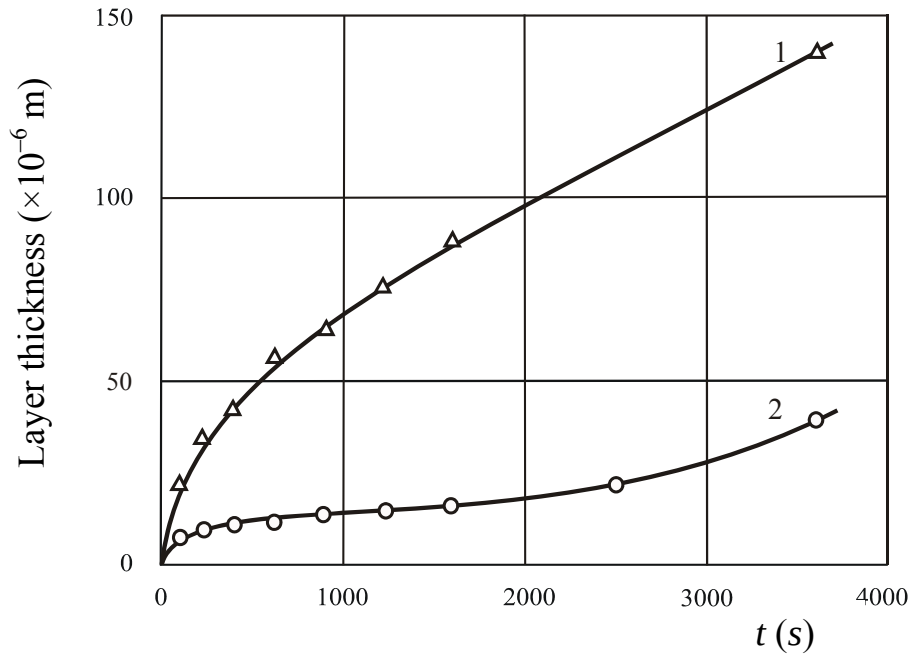


Fig. 5.19. The effect of dissolution on the process of intermetallic compound-layer formation at 700 °C for a 90 % Fe–10 % Cr alloy [414]. 1, total thickness of the Fe_2Al_5 and Fe_2Al_7 layers, saturated aluminium melt; 2, thickness of the Fe_2Al_5 layer (Fe_2Al_7 layer is missing), undersaturated aluminium melt, angular speed of disc rotation 24.0 rad s^{-1} .

1. If a single-phase intermetallic layer occurs in the case of both saturated and undersaturated melts, its value is found from the experimental layer thickness-time dependence for the saturated melt.

2. The layer growth-rate constant is evaluated by equation (5.30) using one or a few initial thickness values of an experimental thickness-time dependence for the undersaturated melt. Then, other values can readily be calculated from this equation, thereby significantly reducing the amount of experimental work.

3. If the data on the solid-state layer-growth rate are available, a value of k_1 can be estimated by extrapolation from the temperature dependence. Clearly, the temperature must not differ considerably in both cases.

With the Fe–Cr alloys investigated, the number of intermetallic layers growing from saturated and undersaturated melts is different (two, namely Fe_2Al_5 and Fe_2Al_7 , in the case of the saturated aluminium melt, and only one, Fe_2Al_5 , from the undersaturated melt). Therefore, the layer-growth constant, k_1 , can only be calculated using a few experimentally determined points of the layer thickness-time dependence for the undersaturated melt, preferably at short times. This makes the calculation of other points of that dependence possible.

Since the dissolution rate diminishes exponentially from b_0 to b_t in the time range $0 - t$, calculations are carried out twice for each point by putting in the denominator of equation (5.30) first equal to $(b_0 + b_t)/2$ and then b_t . Thus, two sets of the Fe_2Al_5 layer thickness are obtained. The first set represents the underestimated values, x_{under} , whereas the second set gives the overestimated ones, x_{over} . Experimental values, x_{exp} , must clearly lie somewhere in between.

For both alloys, the layer growth-rate constant, k_1 , was calculated from equation (5.30) using the first two points $t = 100$ s and $t = 225$ s, with $x_{\text{exp}} = 9 \times 10^{-6}$ m and $x_{\text{exp}} = 10 \times 10^{-6}$ m for a 90 % Fe–10 % Cr alloy and $x_{\text{exp}} = 5.0 \times 10^{-6}$ m and $x_{\text{exp}} = 5.2 \times 10^{-6}$ m for a 75 % Fe–25 % Cr alloy. Appropriate values of k_1 were found to be $14.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $5.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. These are the average of $b_0 x_{100}$ and $b_{100} x_{225}$ (subscripts designate time). Other necessary quantities were as follows.

1. 90 % Fe–10 % Cr alloy:

- (1) $k = 4.2 \times 10^{-5} \text{ m s}^{-1}$ [413],
- (2) $c_s = 66.72 \text{ kg m}^{-3}$ (2.5 % Fe + 0.28 % Cr [413]),
- (3) $a = 4.2 \times 10^{-4} \text{ s}^{-1}$,
- (4) $b_0 = 1.51 \times 10^{-6} \text{ m s}^{-1}$;

2. 75 % Fe–25 % Cr alloy:

- (1) $k = 3.0 \times 10^{-5} \text{ m s}^{-1}$ [413],
- (2) $c_s = 70.08 \text{ kg m}^{-3}$ (2.2 % Fe + 0.72 % Cr [413]),
- (3) $a = 3.0 \times 10^{-4} \text{ s}^{-1}$,
- (4) $b_0 = 1.13 \times 10^{-6} \text{ m s}^{-1}$.

The final results are presented in Tables 5.11 and 5.12. From these tables, equation (5.30) is seen to produce a satisfactory fit to the experimental data.

Note that the intermetallic layer growth-rate constant, k_1 , tends to rise slightly with increasing time because of the anisotropy of growth of the Fe_2Al_5 phase [170]. Therefore, as might be expected, the experimental values of the Fe_2Al_5 layer thickness, calculated with the use of a smaller value of this constant determined from the initial points of the layer thickness-time plots, are closer to the overestimated than to underestimated ones.

Table 5.11. Calculated and experimental thicknesses, x , of the Fe_2Al_5 intermetallic layer for a 90 % Fe–10 % Cr alloy and the undersaturated aluminium melt at a temperature of 700 °C and $\omega = 24.0 \text{ rad s}^{-1}$.

Time (s)	$(b_0 + b_t)/2$ ($\times 10^{-6} \text{ m s}^{-1}$)	x_{under} ($\times 10^{-6} \text{ m}$)	b_t ($\times 10^{-6} \text{ m s}^{-1}$)	x_{over} ($\times 10^{-6} \text{ m}$)	x_{exp} ($\times 10^{-6} \text{ m}$)
100	1.48	-	1.45	-	9.0
225	1.44	-	1.37	-	10.0
400	1.39	10.1	1.28	11.0	11.0
625	1.33	10.6	1.16	12.2	12.0
900	1.27	11.1	1.03	13.7	13.5
1225	1.20	11.8	0.90	15.7	15.0
1600	1.14	12.4	0.77	18.3	16.0
2500	1.02	13.8	0.53	26.6	22.5
3600	0.92	15.3	0.33	42.7	40.0

Table 5.12. Calculated and experimental thicknesses, x , of the Fe_2Al_5 intermetallic layer for a 75 % Fe–25 % Cr alloy and the undersaturated aluminum melt at a temperature of 700°C and $\omega = 24.0 \text{ rad s}^{-1}$.

Time (s)	$(b_0 + b_t)/2$ ($\times 10^{-6} \text{ m s}^{-1}$)	x_{under} ($\times 10^{-6} \text{ m}$)	b_t ($\times 10^{-6} \text{ m s}^{-1}$)	x_{over} ($\times 10^{-6} \text{ m}$)	x_{exp} ($\times 10^{-6} \text{ m}$)
100	1.11	-	1.10	-	5.0
225	1.10	-	1.06	-	5.2
400	1.06	5.2	1.00	5.5	5.5
625	1.03	5.3	0.94	5.9	6.0
900	1.00	5.5	0.86	6.4	6.5
1225	0.95	5.8	0.78	7.1	7.0
1600	0.91	6.0	0.70	7.9	8.0
2500	0.83	6.6	0.53	10.4	9.5
3600	0.75	7.3	0.38	14.5	12.0

5.5: Interfacial interaction of nickel and cobalt with liquid Pb-free soldering alloys

Since lead falls into the range of toxic metals, conventional Sn-Pb solders are gradually being replaced with other soldering alloys. It is not surprising, therefore, that Pb-free solders are receiving marked attention in scientific and technical communities. As evidenced from the literature [276, 419-449], most frequently employed components of new Pb-free solders are Ag, Au, Cu, Bi, In, Sb, Sn and Zn. In this section, dissolution kinetics and the effect of dissolution on the growth rate of intermetallic layers at the interface of solid nickel and cobalt with liquid bismuth- and tin-based alloys will be considered [450-455].

Experimental procedure did not differ essentially from that described in preceding sections. The materials used were electrolytic-grade nickel (99.98 % Ni) and cobalt (99.98 % Co) plates, tin (99.93 % Sn), bismuth (99.999 % Bi) and indium (99.999 % In) and antimony (99.91 % Sb) slabs, and zinc granules (99.94 % Zn).

5.5.1: Interaction of solid nickel with liquid bismuth and bismuth-based alloys

The investigation was aimed mainly at (i) determining the parameters characterizing dissolution kinetics of solid nickel in bismuth and 51 % Bi–42 % Sn–5 % In–2 % Zn alloy melts, (ii) establishing which of the intermetallic compounds (NiBi or NiBi₃ or both) are formed as separate layers between solid nickel and liquid bismuth or its alloy, (iii) visualising the effect of dissolution on the rate of growth of an intermetallic-compound layer and its morphology [450].

The Nernst-Shchukarev relation (equations (5.8)-(5.10)) was found to give a good fit to the experimental data on dissolution kinetics of nickel in liquid bismuth and its alloy. The Ni solubility in bismuth is 0.32 ± 0.02 % at 300 °C and 0.39 ± 0.03 % at 350 °C. Somewhat unexpectedly, much lower solubility values, 0.0053 ± 0.0009 % at 300 °C and 0.015 ± 0.003 % at 350 °C, were obtained for a 51 % Bi–42 % Sn–5 % In–2 % Zn alloy. Therefore, experiments were also carried out at 250, 400 and 450 °C to establish the solubility temperature dependence and then to find from it by extrapolation the solubility value at temperatures close to the melting point of the alloy. This dependence was found to obey a relation of the Arrhenius type

$$c_s = (3.5^{+0.4}_{-0.3}) \times 10^3 \exp [-(63.5 \pm 0.5) \text{ kJ mol}^{-1} / RT] \text{ \%}.$$

From this equation, a value of 0.00005 % is obtained by extrapolation for the solubility of nickel in the alloy at 150 °C. Low solubility values, 0.00005 to 0.094 % in the 150–450 °C temperature range, of nickel in the alloy could hardly be expected judging from the solubility values in binary systems of nickel with the main alloy constituents bismuth (for example, at 300 °C $c_s = 0.32$ % Ni) and tin ($c_s = 0.26$ % Ni at that temperature [456]). In view of their relatively low content, the influence of indium and zinc cannot be essential. Probably, a large drop in solubility arises because the alloy composition is close to that of the binary eutectic Bi-Sn (57 % Bi and 43 % Sn) [157, 159].

Differential thermal analysis showed that the alloy starts melting at 139 °C. This is just the eutectic temperature of the Bi-Sn binary system. It still remains to find out whether lowering the solubility of a transition metal in low-melting alloys of near-eutectic composition, compared to its solubility in pure alloy components, is characteristic only of the system investigated or of others as well.

Though at a given temperature the solubility values of nickel in liquid bismuth and the alloy differ considerably, appropriate dissolution-rate constants are close. For example, at 350 °C c_s is 0.39 % Ni for bismuth and 0.015 % Ni for the alloy, while k is $4.0 \times 10^{-5} \text{ m s}^{-1}$ for the former and $3.8 \times 10^{-5} \text{ m s}^{-1}$ for the latter at $\omega = 24.0 \text{ rad s}^{-1}$ (Table 5.13). Listed in Table 5.13 are also diffusion coefficients of nickel into liquid bismuth and a 51% Bi–42% Sn–5% In–2% Zn alloy.

Table 5.13. Dissolution-rate constants at $\omega = 24.0 \text{ rad s}^{-1}$ and diffusion coefficient of nickel into liquid bismuth and a 51 % Bi–42 % Sn–5 % In–2 % Zn alloy

Temperature (°C)	Liquid phase	$k (\times 10^{-5} \text{ m s}^{-1})$	$D (\times 10^{-9} \text{ m}^2 \text{ s}^{-1})$
300	Bi	1.5	0.23 ± 0.03
350	Bi	4.0	1.0 ± 0.1
300	alloy	1.2	0.17 ± 0.04
350	alloy	3.8	0.96 ± 0.09

With bismuth as a melt material, a single-phase intermetallic layer was found to form from both saturated and undersaturated melts, as illustrated in Fig. 5.20. Average contents of the components determined by EPMA are 24.9 at.% Ni and 75.1 at.% Bi. These values are in accordance with the stoichiometry of the NiBi_3 intermetallic compound. No evidence of the presence of the NiBi intermetallic compound at the interface of nickel and molten bismuth was found.

From Fig. 5.20, it is easy to notice that the NiBi_3 layer thickness is much less in the case of the undersaturated melt compared to the case of the saturated melt, other conditions being identical. Thus, the effect of dissolution on the layer-growth rate is very appreciable.

It should be noted that thick NiBi_3 layers tend to be destroyed under the influence of the saturated bismuth melts. Clearly, in such a case it was hardly possible to establish a reliable layer thickness-time dependence. Therefore, a value of the layer growth-rate constant, k_1 , necessary for calculations of layer thicknesses using equation (5.30), was evaluated by extrapolation from the temperature dependence [164]

$$k_1 = 0.49 \times 10^{-6} \exp(-67100/RT) \text{ m}^2 \text{ s}^{-1}$$

where R is in $\text{J mol}^{-1} \text{ K}^{-1}$ and T in K .

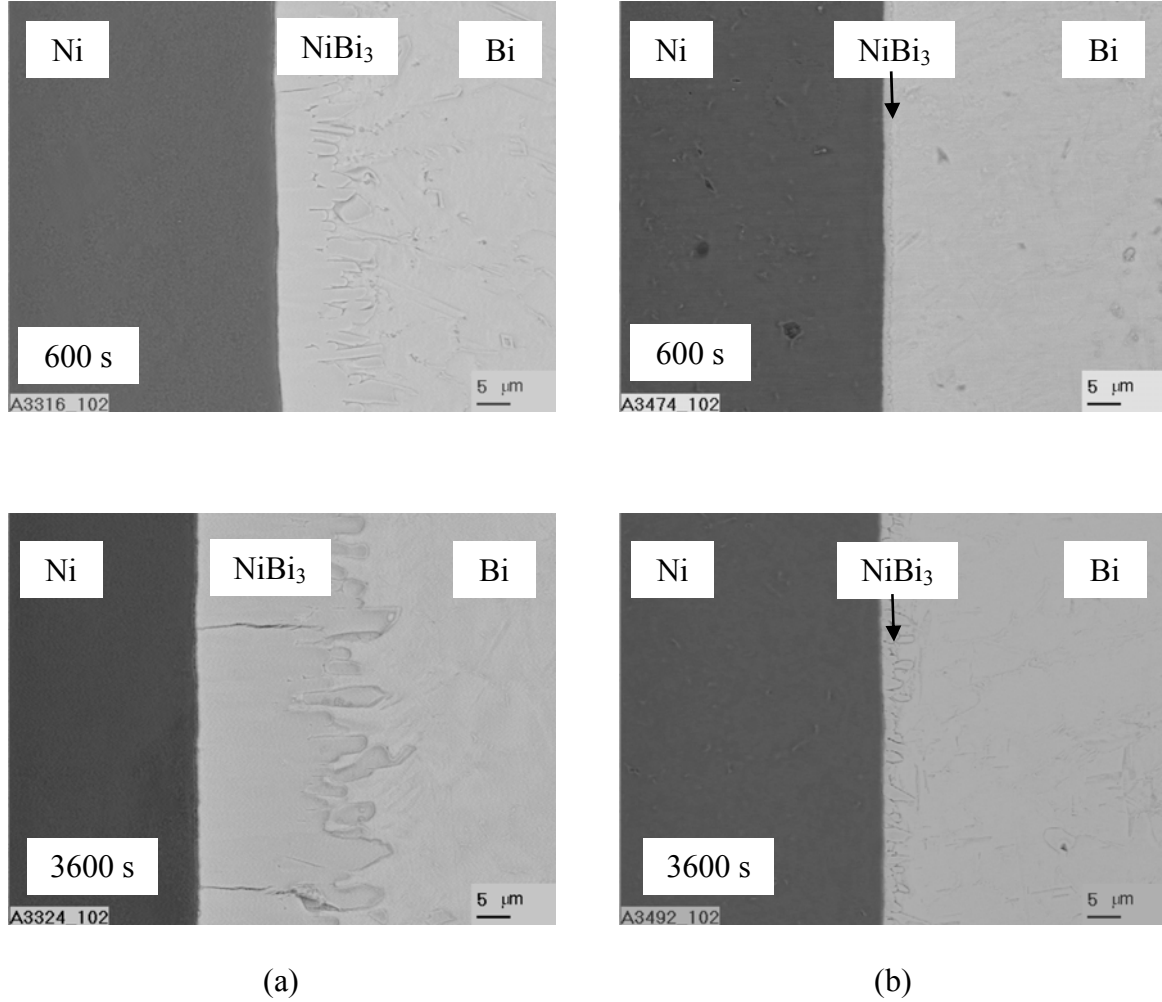


Fig. 5.20. Backscattered electron image (BEI) of the transition zone formed between nickel and bismuth at a temperature of 350 °C. (a) saturated melts, (b) undersaturated melts, $\omega = 24.0 \text{ rad s}^{-1}$ [450].

This dependence was obtained when investigating the NiBi_3 layer-growth kinetics between two solid phases (nickel and bismuth). Extrapolation yields for k_1 a value of $3.7 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ at 300 °C and $1.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 350 °C. The other quantities used in calculations were as follows.

1. 300 °C:

- (1) $k_1 = 3.7 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$
- (2) $k = 1.5 \times 10^{-5} \text{ m s}^{-1}$
- (3) $c_s = 27.04 \text{ kg m}^{-3}$ (0.32% Ni in Bi [450])
- (4) $\rho_{\text{int}} = 10.1 \times 10^3 \text{ kg m}^{-3}$ [165]
- (5) $s/\nu = 10.0 \text{ m}^{-1}$
- (6) $a = 1.5 \times 10^{-4} \text{ s}^{-1}$
- (7) $b_0 = 4.70 \times 10^{-7} \text{ m s}^{-1}$

2. 350 °C:

- (1) $k_1 = 1.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$
- (2) $k = 4.0 \times 10^{-5} \text{ m s}^{-1}$
- (3) $c_s = 32.76 \text{ kg m}^{-3}$ (0.39% Ni in Bi [450])
- (4) $\rho_{\text{int}} = 10.1 \times 10^3 \text{ kg m}^{-3}$ [165]
- (5) $s/\nu = 10.0 \text{ m}^{-1}$
- (6) $a = 4.0 \times 10^{-4} \text{ s}^{-1}$
- (7) $b_0 = 1.52 \times 10^{-6} \text{ m s}^{-1}$

Final results are presented in Table 5.14. Equation (5.30) again produces a quite satisfactory fit to the experimental data. It is also worth noting that the range in which the intermetallic-layer thickness can vary is rather narrow, even though the time interval (600-3600 s) is relatively wide.

Table 5.14. Comparison of experimental thicknesses of the NiBi₃ layer grown from undersaturated bismuth melts at $\omega = 24.0 \text{ rad s}^{-1}$ with those calculated from equation (5.30)

Temperature (°C)	Time (s)	x_{under} ($\times 10^{-6} \text{ m}$)	x_{exp} ($\times 10^{-6} \text{ m}$)	x_{over} ($\times 10^{-6} \text{ m}$)
300	600	0.82	0.85 ± 0.10	0.86
	3600	1.00	1.25 ± 0.15	1.35
350	600	0.88	0.90 ± 0.15	1.00
	3600	1.3	2.5 ± 0.5	3.3

With a 51 % Bi–42 % Sn–5 % In–2 % Zn alloy as a melt material, a thin intermetallic layer occurs at the Ni-alloy interface. After 10800 s (3 h) holding at 350 °C and an angular disc rotation speed of 6.45 rad s^{-1} , its thickness is around $1.5 \text{ }\mu\text{m}$, as illustrated in Fig. 5.21. With saturated melts, the layer thickness varies at this temperature from about $0.8 \text{ }\mu\text{m}$ at a holding time of 600 s to $2.0 \text{ }\mu\text{m}$ at 3600 s. From those values, the layer growth-rate constant can be estimated from a parabolic relation of the type $k_1 = x^2/2t$ as $5.5 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$.

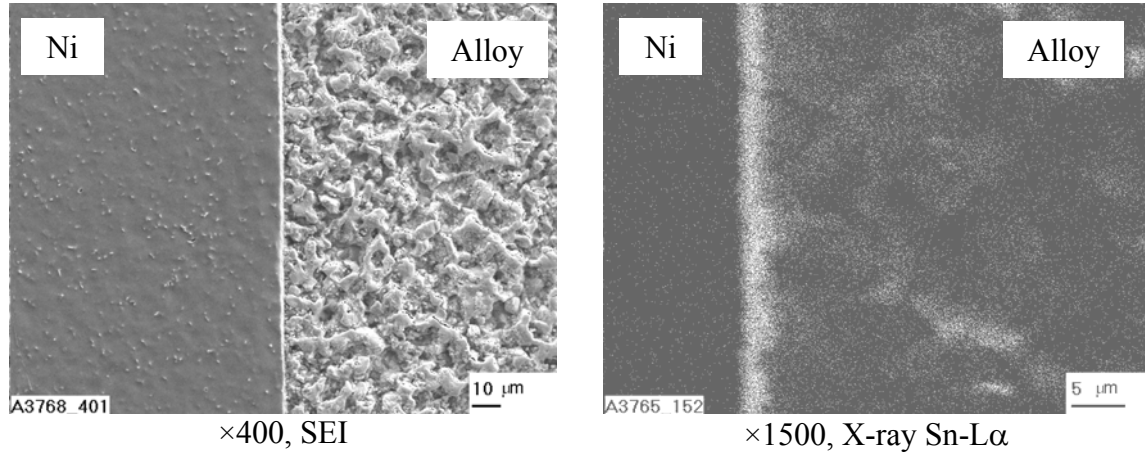


Fig. 5.21. Secondary electron image (SEI) and X-ray map of the transition zone formed between nickel and a 51 % Bi–42 % Sn–5 % In–2 % Zn alloy after 3h holding at 350 °C and a disc rotational speed of 6.45 rad s^{-1} [450].

At a temperature of 300 and 350 °C, a disc rotational speed of 24.0 rad s^{-1} and a holding time of up to 3600 s, no intermetallic layer was found to form at the solid-liquid interface under conditions of dissolution of nickel in the undersaturated 51 % Bi–42 % Sn–5 % In–2 % Zn alloy melt [450]. It means that the rate of chemical interaction at the layer interfaces, resulting in the growth of the layer, is less than the rate of its dissolution in the melt, so that in equation (5.26) $k_0 < b$ at any value of t in the 600–3600 s range. Hence, in the case under consideration the layer formation can readily be prevented, if the rate of dissolution is maintained sufficiently high. Small additions of Sb (1 %), Te and Se (0.5 % each), instead of corresponding amounts of Sn and Zn, do not change significantly the intermetallic-layer thickness [450].

5.5.2: Interaction of solid nickel with liquid Sn–Bi–In–Zn–Sb alloys

Interfacial reactions of nickel with 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb and 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb soldering alloys have been investigated [451– 453]. As evidenced in Fig. 5.22, temperature dependence of the solubility of nickel in those alloys

obeys a relation of the Arrhenius type. Application of the least-squares fit method yields the following equations:

$$c_s = 4.94 \times 10^2 \exp(-39500/RT) \%$$

for a 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb alloy,

$$c_s = 4.19 \times 10^2 \exp(-40200/RT) \%$$

for a 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb alloy,

where R is in $\text{J mol}^{-1} \text{K}^{-1}$ ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$) and T in K. The linear regression coefficient is 0.99963 for the former alloy and 0.99969 for the latter.

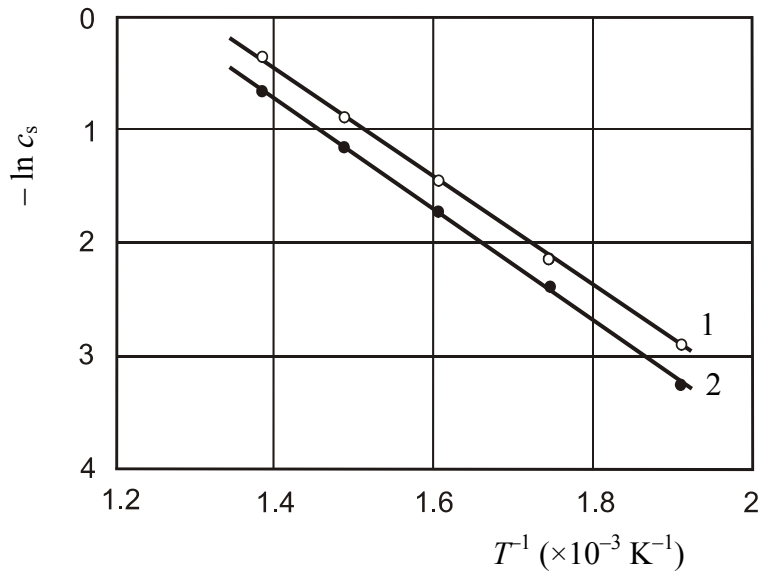


Fig. 5.22. Temperature dependence of the solubility of nickel in liquid soldering alloys. (1) 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb alloy, (2) 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb alloy.

Note that relatively small amounts of additives produce a very considerable effect on the solubility of nickel in tin-based soldering alloys. The temperature dependence of the nickel solubility in pure tin at 300–700 °C is reported to obey the equation [456]

$$c_s = 5.34 \times 10^2 \exp(-36900/RT) \%.$$

Comparison of the solubility values calculated from these three temperature dependences is provided in Table 5.15. Twenty percent of additives (Bi, In, Zn and Sb) are seen to produce more than a two-fold decrease in nickel solubility values. Such a large drop could not be expected judging from the solubility values in binary systems of nickel with the main alloy constituents tin and bismuth.

Table 5.15. Comparison of nickel solubility values in tin and soldering alloys

Temperature (°C)	Nickel solubility, c_s (%)		
	100 % Sn [456]	87.5 % Sn...	80 % Sn...
250	0.11	0.056	0.040
300	0.23	0.12	0.091
350	0.43	0.24	0.18
400	0.73	0.42	0.32
450	1.15	0.69	0.52

For example, at 350 °C c_s is 0.43 % Ni for tin [456] and 0.39 % Ni for bismuth [450]. In view of their relatively low content in soldering alloys, the influence of indium, zinc and antimony is insignificant. Note that for a similar alloy containing 51 % Bi, 42 % Sn, 5 % In and 2 % Zn the nickel solubility at 350°C is much lower, namely, 0.015 % [450]. These data again provide evidence that the solubility of nickel decreases as the solder composition approaches that of the binary Bi-Sn eutectic.

Probably, lowering the nickel solubility with increasing bismuth content of the alloys is connected with the increasing degree of ordering of the liquid structure that becomes most perfect at the eutectic composition. In the structure corresponded to the eutectic composition, little room remains to accommodate foreign (nickel) atoms. Direct experimental evidence, for example from X-ray diffraction, is needed to verify this viewpoint.

Dissolution-rate constants of nickel in Sn–Bi–In–Zn–Sb soldering alloys at an angular rotational speed of 24.0 rad s⁻¹ are presented in Table 5.16. Also included in the table are appropriate diffusion coefficients.

Two sets of experiments, with saturated and undersaturated melts, were again carried out to visualize the effect of dissolution on the process of intermetallic compound-layer formation at the interface between nickel and liquid soldering alloys. In the case of undersaturated melts, the nickel disc was being rotated during the run at an angular speed of 24.0 rad s⁻¹.

With both soldering alloys, a single-phase intermetallic layer was found to form from both saturated and undersaturated melts, as illustrated in Fig. 5.23. Phase identification was carried out by X-ray diffraction (XRD). Experimental values of 2θ and interplanar distances (d -spacing) were found to agree fairly well with those reported for the Ni₃Sn₄ intermetallic compound having monoclinic unit cell parameters $a = 1.2200$ nm, $b = 0.4055$ nm, $c = 0.5215$ nm, $\beta = 105.03^\circ$ [457].

Table 5.16. Dissolution-rate constants at $\omega = 24.0 \text{ rad s}^{-1}$ and diffusion coefficient of nickel in liquid Sn–Bi–In–Zn–Sb soldering alloys

Alloy	Temperature (°C)	k ($\times 10^{-5} \text{ m s}^{-1}$)	D ($\times 10^{-9} \text{ m}^2 \text{ s}^{-1}$)	
			Eq. (5.6)	Eq. (5.7)
87.5 % Sn...	250	1.3	0.20	0.22
	300	2.7	0.55	0.59
	350	4.6	1.21	1.33
	400	5.4	1.52	1.68
	450	6.2	1.82	2.02
80 % Sn...	250	1.1	0.15	0.16
	300	2.6	0.52	0.56
	350	4.5	1.17	1.28
	400	5.3	1.48	1.63
	450	6.1	1.77	2.02

The small difference observed is most probably due to the existence of the Ni_3Sn_4 homogeneity range of about 1.5 at.% Ni [241]. Note that another set of lattice parameters $a = 1.2214 \text{ nm}$, $b = 0.4060 \text{ nm}$, $c = 0.5219 \text{ nm}$, $\beta = 105.0^\circ$ is also available in the literature for Ni_3Sn_4 [458]. Accordingly, for the most intensive $\{111\}$ reflection appropriate values of 2θ and d are 30.47° and 0.29338 nm [390] or 30.43° and 0.29373 nm [458].

XRD data were confirmed by electron probe microanalysis (EPMA). The results of measurements made at random on the surface of the specimens used for XRD were in accordance with the stoichiometry of the Ni_3Sn_4 intermetallic compound.

EPMA measurements were also carried out across the transition zone between the nickel and the soldering alloy. The phases revealed were Ni, Ni_3Sn_4 and the alloy. No evidence of the presence of other Ni–Sn intermetallics at the nickel–alloy interface was found. Their absence is most probably due to kinetic reasons (see Chapters 2 and 3).

Low content of bismuth (around 0.1 at.% with a 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb soldering alloy and 0.2 at.% with a 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb soldering alloy) in the the Ni_3Sn_4 layer is worth noting. The content of indium was 0.10–0.15 at.% with both alloys, whereas zinc and antimony were practically missing from the intermetallic layer.

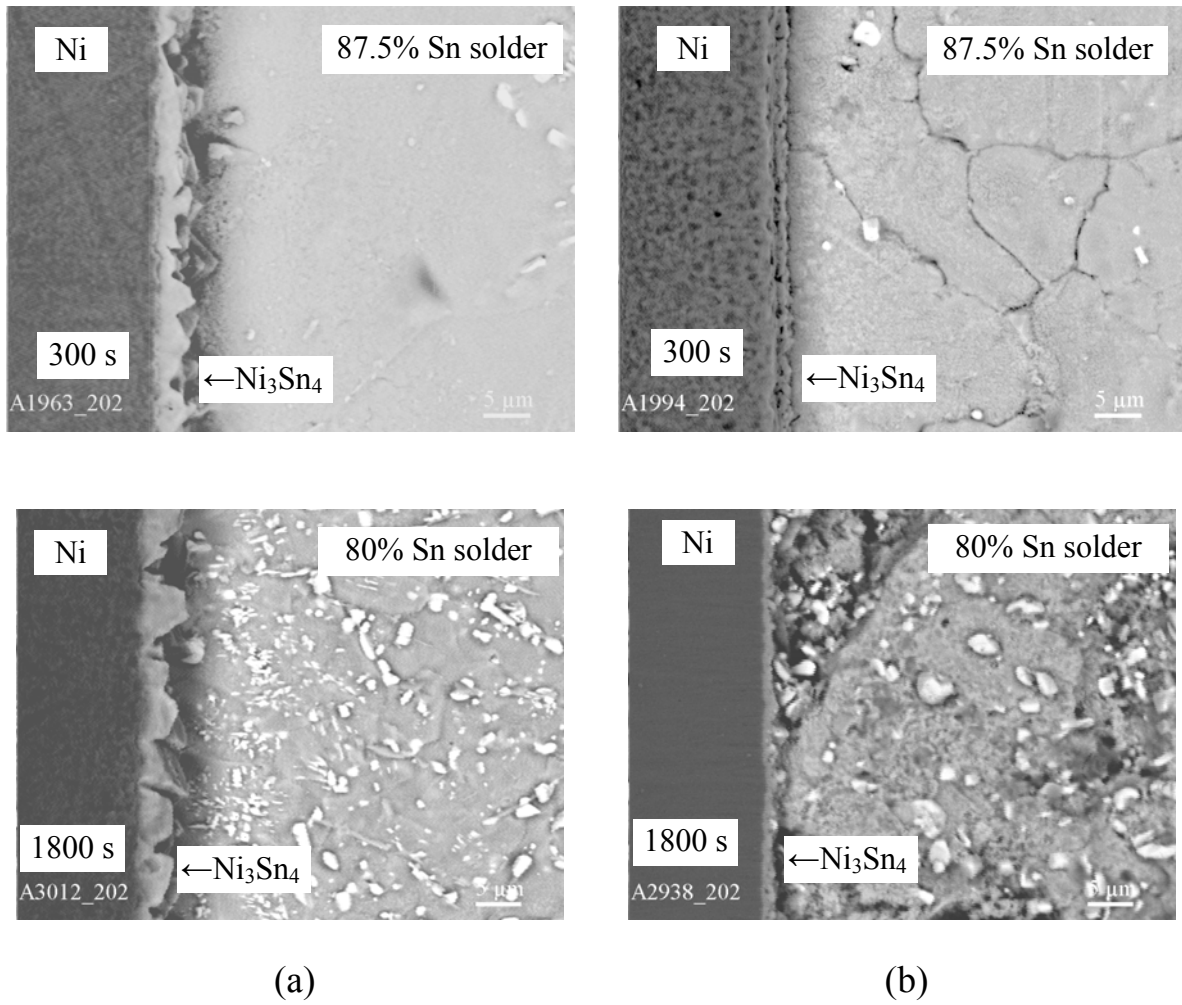


Fig. 5.23. Backscattered electron image (BEI) of the transition zone formed between nickel and liquid soldering alloys at a temperature of 350 °C. (a) saturated melts, (b) undersaturated melts ($\omega = 24.0 \text{ rad s}^{-1}$) [450].

Like NiBi_3 , the Ni_3Sn_4 intermetallic-compound layer also tends to be destroyed under the influence of the liquid phase. This effect is typical of thick layers formed from saturated melts. Nonetheless, from Fig. 5.23 it is seen that the Ni_3Sn_4 layer thickness is much less in the case of the undersaturated melt compared to the case of the saturated melt, indicative of the profound effect of dissolution on the layer-growth kinetics.

To estimate the magnitude of this effect, calculations of the thickness of the Ni_3Sn_4 layer grown from undersaturated solder melts were again carried out using equation (5.30). For example, in the case of the saturated 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb alloy melt, the experimental value of the Ni_3Sn_4 layer thickness (whenever it has not been destroyed under the influence of the liquid phase) was found to be $16.0 \times 10^{-6} \text{ m}$ at 450 °C and a dipping time of 300 s. Hence, $k_1 = x^2/2t = 4.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.

Other quantities necessary for calculations are $k = 6.2 \times 10^{-5} \text{ m s}^{-1}$ at $\omega = 24.0 \text{ rad s}^{-1}$, $c_s = 48.5 \text{ kg m}^{-3}$ (0.69% Ni in the soldering alloy), $\rho_{\text{int}} = 8.68 \times 10^3 \text{ kg m}^{-3}$ [457], $\phi = 0.27$, $s/\nu = 10.0 \text{ m}^{-1}$, $b_0 = 1.28 \times 10^{-6} \text{ m s}^{-1}$. Using these data, one obtains the limiting values, $x_{\text{under}} = 0.6 \times 10^{-6} \text{ m}$ and $x_{\text{over}} = 1.5 \times 10^{-6} \text{ m}$, for the thickness of the Ni_3Sn_4 layer grown from the undersaturated solder melt at 450°C and a dipping time of 2400 s. The experimental value, x_{exp} , is $(1.2 \pm 0.2) \times 10^{-6} \text{ m}$. The agreement of these values appears to be quite sufficient for practical purposes to roughly evaluate the intermetallic layer thickness at the solid-liquid interface.

Whenever the layer growth-rate constant, k_1 , could not be determined from the layer thickness-time dependence for the saturated melt, it was estimated from that for the undersaturated melt. For example, in the case of the undersaturated 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb alloy melt at 350°C , $k = 4.6 \times 10^{-5} \text{ m s}^{-1}$ at $\omega = 24.0 \text{ rad s}^{-1}$, $c_s = 17.0 \text{ kg m}^{-3}$ (0.24% Ni in the soldering alloy [453]), $b_0 = 3.34 \times 10^{-6} \text{ m s}^{-1}$; ρ_{int} , ϕ and s/ν are as before.

The experimental value, x_{exp} , of the Ni_3Sn_4 layer thickness at this temperature and a dipping time of 300 s is $1.0 \times 10^{-6} \text{ m}$. By assuming $x_{\text{exp}} = x_{\text{max}}$, one obtains from equation (5.30) $k_1 = x_{\text{max}} (b_0 + b_{300})/2 = 3.13 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Note that the accuracy of this estimation is rather high, with the overestimated value of k_1 being $3.34 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ and the underestimated one $2.91 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.

Comparison of calculated and experimental values of the Ni_3Sn_4 layer thickness is provided in Table 5.17. Also included in the table are the results for a 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb alloy melt, obtained using the following quantities: $k = 4.5 \times 10^{-5} \text{ m s}^{-1}$ at $\omega = 24.0 \text{ rad s}^{-1}$, $c_s = 13.0 \text{ kg m}^{-3}$ (0.18% Ni in the soldering alloy [453]), $b_0 = 2.50 \times 10^{-6} \text{ m s}^{-1}$, $x_{\text{exp}} = 0.9 \times 10^{-6} \text{ m}$ at $t = 300 \text{ s}$, $k_1 = 2.11 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Again, the agreement of experimental and calculated layer thicknesses is fairly good.

5.5.3: Reactions of solid cobalt with liquid Sn–Bi–In–Zn–Sb alloys

Like nickel, reactions of cobalt with 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb and 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb soldering alloys have also been studied [454, 455]. As evidenced in Fig. 5.24, temperature dependence of the solubility of cobalt in those alloys obeys a relation of the Arrhenius type.

The least-squares fit method yields the following equations:

$$c_s = 4.08 \times 10^2 \exp(-45200/RT) \%$$

for tin,

$$c_s = 4.06 \times 10^2 \exp(-46300/RT) \%$$

for a 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb alloy,

$$c_s = 5.46 \times 10^2 \exp(-49200/RT) \%$$

for a 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb alloy,

where R is in $\text{J mol}^{-1} \text{K}^{-1}$ and T in K. Appropriate linear regression coefficients are 0.9966, 0.9987 and 0.9963.

Table 5.17. Comparison of experimental thicknesses of the Ni_3Sn_4 layer grown from undersaturated bismuth melts at 350°C and $\omega = 24.0 \text{ rad s}^{-1}$ with those calculated using equation (5.30)

Soldering alloy	Time (s)	x_{under} ($\times 10^{-6} \text{ m}$)	x_{exp} ($\times 10^{-6} \text{ m}$)	x_{over} ($\times 10^{-6} \text{ m}$)
87.5 % Sn...	600	1.06	1.1 ± 0.1	1.24
	900	1.13	1.3 ± 0.1	1.42
	1200	1.19	1.5 ± 0.2	1.63
	1800	1.30	1.8 ± 0.2	2.14
	2400	1.40	2.2 ± 0.3	2.82
80 % Sn...	600	0.95	1.0 ± 0.1	1.10
	900	1.01	1.2 ± 0.1	1.26
	1200	1.07	1.3 ± 0.1	1.46
	1800	1.17	1.5 ± 0.2	1.90
	2400	1.26	1.8 ± 0.2	2.48

Comparison of the solubility values calculated from these temperature dependences (smoothed solubilities) is provided in Table 5.18. The additives Bi, In, Zn and Sb are seen to produce a considerable decrease of the cobalt solubility in the solder melts.

From the data of Table 5.18, it must be clear why conventional methods employed to investigate phase equilibria, for example differential scanning calorimetry, do not yield satisfactory results in the liquidus determination with systems like Co–Sn. Firstly, the solubility values of cobalt in liquid tin are rather small. Secondly, the liquidus curve ascends very abruptly from the eutectic point to the peritectic temperature of formation of the CoSn_2 compound (see Fig. 5.25). For these reasons, any arrests on the thermal heating-cooling curves, corresponding to the cobalt solubility in tin (and the soldering alloys) at a given temperature, cannot be determined with confidence.

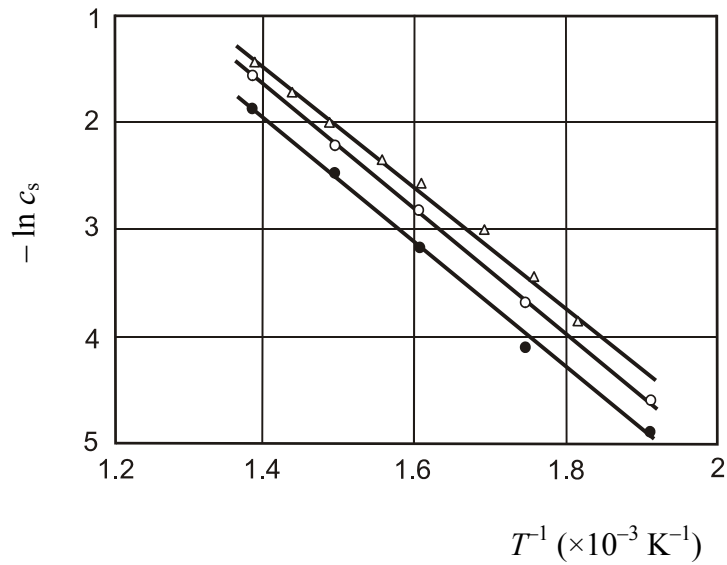


Fig. 5.24. Temperature dependence of the solubility of cobalt in tin and liquid soldering alloys. Δ , tin; $\circ$, 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb alloy; $\bullet$, 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb alloy.

Table 5.18. Comparison of smoothed cobalt solubility values in tin and soldering alloys at 250–450 °C

Temperature (°C)	Cobalt solubility, c_s (%)		
	100 % Sn	87.5 % Sn...	80 % Sn...
250	0.012	0.0092	0.0067
300	0.031	0.024	0.018
350	0.066	0.053	0.041
400	0.13	0.10	0.083
450	0.22	0.18	0.15

In contrast, the kinetic method employed here is sufficiently accurate, because the degree of saturation of the liquid can easily be controlled by chemical and physical means. Since the experiment is carried out at constant temperature and pressure, no supersaturation of the liquid is possible. Sooner or later, an equilibrium intermetallic phase is formed at the cobalt-solder interface (see Section 3.2). At long dipping times, the layer of this (and perhaps some other) phase will grow until all the cobalt (the solder is usually taken in excess) is consumed completely.

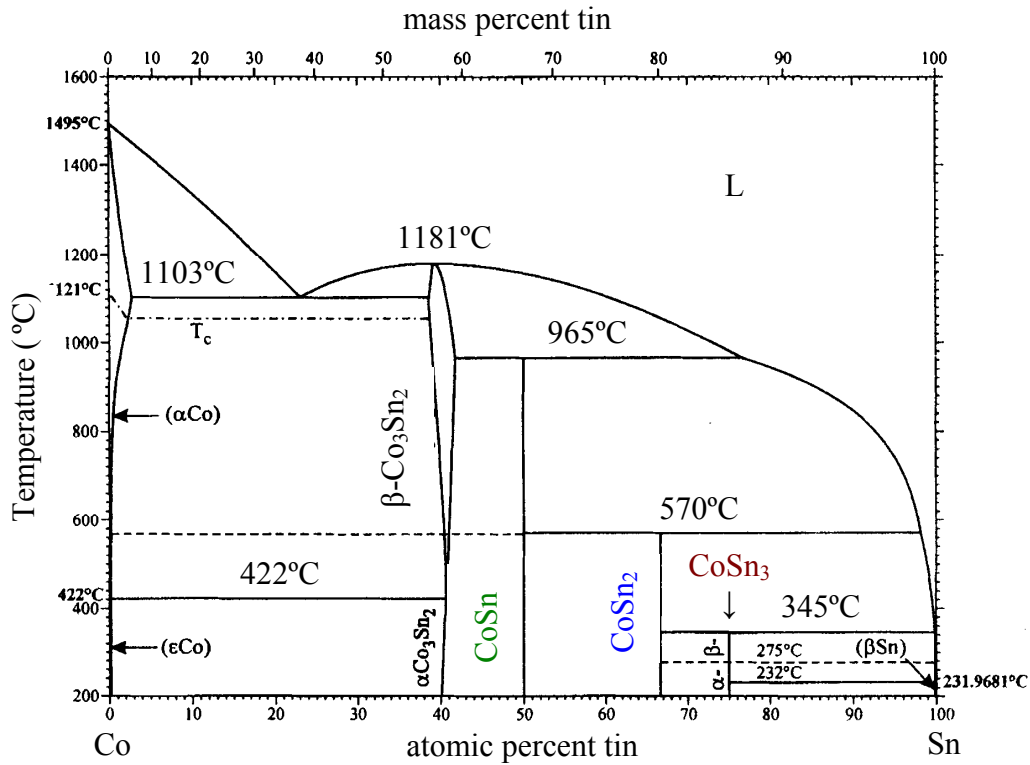


Fig. 5.25. Phase diagram of the Co–Sn binary system according to the works of M. Jiang *et al.* [459] and H. Okamoto [460].

Note that for the liquid-tin phase to reach saturation, it does not matter whether the saturation process is carried out from the cobalt phase, or from the nearest (to tin) intermetallic compound, or from any other intermetallic compound of the Co–Sn binary system because cobalt exists in the saturated metallic melt in the form of atoms, and therefore any initial phase decomposes during its dissolution in tin. No compounds can occur within the liquid-tin bulk unless the temperature is lowered enough to cause supersaturation of the melt (pressure is usually constant in the course of experiments).

Dissolution-rate constants of cobalt in Sn–Bi–In–Zn–Sb soldering alloys at an angular disc rotational speed of 24.0 rad s^{-1} are presented in Table 5.19. Also listed in the table are appropriate diffusion coefficients. As seen from Tables 5.16 and 5.19, both quantities are close to those for nickel. It is not surprising because many physical and chemical properties of cobalt and nickel are similar.

Table 5.19. Dissolution-rate constants at $\omega = 24.0 \text{ rad s}^{-1}$ and diffusion coefficients of cobalt in liquid Sn–Bi–In–Zn–Sb soldering alloys

Alloy	Temperature (°C)	k ($\times 10^{-5} \text{ m s}^{-1}$)	D ($\times 10^{-9} \text{ m}^2 \text{ s}^{-1}$)	
			Eq. (5.6)	Eq. (5.7)
87.5 % Sn...	250	1.2	0.17	0.19
	300	2.7	0.55	0.59
	350	4.5	1.17	1.28
	400	5.2	1.44	1.58
	450	6.2	1.82	2.02
80 % Sn...	250	1.1	0.15	0.16
	300	2.4	0.46	0.49
	350	4.4	1.14	1.24
	400	5.2	1.44	1.58
	450	6.2	1.82	2.02

To appreciate the influence of dissolution on the intermetallic layer-growth kinetics, experiments with both saturated and undersaturated Sn–Bi–In–Zn–Sb alloy melts were carried out. A few backscattered electron images of the cobalt-solder transition zone are shown in Fig. 5.26 as an example. With both solders, a single-phase layer of the CoSn_3 intermetallic compound was found to form from saturated and undersaturated melts at 250°C and dipping times up to 1800 s. The layer of CoSn_2 occurs at 350 and 450 °C. Besides, the formation of an additional intermetallic layer around 1.5 μm thick was observed at a temperature of 450 °C and a dipping time of 1800 s (Fig. 5.27).

Phase identification was carried out by X-ray diffraction (XRD). To prepare a specimen for X-ray examination, the melt material adhering to the solid cobalt base was removed by its rapid melting at an appropriate experimental temperature of 250, 350 or 450 °C. After slight polishing to remove the remainder of the melt material, cobalt specimens with adherent intermetallic layers proved suitable for X-ray analysis. Diffraction patterns were taken immediately from their surface.

At each temperature, similar patterns have been obtained with both soldering alloys investigated. To identify intermetallic phases formed at the interface between solid cobalt and liquid solders, comparison of X-ray results with the literature data for the Co–Sn intermetallics [461-470] was undertaken. Examples are shown in Figs 5.28 and 5.29.

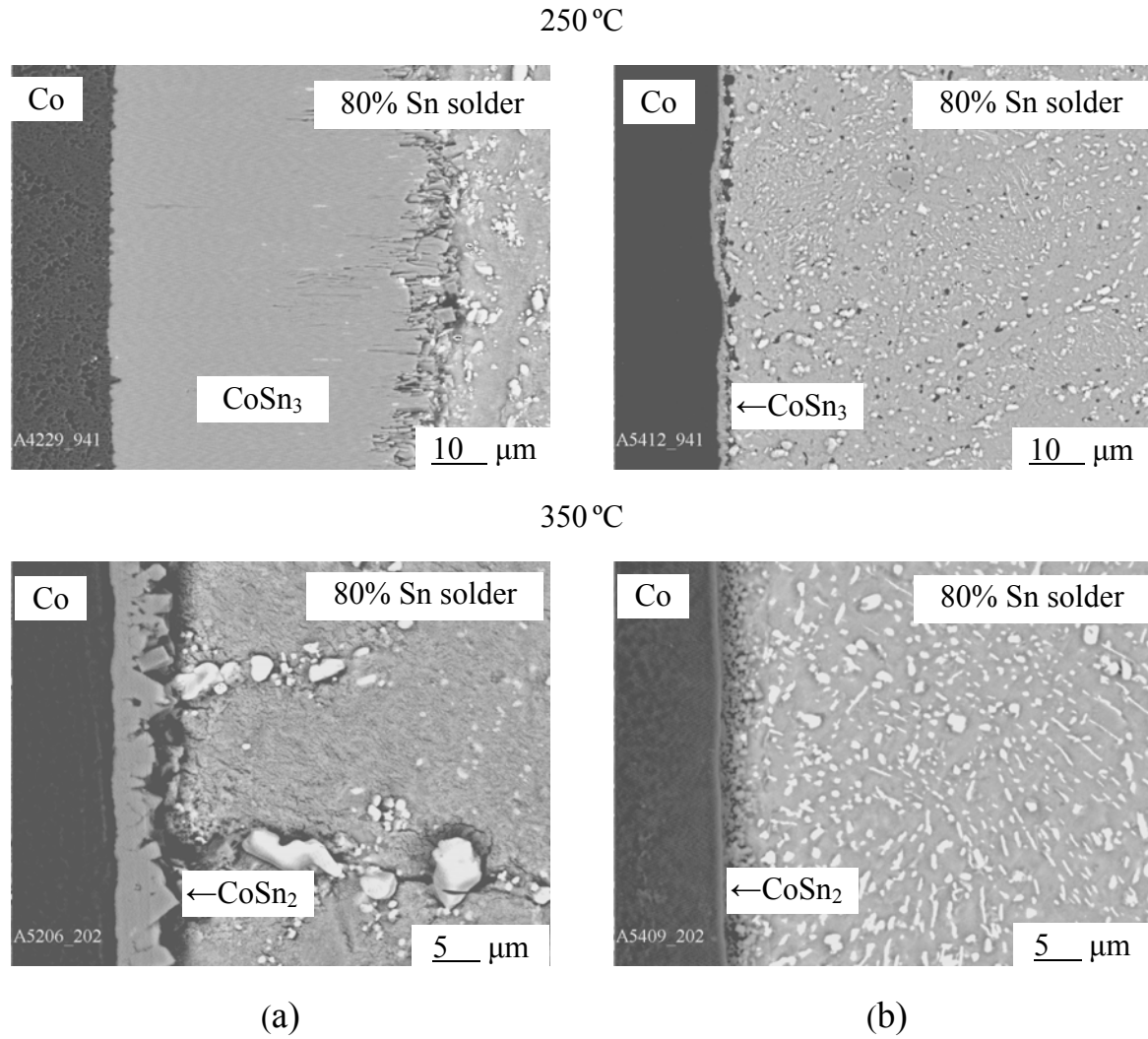


Fig. 5.26. Backscattered electron images of the transition zone formed between cobalt and liquid soldering alloys at a dipping time of 1800 s: (a) saturated melts; (b) undersaturated melts ($\omega = 24.0 \text{ rad s}^{-1}$).

Experimental values of 2θ and interplanar distances (d -spacing) were in fair agreement with those reported in the literature for the α - CoSn_3 intermetallic compound having orthorhombic unit cell parameters $a = 1.6864 \text{ nm}$, $b = 0.6268 \text{ nm}$, $c = 0.6270 \text{ nm}$ [461, 468, 469]. However, two significant distinctions are worth noting.

Firstly, experimental peak intensities were found to differ considerably from those reported in the literature. It should be emphasised that the literature data themselves are somewhat confusing in this respect, giving quite different values of intensity for the same reflections. Most striking example is the intensity of the $\{312\}$ reflection ($d = 0.2509 \text{ nm}$). One database [401] reports $I = 1000$ for this reflection, while the other [402] indicates $I = 0$. This discrepancy is difficult to explain because both are based on the same work of A. Lang and W. Jeitschko [461].

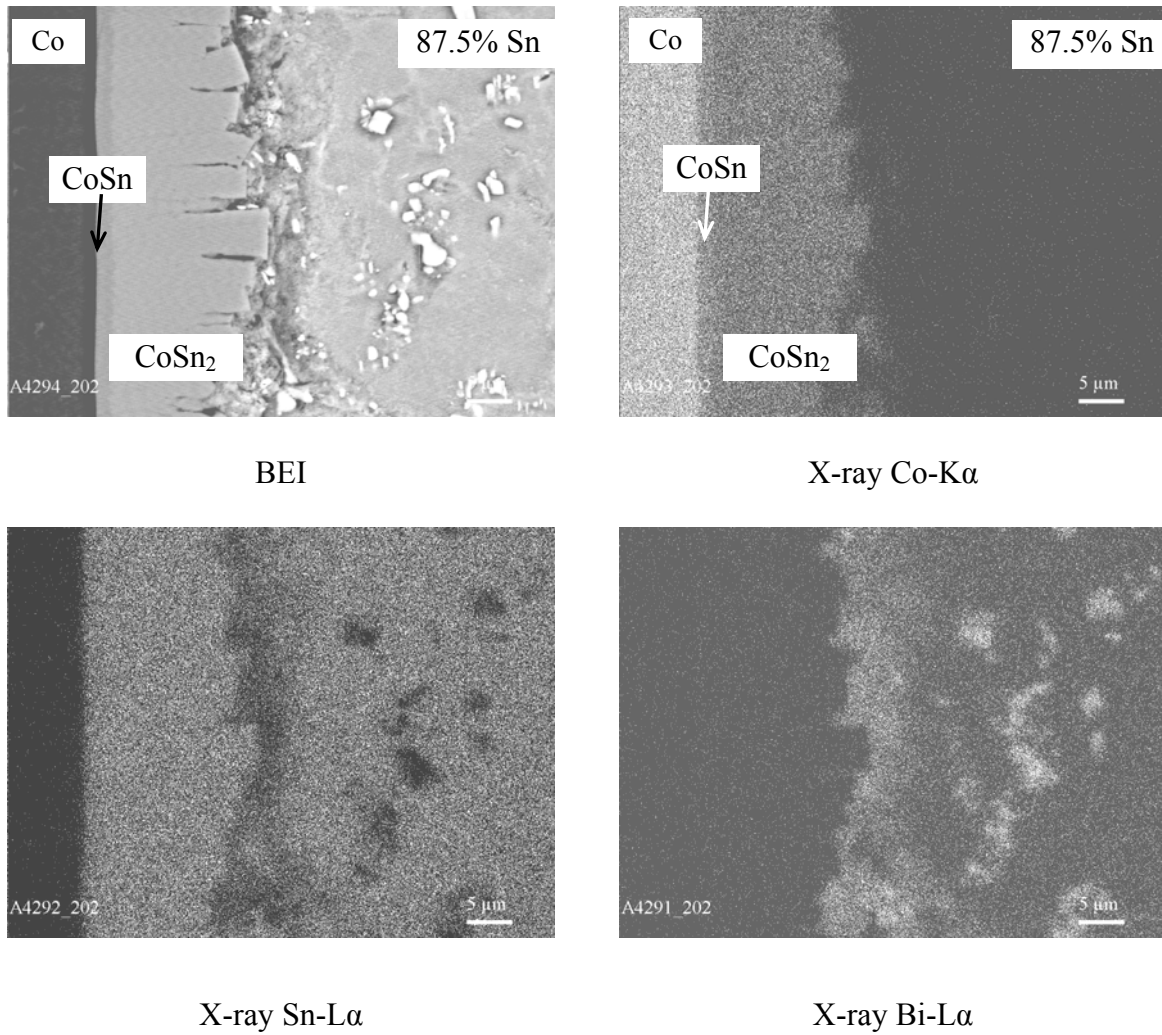


Fig. 5.27. Backscattered electron image (BEI) and X-ray maps (the brighter the region, the greater the amount of an appropriate element) of intermetallic-compound layers formed between solid cobalt and liquid saturated soldering alloys at 450 °C and a dipping time of 1800 s.

Secondly, experimental X-ray patterns for the α -CoSn₃ intermetallic compound contain a very broad, poorly resolved peak at about $2\theta = 14.1^\circ$ ($d = 0.6278$ nm), missing from any pattern reported in the literature. If the intermetallic phases formed as separate layers growing between cobalt and solders at 250 °C are indeed the orthorhombic α -CoSn₃ compound, then this peak may originate from the {001} and {010} reflections.

It should be noted that earlier Y.-H. Chao *et al.* [470] also found the peak intensities to differ considerably from those reported for the equilibrium α -CoSn₃ intermetallic compound. Further X-ray work is needed to clarify the situation.

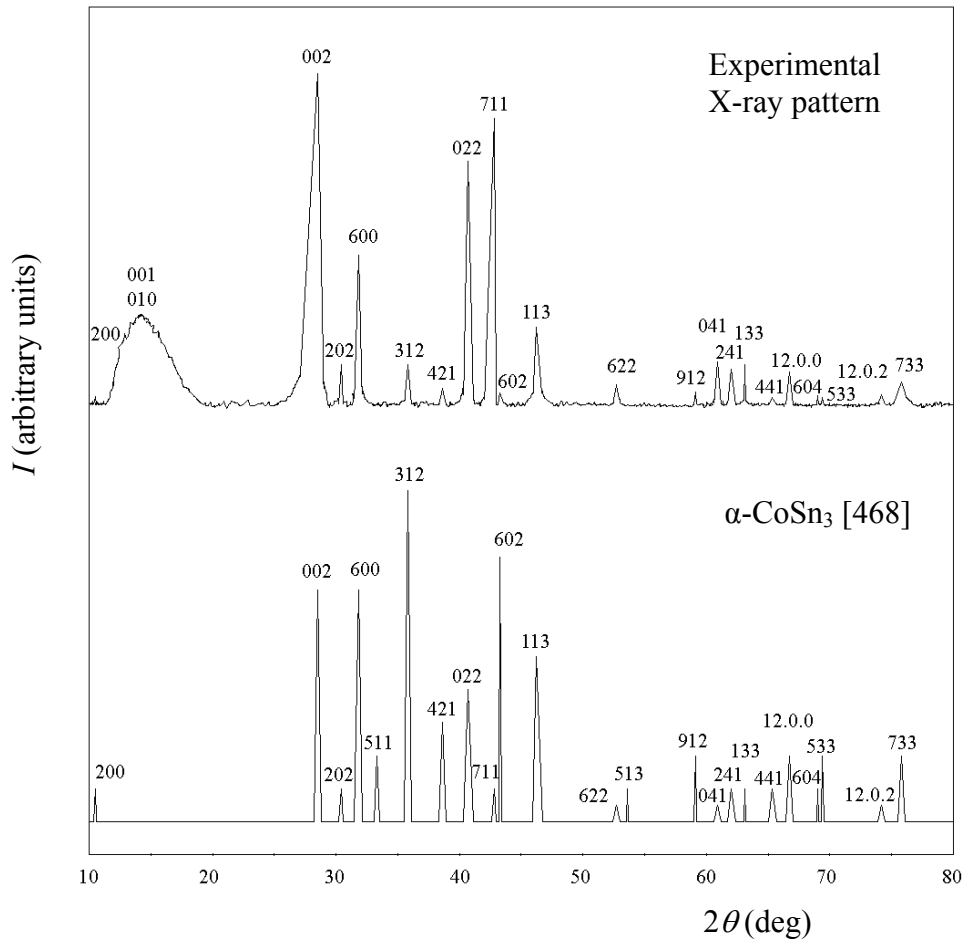


Fig. 5.28. Comparison of an experimental X-ray diffraction pattern (top) for an intermetallic phase formed at the interface between solid cobalt and a liquid cobalt-saturated 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb soldering alloy at 250 °C and a dipping time of 1800 s with that (bottom) available in the literature for the α -CoSn₃ compound [468]. Cu-K α radiation.

Literature XRD data for CoSn₂ are much more numerous than for CoSn₃ and agree very well with each other [462–467, 469]. Good agreement is observed between those and experimental X-ray results obtained at 350 and 450 °C (Fig. 5.29). Hence, the constituent phase of intermetallic layers formed at the cobalt-solder interface at these temperatures is CoSn₂.

XRD data were confirmed by electron probe microanalysis (EPMA). The results of EPMA measurements were in accordance with the stoichiometry of the CoSn₃ and CoSn₂ intermetallic compounds. The distribution of cobalt and tin in the cobalt-solder transition zone is shown in Fig. 5.30. Both compounds appear to have a noticeable homogeneity range. It was estimated as 25.5–22.5 at.% (14.5–12.5 %) Co for CoSn₃ at 250 °C and 34.6–31.1 at.% (20.8–18.3 %) Co for CoSn₂ at 450 °C.

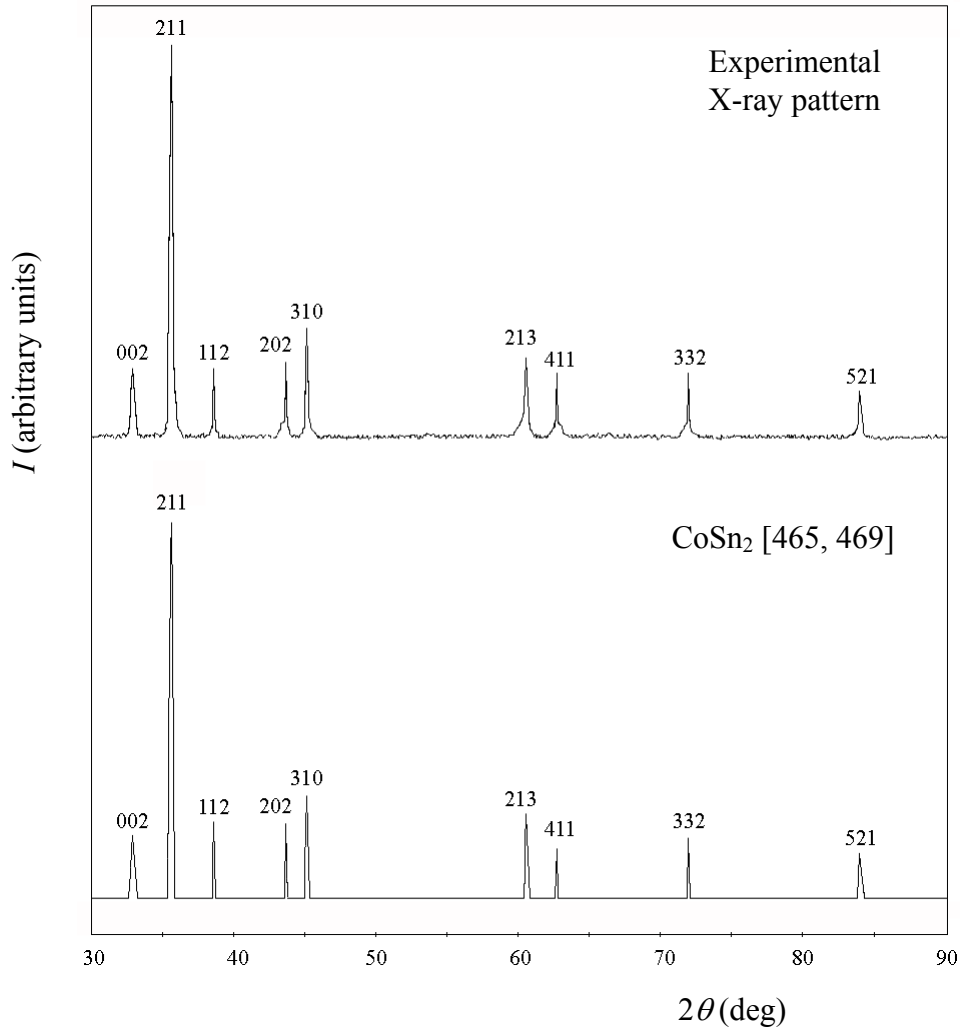


Fig. 5.29. Comparison of an experimental X-ray diffraction pattern (top) for an intermetallic phase formed at the interface between solid cobalt and a liquid cobalt-saturated 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb soldering alloy at 450 °C and a dipping time of 1800 s with that (bottom) available in the literature for the CoSn₂ compound [465, 469]. Cu-K α radiation.

EPMA measurements showed a thin intermetallic layer formed between cobalt and CoSn₂ at 450 °C and a dipping time of 1800 s (see Fig. 5.27) to be CoSn. Average content of the components of this compound was found to be 49.65 at.% (32.85 %) Co, 50.05 at.% (66.69 %) Sn, 0.06 at.% (0.14 %) Bi, 0.12 at.% (0.16 %) In, 0.12 at.% (0.16 %) Sb and 0.00 at.% (0.00 %) Zn. Note that, when studying the reaction kinetics of cobalt with pure tin, WenJun Zhu *et al.* [471] found the CoSn₂ layer to form at 400 and 500 °C, while the CoSn phase only occurred at 600 °C.

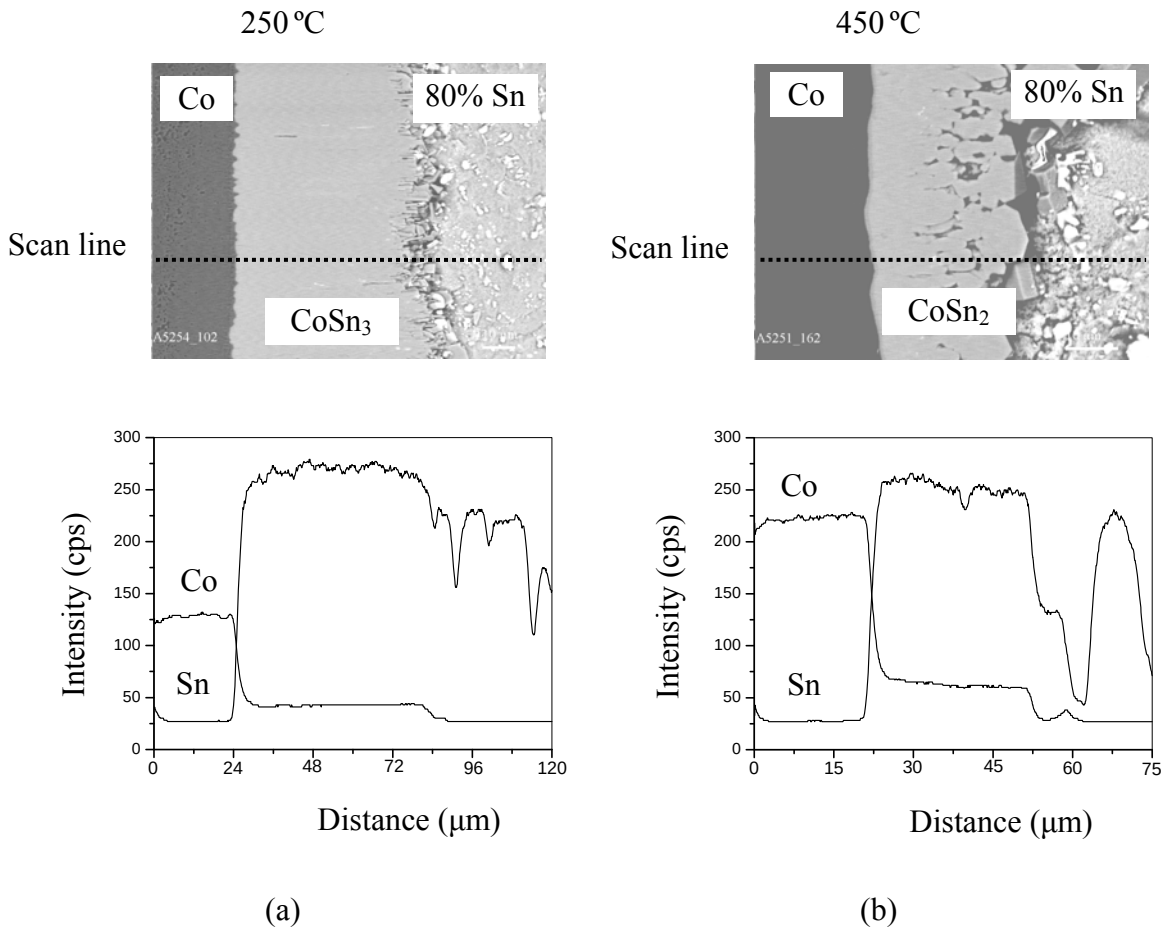


Fig. 5.30. Microstructure of the transition zone between solid cobalt and a liquid soldering alloy, and concentration profiles of cobalt and tin in (a) CoSn_3 and (b) CoSn_2 intermetallic layers. Cobalt-saturated solder melts, dipping time 1800 s.

It is worth noting that, in addition to four intermetallic compounds Co_3Sn_2 , CoSn , CoSn_2 and CoSn_3 (see Fig. 5.25), formation of the CoSn_4 layer was observed by Chao-hong Wang and Sinn-wen Chen at the corners of the Co-Sn diffusion couples reacted at 180-190 °C as shown in Fig. 5.31 [472]. It is yet unclear whether the CoSn_4 phase is stable or metastable.

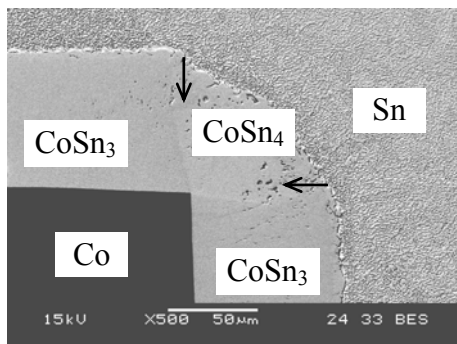


Fig. 5.31. BEI micrograph of the Co-Sn diffusion couple reacted at a temperature of 180 °C for 432×10^3 s (120 h) [472]. Photograph kindly provided by Prof. Sinn-wen Chen.

Most probably, occurrence of this phase is a result of the secondary reaction $\text{Sn}_{\text{dif}} + \text{CoSn}_3 = \text{CoSn}_4$ taking place at the CoSn_3 – CoSn_4 interface where any contact between Co and CoSn_3 is lacking, *i.e.* actually in the CoSn_3 –Sn diffusion couple. In the Co– CoSn_3 –Sn couple, the CoSn_4 layer can hardly compete with the fast-growing CoSn_3 layer and is therefore missing.

The absence of the CoSn_4 compound from the equilibrium phase diagram might be due to the difficulty of attaining the equilibrium state of Co–Sn alloys during their annealing at low temperatures. Further work is required to establish phase equilibria in Sn-rich alloys of the Co–Sn binary system. Investigation of reaction kinetics in CoSn_3 –Sn diffusion couples might be helpful in this respect.

Effect of dissolution on the intermetallic layer-growth kinetics is seen in Fig. 5.26 to be very profound. To estimate its magnitude, calculations of the thickness of intermetallic layers grown from undersaturated solder melts were again carried out using equation (5.30). For example, in the case of the saturated 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb alloy melt, the experimental value of the CoSn_2 layer thickness was found to be 33.0×10^{-6} m at 450 °C and a dipping time of 1800 s. Hence, $k_1 = x^2/2t = 3.0 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Other quantities necessary for calculations are $k = 6.2 \times 10^{-5} \text{ m s}^{-1}$ at $\omega = 24.0 \text{ rad s}^{-1}$, $c_s = 10.74 \text{ kg m}^{-3}$ (0.15 % Co in the soldering alloy [454]), $\rho = 8.91 \times 10^3 \text{ kg m}^{-3}$ [466], $\varphi = 0.1989$ (19.89 % Co in CoSn_2), $s/v = 10.0 \text{ m}^{-1}$, $b_0 = 3.76 \times 10^{-7} \text{ m s}^{-1}$.

Comparison of calculated values of the CoSn_2 layer thickness, x_{under} and x_{over} , with experimental ones is provided in Table 5.20. Since the duration of the soldering procedure rarely exceeds a few minutes, the agreement of these values appears to be quite sufficient for practical purposes to estimate the intermetallic-layer thickness at the solid-liquid interface.

Table 5.20. Comparison of experimental thicknesses of the CoSn_2 layer grown from undersaturated 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb solder melts at 450 °C and $\omega = 24.0 \text{ rad s}^{-1}$ with those calculated using equation (5.30)

Time (s)	b_t ($\times 10^{-7} \text{ m s}^{-1}$)	$(b_0 + b_t)/2$ ($\times 10^{-7} \text{ m s}^{-1}$)	x_{under} ($\times 10^{-6} \text{ m}$)	x_{exp} ($\times 10^{-6} \text{ m}$)	x_{over} ($\times 10^{-6} \text{ m}$)
300	3.12	3.44	0.80	0.8 ± 0.1	0.87
600	2.59	3.18	0.94	1.0 ± 0.2	1.16
1200	1.79	3.02	1.00	1.5 ± 0.2	1.68
1800	1.23	2.50	1.20	1.8 ± 0.2	2.43

Another example of calculations is the case of the undersaturated 87.5 % Sn–7.5 % Bi–3 % In–1 % Zn–1 % Sb alloy melt at 350°C, in which $k = 4.5 \times 10^{-5} \text{ m s}^{-1}$ at $\omega = 24.0 \text{ rad s}^{-1}$, $c_s = 3.75 \text{ kg m}^{-3}$ (0.053 % Co in the soldering alloy [454]), $b_0 = 9.52 \times 10^{-8} \text{ m s}^{-1}$; ρ_{int} , φ and s/v are as before. The experimental value, x_{300} , of the CoSn_2 layer thickness at this temperature and a dipping time of 300 s is $0.6 \times 10^{-6} \text{ m}$. By assuming $x_{300} = x_{\text{max}}$, one obtains from equation (5.30) $k_1 = x_{\text{max}} (b_0 + b_{300})/2 = 5.4 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. Comparison of calculated and experimental values of the CoSn_2 layer thickness is provided in Table 5.21.

Table 5.21. Comparison of experimental thicknesses of the CoSn_2 layer grown from undersaturated solder melts at 350°C and $\omega = 24.0 \text{ rad s}^{-1}$ with those calculated using equation (5.30)

Soldering alloy	Time (s)	b_t ($\times 10^{-8} \text{ m s}^{-1}$)	$(b_0 + b_t)/2$ ($\times 10^{-8} \text{ m s}^{-1}$)	x_{under} ($\times 10^{-6} \text{ m}$)	x_{exp} ($\times 10^{-6} \text{ m}$)	x_{over} ($\times 10^{-6} \text{ m}$)
87.5 % Sn	600	7.27	8.40	0.64	0.7 ± 0.1	0.74
	1200	5.55	7.54	0.72	0.8 ± 0.2	0.97
	1800	4.24	6.88	0.78	1.1 ± 0.3	1.27
80 % Sn	600	6.44	6.90	0.54	0.6 ± 0.1	0.62
	1200	5.64	6.50	0.60	0.8 ± 0.2	0.81
	1800	4.33	5.84	0.66	1.0 ± 0.3	1.05

Also included in the table are the results for an 80 % Sn–15 % Bi–3 % In–1 % Zn–1 % Sb alloy, obtained using the following quantities: $k = 4.4 \times 10^{-5} \text{ m s}^{-1}$ at $\omega = 24.0 \text{ rad s}^{-1}$, $c_s = 2.96 \text{ kg m}^{-3}$ (0.041 % Co in the soldering alloy [454]), $b_0 = 7.35 \times 10^{-8} \text{ m s}^{-1}$, $x_{\text{exp}} = 0.5 \times 10^{-6} \text{ m}$ at $t = 300 \text{ s}$, $k_1 = 3.5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. Again, the agreement of calculated and experimental values of the layer thickness is seen to be quite satisfactory for both alloys.

5.6: Basic kinetic dependences in solid-gas systems

Kinetics of interfacial interaction of solids with gases have been considered in the books by V.I. Arkharov [1], O. Kubaschewski and B.E. Hopkins [4], K. Hauffe [6], U.R. Evans [7], W. Jost [8], I.N. Frantsevich *et al.* [11], P. Kofstad [13, 14], N.A. Kolobov and M.M. Samokhvalov [17], A.T. Fromhold [18, 19], N. Birks and G.H. Meier [24], I.I. Kornilov and V.V. Glazova [122], R.F. Voitovich and E.I. Golovko [125], M.W. Roberts and C.S. McKee [473], R.F. Voitovich [474], V.A. Lavrenko and V.L. Tikush [475], and other researchers. Various aspects of solid-gas reactions have been analysed in the papers by

R.A. Rapp [28], A.T. Fromhold and N. Sato [55], M. Danielewski [58], J.R. Ligenza [59, 60], B.E. Deal and A.S. Grove [61], E.A. Irene [62], Y. Kamigaki and Y. Itoh [63], M.P. Murell *et al.* [160], S. Tinkler and R. Dieckmann [174], A.C.S. Sabioni *et al.* [175-178], K. Motzfeldt [191], S.S. Kristy and J.B. Condon [192], W.K. Chen and N.L. Peterson [198, 199], G.R. Wallwork and A.Z. Hed [476], M. Dechamps and P. Lehr [477], R.L. Rawe and C.J. Rosa [478], J.E. Lopes Gomes and A.M. Huntz [479], M.J. Graham and R.J. Hussey [480], P. Lefort *et al.* [481], A.G. Ritchie [482-484], A. Takei and K. Nii [485], F.M. d'Heurle [486], V.I. Zmii *et al.* [487], B.S. Lee and R.A. Rapp [488], V.A. Lavrenko *et al.* [489], M.A. Nicolet [490], V.I. D'yachkov [491, 492], F.M. d'Heurle *et al.* [493], M. Paljević [494-431], R.A. Ploc [497], D. Nicolas-Chaubet *et al.* [498], S.L. Zhang *et al.* [499], L. Stolt *et al.* [500], O. Thomas *et al.* [501], H. Taimatsu [502], V. Ucakar *et al.* [503], M. Dopita *et al.* [504], H.J. Grabke [505], D. Monceau *et al.* [506], H. Li *et al.* [507], C. Piehl *et al.* [508], G. Calvarin-Amiri *et al.* [509], B. Lesage *et al.* [510], Z. Jurasz *et al.* [511], Z. Grzesik *et al.* [512], C. H. Zhou *et al.* [513], M. Steinbrück [514], S. Hayashi and B. Gleeson [515], H. Svensson *et al.* [516], L. Sánchez *et al.* [517], A.N. Hansson *et al.* [518] and many others.

Therefore, consideration will here be restricted to a few comments regarding the shape of the layer thickness-time dependence. First, the most probable dependence in the case of formation of non-volatile chemical compounds between solid *A* and gas *B* will be analyzed, assuming that *B* is insoluble in *A* at a given temperature. Then, the effect of evaporation on the layer-growth kinetics will be illustrated. Also, soft oxidation of chemical compounds will briefly be considered.

5.6.1: Compound layer thickness-time relationships

Although there are no essential difference in the processes of formation of the solid layers of chemical compounds at the interface of either two solid substances, or a solid and a liquid, or a solid and a gas, nevertheless in the latter case the experimentally observed layer thickness-time dependences are more diverse and complicated than in the first two cases because the growth kinetics of compound layers in the solid-gas systems are usually investigated by thermogravimetry over a comparatively long time range. Under such conditions, significant changes of the layer-growth mechanism may take place, and this must be reflected on the kinetic dependences observed. Therefore, the number of equations proposed for the mathematical description of those dependences is considerably greater than in the case of systems formed, for example, by two solids. Of these, different forms of linear, parabolic, parilinear, cubic and logarithmic laws are employed most frequently.

According to U.R. Evans [7], logarithmic equations (direct, reverse and asymptotic) are low-temperature laws. The reverse logarithmic law is valid if the layer-growth process is controlled by the electric potential gradient. This is probably the case with thin films of ionic compounds [6, 200]. The asymptotic and direct logarithmic laws are due to the transport of matter through pores whose number varies in the course of interaction between a solid and a

gas. In such a case, the growth process may happen to be more dependent upon the presence of macroscopic defects in a growing layer than upon its microscopic mechanism.

In the case of a single non-volatile chemical compound layer, some initial region of the layer thickness-time dependence is close to linear, followed by the gradual transition to a parabola (see Fig. 1.11 of Chapter 1). Such dependences are almost always observed in the oxidation, nitridation or sulphidation of metals, if temperature is not too high and the course of the process is monitored by a sufficiently sensitive investigation technique. For example, B.S. Lee and R.A. Rapp [488] found the kinetics of gaseous sulphidation of molybdenum to be linear-parabolic at a temperature as high as 750 °C, with the linear growth period extending at least to 2h (Fig. 5.32).

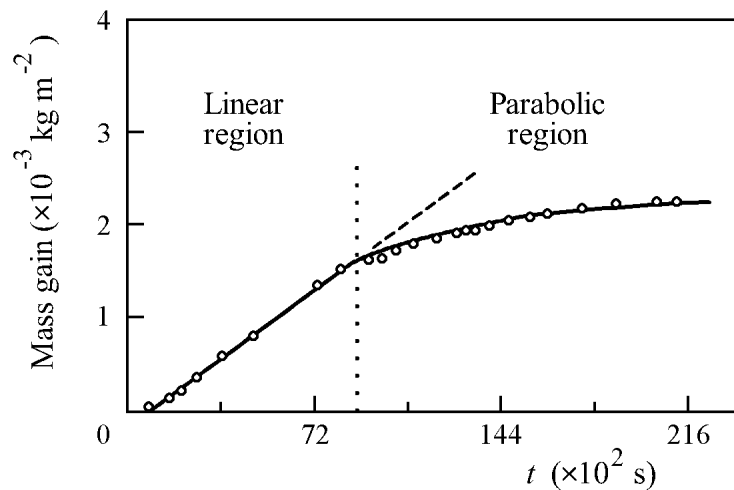


Fig. 5.32. Sulphidation kinetics of molybdenum from the gaseous phase at 750 °C and a sulphur vapour pressure of 4 Pa (0.03 mm Hg) according to the experimental data by B.S. Lee and R.A. Rapp [488]. Growth of the MoS₂ layer is initially linear and then parabolic.

The higher the temperature, the narrower the time range of linear growth was. Above 800 °C, the linear growth region was too narrow and therefore hardly observable. Note that the linear-to-parabolic transition took place at the MoS₂ layer thickness in the vicinity of 0.5 μm , which value is close to those for intermetallics and silicides. Growth of the MoS₂ layer is due to diffusion of sulphur ions or atoms across its bulk, followed by their subsequent interaction with the molybdenum atoms at the Mo–MoS₂ interface. Therefore, inert markers are found after the reaction at the interface between MoS₂ and the gaseous phase [488].

It seems relevant to remind once again that in the case of formation of a single-phase compound layer, the reverse (parabolic-to-linear) transition is impossible. From a physico-chemical viewpoint, it is only possible during the simultaneous occurrence of two or more compound layers, as is indeed observed experimentally [13, 122-124]. Parabolic-to-linear

growth kinetics are thus indicative of the formation of multiple layers of oxides, nitrides, sulphides, *etc.*, even though some of them may be hardly identifiable due to their extremely small thickness.

If two layers A_pB_q and A_rB_s are formed, the kinetic dependence is more complicated and can scarcely be described by any single analytical function. One of its most probable variants is shown schematically in Fig. 5.33. Both layers are assumed to form from the very beginning of interaction of solid A with gas B . Their growth kinetics are described by the system of differential equations (2.27).

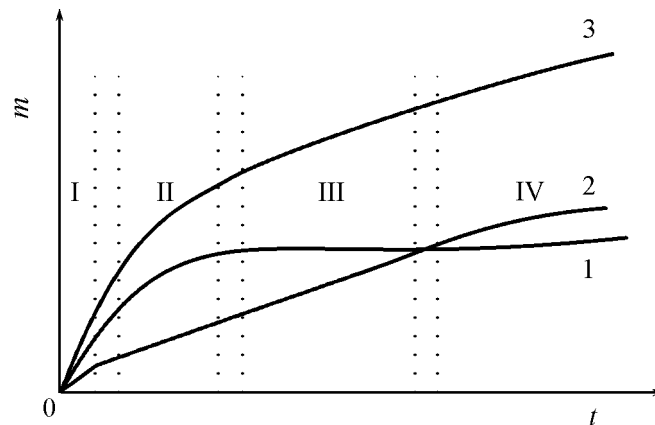


Fig. 5.33. Schematic diagram to illustrate one of possible kinetic relationships in the case of formation of two compound layers at the interface between solid A and gas B . 1, mass of the A_pB_q layer; 2, mass of the A_rB_s layer; 3, total mass gain of a solid specimen.

In general, the initial region of the dependence of the mass of each of the two layers as well as their total mass upon time must be linear (region I in Fig. 5.33). It is the region of chemical control, with fast diffusion of both species across the bulks of both layers and slow chemical interaction at the layer interfaces. At longer times and an appropriate ratio of the chemical and diffusional constants, the layer, for example, A_pB_q may happen to grow over some period of time in the diffusion controlled regime with regard to both components, while the A_rB_s layer in the reaction controlled regime with regard to component B (see Chapter 2). In such a case, the thickness and hence the mass of the A_pB_q layer tends with increasing time to a limiting value determined by equation (2.41), whereas the thickness (mass) of the A_rB_s layer increases linearly. The summation of the masses of both layers yields a dependence which in region II is close to parabolic, while in region III is linear. This is *paralinear* growth kinetics.

During further isothermal holding, a time will come for the A_rB_s layer to grow in the diffusion controlled regime with regard to component B . As a result, the A_pB_q layer loses a source of B atoms and therefore its growth must have slowed down considerably. However, this effect is in fact not so profound and practically unobservable since a significant reduction in the growth rate of the A_rB_s layer due to a change of the growth regime causes the A_pB_q layer to grow more rapidly, thereby compensating its decrease due to the former reason. Therefore, the A_pB_q layer thickness will start to increase, instead of being constant. Region IV thus corresponds to the so-called *postlinear* (or, more precisely, *postparalinear*) growth period [13] that is described by the system of differential equations (2.46).

It should be noted that at this stage the rate of increase of the total mass of the layers would be less than that which could be expected on the basis of a parabolic law. Therefore, if the kinetic data are formally treated using a power law, its exponent must in all likelihood be greater than 2. The cubic law may presumably hold in this region of growth of compound layers, though experimental values of the exponent are rarely observed to be constant and equal to 3. Most frequently, its value varies in the range 2.0-3.5 [7].

In such a case, it seems reasonable to treat the kinetic data using equations (2.46) and (2.53). However, thermogravimetric measurements alone, providing no information regarding the number of growing compound layers, their composition, thickness and structure, are insufficient for this purpose. It is necessary to use a few additional independent methods of investigation (metallography, X-ray diffraction, electron microscopy, electron probe microanalysis, Rutherford backscattering spectroscopy, *etc.*) in order to determine the phase identity and the thickness (or mass) of each of the layers formed.

Clearly, the relative duration of those growth stages in a particular solid-gas system may differ considerably. It results in a complicated kinetic curve, with its slope changing a few times due to the change in the number of growing compound layers and in their growth regimes (see Chapter 2).

Since the solid phase under investigation may be not only an elementary substance but also a material of rather complicated chemical composition, interpretation of experimental results is in many cases a not so easy task which not always can be solved unambiguously. Further complications arise from layer cracking due to stress and other reasons. After reaching a certain thickness, compound layers often cracks along the whole interface or at local areas, providing direct access to the gas attack. Then, subsequent healing of cracks occurs until the cracking thickness is attained again. The cracking process is repeated again and again, thus being a continuous one over the surface of the solid phase as a function of time. Note that the sudden release of stress by the layer fracture may even cause an occasional vibration of the microbalance spring during thermogravimetric measurements, as observed B.S. Lee and R.A. Rapp [488] during the sulphidation of molybdenum. Difficulties in interpreting the experimentally observed kinetic dependences are significantly aggravated, if volatile chemical compounds are formed in the course of interaction of solids with gases.

5.6.2: Influence of evaporation on the growth rate of a chemical compound layer

The process of evaporation of the volatile compound A_pB_q is described by equations similar to (5.15) and (5.16) [145]:

$$\frac{dx_{\text{evap}}}{dt} = kc_s V_{A_pB_q} \exp\left(-\frac{kSt}{v}\right) \quad (5.35)$$

and

$$x_{\text{evap}} = \frac{V_{A_pB_q} c_s v}{S} \left[1 - \exp\left(-\frac{kSt}{v}\right) \right], \quad (5.36)$$

where x_{evap} is the thickness of the evaporated portion of the A_pB_q layer, m; t is the time, s; k is the evaporation-rate constant, m s^{-1} ; c_s is the concentration of the A_pB_q compound in the diffusion boundary layer at the surface of a solid, mol m^{-3} ; $V_{A_pB_q}$ is the molar volume of the A_pB_q compound, $\text{m}^3 \text{mol}^{-1}$; v is the volume of the gaseous phase, m^3 ; S is the surface area of the solid specimen, m^2 .

In deriving equations (5.35) and (5.36) the A_pB_q compound was assumed to evaporate without decomposition. In such a case, growth kinetics of the A_pB_q compound layer between solid A and gas B are described by equation (5.19) in which $b = kc_s V_{A_pB_q}$ [145, 151-155].

For solid-gas systems, in most cases the condition $\exp(-kSt/v) \approx 1$ is satisfied. Indeed, one of the following two variants is usually realised in experiments.

- (1) Large volume of a gas is used. Hence, during the reaction time the chemical composition of the gaseous phase does not change significantly.
- (2) Investigations are carried out in a flowing gas or under vacuum. Therefore, the reaction product is continuously removed away from the reaction site.

If so, the rate of evaporation of the growing A_pB_q layer is constant and equal to b . Consequently, the kinetics of layer formation are described by equation (5.22). It should be noted that a simpler equation, analogous to (5.24) but differing by the meaning of the coefficients, was first derived by I.N. Frantsevich *et al.* [11] in the framework of the electrochemical approach. Then, it was re-discovered a few times by other researchers, probably independently of each other.

In general, the volatile A_pB_q compound formed during the interaction of substances A and B is partitioned between the solid and gaseous phases, *i.e.* some its portion forms a solid layer adherent to the surface of substance A , whereas another portion evaporates into the gaseous phase. If $k_0 > b$ (or more generally $k_{0B1} + k_{0A2} > b$, see equation (5.31)), then the solid layer A_pB_q forms and grows at the A – B interface from the very beginning of interaction between solid A and gas B .

This happens when the sum of the rates of chemical transformations at the layer interfaces with initial substances exceeds its evaporation rate. In such a case, the A_pB_q layer adherent to the surface of substance A reaches a maximal possible thickness determined by equation (5.26) and then grows no longer. Note that certain regions of the layer mass-time dependence may be either linear (at $k_0 \ll k_1/x$) or parabolic (at $k_0 \gg b$ and $k_1/x \gg b$).

When the thickness of the A_pB_q layer has reached its highest value $x_{\max}$, the stationary state is established in which the mass loss of the solid phase due to evaporation is just compensated by the mass gain due to partial chemical reactions proceeding at the layer interfaces with initial substances A and B . Subsequently, the mass of the A_pB_q layer adherent to phase A remains constant, whereas the mass of its evaporated portion increases linearly. As a result, the mass of a solid specimen (substance A plus layer A_pB_q) first increases, goes through a maximum, then begins to decrease and at t_0 proves equal to its initial value (Fig. 5.34). Thereafter, mass loss takes place instead of mass gain.

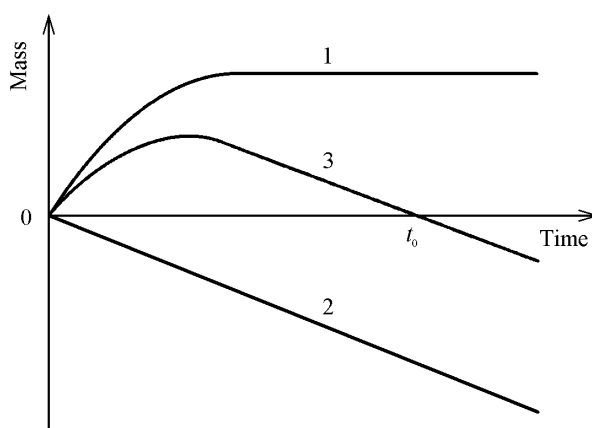


Fig. 5.34. Typical kinetic dependence in the case of formation of a volatile chemical compound evaporating at a constant rate. 1, mass of the solid A_pB_q layer adherent to phase A ; 2, mass of the evaporated portion of the A_pB_q layer; 3, change of the total mass of a solid specimen relative to its initial value.

Such a dependence is frequently observed experimentally in the oxidation of transition metals forming volatile oxides [11, 13, 122-125] and also of their alloys, carbides, nitrides, borides, silicides and other chemical compounds [474, 489]. An example based on the experimental results of E.A. Gulbransen and K.F. Andrew [519] is provided in Fig. 5.35.

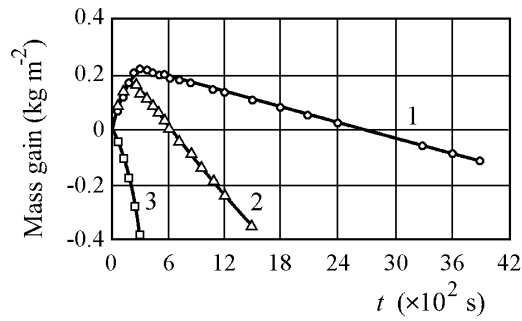


Fig. 5.35. Oxidation kinetics of tungsten wires at an oxygen pressure of 1.0×10^4 Pa (0.1 atm) according to the data by E.A. Gulbransen and K.F. Andrew [519]. Temperature: 1, 1100 °C; 2, 1150; 3, 1200.

At temperatures up to about 1150 °C there were time periods of the mass gain of tungsten wires, whereas at a temperature of 1200 °C or higher no mass gain was observed from the very beginning of their experiments since the volatile oxide WO_3 formed in the course of oxidation entirely evaporated into the gaseous phase. The boiling point of this compound is 1670 °C [167]. It is known to appreciably volatilise at a temperature of 800 °C.

With technetium, no mass gain has been found by V.I. Spitsin *et al.* [520] at temperatures as low as 300 °C. The mass loss of its sheets strictly followed a linear relation. The reaction product was Tc_2O_7 (boiling point 311 °C [167]).

The effect of decreasing pressure on the rate of oxidation of tungsten samples was similar to that of increasing temperature, as illustrated in Fig. 5.36. As E.A. Gulbransen and K.F. Andrew have introduced no correction for the change in the surface area during the reaction, mass loss plots in Figs 5.35 and 5.36 are seen to be somewhat curved, instead of being straight lines. Note that the pure WO_3 taken alone evaporates at a higher rate than its layer formed in the course of oxidation of tungsten (see line 8 in Fig. 5.36).

Evidently, at a time t_0 when the mass of a solid specimen again becomes equal to its initial value, the condition $x_{\max} = x_{\text{evap}}$ is satisfied (see Fig. 5.34). Since $x_{\text{evap}} = bt$, equation (5.26) yields

$$t_0 = \frac{k_1(k_0 - b)}{k_0 b^2}. \quad (5.37)$$

At $t > t_0$, the process of interaction between initial substances A and B actually only consists in the transport of substance A , combined into the $A_p B_q$ compound, into the gaseous phase. The amount of component B in the solid and the gas phases remains constant. If the state (free or combined) in which substance A is present in the gaseous phase is neglected, the final result is seen to be such as if A simply evaporated at a constant rate.

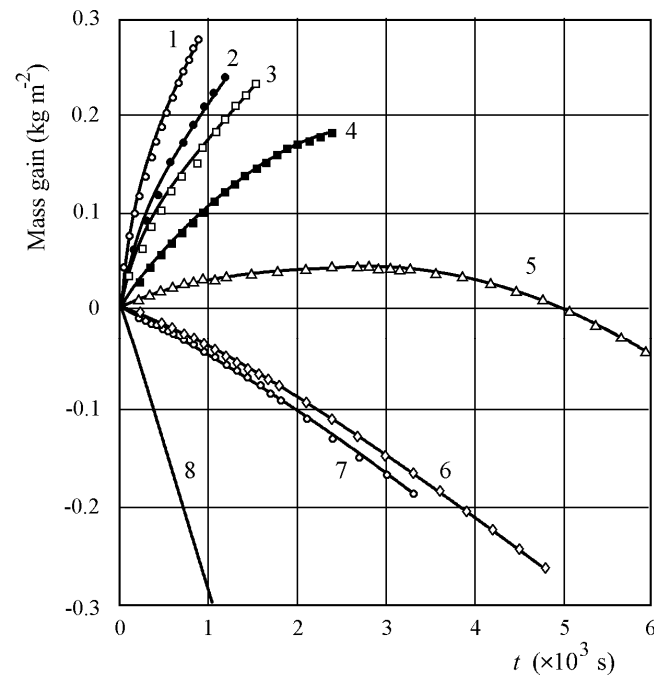


Fig. 5.36. Effect of oxygen pressure on oxidation kinetics of tungsten at a temperature of 1050 °C according to the data by E.A. Gulbransen and K.F. Andrew [519]. Pressure: 1, 1.0×10^4 Pa (0.1 atm); 2, 5.12×10^3 Pa (0.0512 atm); 3, 2.63×10^3 Pa (0.0263 atm); 4, 1.12×10^3 Pa (0.0112 atm); 5, 0.66×10^3 Pa (0.0066 atm); 6, 0.33×10^3 Pa (0.0033 atm); 7, 0.131×10^3 Pa (0.00131 atm); 8, volatility of WO_3 in vacuum.

If at a given temperature and pressure $k_0 < b$ (or more generally $k_{0B1} + k_{0A2} < b$, see equation (5.22)), the A_pB_q compound is not formed as a solid layer between substances A and B . In this case, the rate of evaporation of the A_pB_q layer exceeds the rate of its formation at the A – B interface. Therefore, the reaction product is entirely removed away from the solid surface into the gaseous phase. In the case under consideration, the rate of evaporation is limited by the rate of interfacial chemical interaction. Its value is clearly less than the evaporation rate, b , of a specimen prepared from the same A_pB_q compound.

It is necessary to differentiate between the two cases just considered, namely, when $k_0 > b$ and when $k_0 < b$. In the former case, the A_pB_q layer of constant thickness is present at the A – B interface, whereas in the latter the surface of substance A remains bare during the whole course of reaction.

It is worth noting that in the case of formation of volatile chemical compounds the effect of temperature on the layer growth are often established by comparing the rate constants obtained from kinetic dependences at a constant observation time. Obviously, the results would be dependent upon whether measurements are made on ascending or descending portions of those dependences.

From curve 3 in Fig. 5.34, it must be clear that if measurements are carried out on its ascending portion, then the treatment of the experimental data using the Arrhenius relation yields positive values of the activation energy, though different at varying observation times. By contrast, if measurements are carried out on its descending portion, negative values of the activation energy will be obtained. It only means that the growth rate of the solid A_pB_q layer between the A and B phases increases with raising temperature at a lower rate than its evaporation rate.

The activation energy thus found reflects the overall effect of temperature on a few parameters characterising the process of interaction of those phases (see equation (5.19)). Not only is the temperature dependence of each of them characterised by its own activation energy, but it may happen to be quite different from temperature dependences of other parameters. Whether these were calculated from the ascending or descending portion of any experimental kinetic relationship, both sets of activation energies prove, therefore, to be of little practical value.

It seems to be much more relevant to establish the temperature dependence of each parameter (chemical and diffusional constants, the evaporation-rate constant, *etc.*) separately. The availability of such data would make it possible to adequately describe the process of growth of a chemical compound layer under conditions of its simultaneous evaporation.

It is important to mention another essential circumstance. The duration of experiments in solid-gas systems is usually long. Therefore, it is just these experiments in which the appearance of departure points on thermogravimetric curves, caused by the transition from the reaction to diffusion controlled regime of growth of chemical compound layers (see Chapter 2), might be revealed. This concerns the case where there are no noticeable changes in the system under investigation (the number of the layers, their phase identity, chemical composition and structure remain unchanged), and nevertheless the dependence of the total mass of solid substances upon time gradually changes, displaying noticeable deviation points.

The occurrence of two such points may be expected, if two compound layers grow simultaneously. If there are three or more compound layers, the kinetic dependence should in addition change considerably when some of those layers disappear after the others have reached their critical thickness with regard to components A and B (see Chapter 3). To avoid misleading conclusions, these peculiarities of multiple-layer formation must be taken into account in interpreting the experimental data on solid-gas interactions.

5.6.3: Partial oxidation of chemical compounds

If the initial solid substance is a chemical compound (an intermetallic, a silicide, *etc.*), then its oxidation can proceed via two different mechanisms, depending upon experimental conditions. Two oxides are formed in the severe oxidation (combustion) usually resulting in the disintegration of the initially compact solid phase. In the partial (soft) oxidation, the

chemical compound undergoes a partial decomposition producing another chemical compound of the same class and an oxide.

Therefore, two solid layers occur at the interface between initial substances. One of these is an oxide layer, while the other is the layer of a chemical compound of the same $A-B$ multiphase binary system, enriched in the non-oxidising element. In the course of partial oxidation, both layers remain more or less compact and adherent to the surface of an initial solid phase.

Consider the process of oxidation of Zr_2Al_3 as a typical example. M. Paljevič has established that the $ZrAl_2$ and ZrO_2 layers occur during its oxidation [496]. The overall chemical reaction of their formation is



However, this equation provides no information about a real mechanism of layer growth. Indeed, reaction (5.38) cannot proceed any more immediately after the occurrence of the $ZrAl_2$ and ZrO_2 layers of appreciable thickness because these separate the reactants Zr_2Al_3 and oxygen from each other. Instead, partial chemical reactions will subsequently take place at appropriate interfaces [521]. Two molecules of Zr_2Al_3 decompose at interface 1 (Fig. 5.37) in accordance with the reaction



yielding three molecules of $ZrAl_2$ and releasing one zirconium atom. This released zirconium atom diffuses across the $ZrAl_2$ layer and then reacts at interface 2 with the oxygen atoms (or ions) to form more ZrO_2 :



An oxygen vacancy occurred at interface 2 moves on native sites of the ZrO_2 lattice to interface 3 where it is filled with an oxygen atom from the oxygen phase. Zirconium atoms are transported by the same mechanism through the $ZrAl_2$ layer. Continuous repeating of the elementary reaction-diffusion acts just described results in the growth of both compound layers.

Note that reaction (5.39) represents the phase transformation of Zr_2Al_3 into $ZrAl_2$ under the influence of reaction diffusion of the zirconium atoms from interface 1 to interface 2. It can proceed at any temperature whenever this reaction diffusion takes place [150-152].

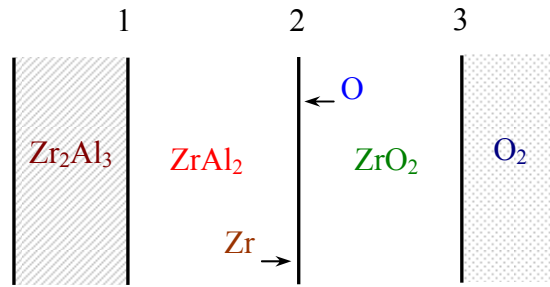


Fig. 5.37. Schematic diagram to illustrate the process of partial oxidation of the Zr_2Al_3 intermetallic compound.

The proposed mechanism [521] of growth of the ZrAl_2 and ZrO_2 layers appears to be more likely than an alternative one [496] involving the simultaneous diffusion of oxygen and aluminium atoms. Indeed, the self-diffusion coefficient of oxygen in ZrO_2 is higher than that of zirconium [522]. Therefore, the diffusion coefficient of aluminium in this phase can hardly be expected to be sufficiently high to ensure a considerable flux of the aluminium atoms across its bulk. Probably, the same applies to the transport of oxygen atoms in the ZrAl_2 lattice.

For these reasons, the growth mechanism of the ZrAl_2 and ZrO_2 layers, involving diffusion of foreign atoms across their bulks, seems to be much less likely. Of course, there are also other conceivable mechanisms. To decide which one of those is operative, marker experiments, though not so easy to carry out with such brittle phases, are strongly desired.

As the Zr–Al–O system is ternary, the ZrAl_2 phase can form either a continuous coherent layer between Zr_2Al_3 and ZrO_2 or separate grains in the Zr_2Al_3 matrix near the Zr_2Al_3 – ZrO_2 interface. Anyway, after successive oxidation of the same Zr_2Al_3 specimen the newly formed portions of the ZrAl_2 and ZrO_2 layers are likely to be revealed by metallographic examination (ZrAl_2 at interface 1 and ZrO_2 at interface 2).

Similar reactions are likely to take place in sintering of powder mixtures consisting of an intermetallic compound and an elementary substance [523, 524]. For example, I.F. Martynova *et al.* [524] found the Fe_2Ti and TiNi_3 layers to grow at the interface between FeTi and nickel (Fig. 5.38a).

The mechanism of their formation probably includes the decomposition of FeTi at interface 1



and the subsequent reaction of the released titanium atoms (after their diffusion across the Fe₂Ti layer to interface 2) with the nickel atoms diffusing across the TiNi₃ layer

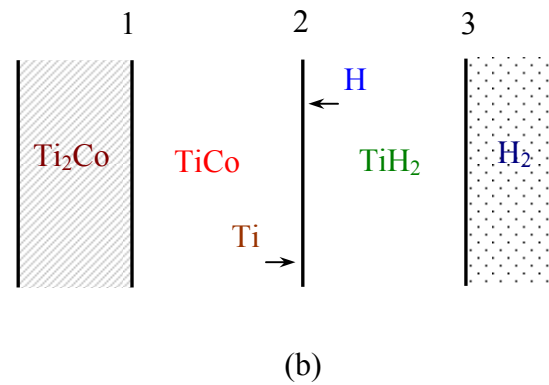
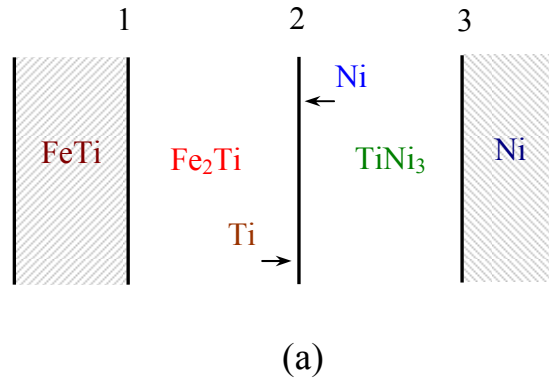


Fig. 5.38. Schematic diagrams to illustrate the process of formation of (a) the Fe₂Ti and TiNi₃ layers at the interface of FeTi with nickel and (b) the TiCo and TiH₂ layers at the interface of Ti₂Co with hydrogen.

When investigating the process of destructive hydrogenation of Ti–X ($X = \text{Co}, \text{Cu}$ and Ni) intermetallics, V.V. Skorokhod *et al.* [525, 526], T.I. Bratanich *et al.* [527-530] and O.V. Kucheriavyi *et al.* [531, 532] found that all the phases available on an appropriate binary phase diagram Ti–X are formed sequentially. The mechanism of their formation appears to be analogous to that of the Fe₂Ti and TiNi₃ layers occurring between FeTi and nickel. For example, formation of the TiCo and TiH₂ (its stoichiometry is more close to TiH_{1.9}) layers at the interface of Ti₂Co and hydrogen is due to partial chemical reactions (Fig. 5.38b)



and



taking place at interfaces 1 and 2, respectively.

After the initial Ti_2Co phase is entirely consumed, further interaction of TiCo with hydrogen yields the layers of TiCo_2 and TiH_2 according to reactions



and



Thus, the sequence of formation of the Ti–Co intermetallic compounds (including the initial Ti_2Co one) is $\text{Ti}_2\text{Co} \rightarrow \text{TiCo} \rightarrow \text{TiCo}_2$, with only two layers (an intermetallic and TiH_2) occurring simultaneously in each intermetallic-hydrogen reaction couple. Similar sequences are observed in hydrogenising of Ti_2Cu and Ti_2Ni [525-532].

It is worth noting that the course of the process of partial oxidation is strongly dependent upon whether an initial chemical compound is taken alone or deposited on a substrate consisting of an oxidising element, as illustrated with the nickel silicide NiSi in Fig. 5.39. If alone, the NiSi compound is partially oxidised by oxygen, giving Ni_2Si and SiO_2 (see Fig. 5.39a).

The reactions of their formation appear to be



and



These take place at interfaces 1 and 2, respectively. In this case, both compound layers grow simultaneously at the expense of the NiSi phase whose thickness steadily decreases with passing time.

By contrast, if a layer of the NiSi compound is deposited on a silicon substrate, then its thickness does not change at all during oxidation, as established by F.M. d'Heurle [486]. It means that the following partial chemical reactions take place (see Fig. 5.39b):

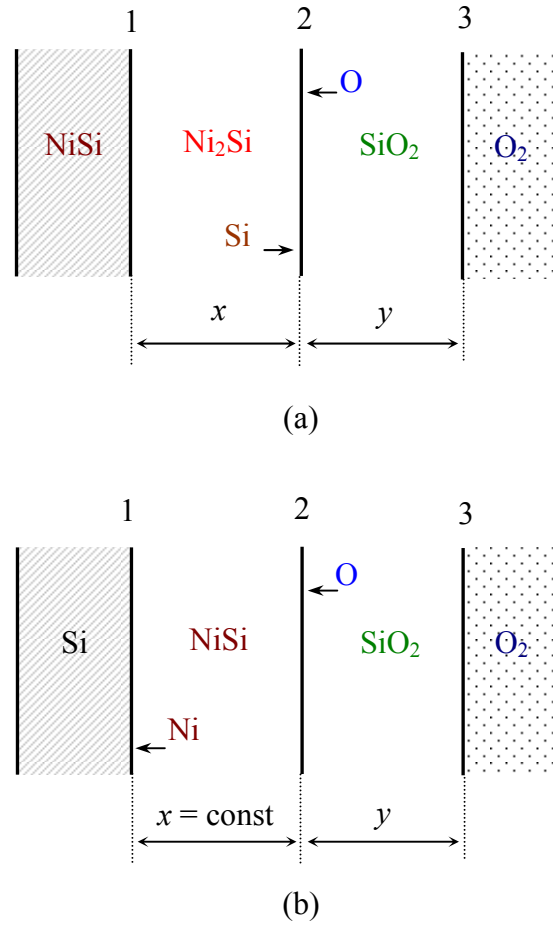


Fig. 5.39. Schematic diagram to illustrate the process of partial oxidation of the NiSi silicide. (a) free, (b) on a silicon substrate.

By contrast, if a layer of the NiSi compound is deposited on a silicon substrate, then its thickness does not change at all during oxidation, as established by F.M. d'Heurle [486]. It means that the following partial chemical reactions take place (see Fig. 5.39b):



and



The former reaction proceeds at interface 2, while the latter at interface 1 after the backward diffusion of the released nickel atoms. The number of NiSi molecules entering into reaction (5.49) is seen to be equal to that occurring as a result of reaction (5.50). Thus,

the disappearance of a NiSi molecule at one of the NiSi interfaces is compensated by its formation at the other. Therefore, the thickness of the NiSi layer remains unchanged, whereas that of the SiO₂ layer increases with passing time. The net reaction is actually the oxidation of silicon from the substrate to form SiO₂. The NiSi layer of constant thickness simply moves as a whole deeper into the substrate bulk, without the loss of its integrity. Similar behaviour is likely to be observed in the course of interaction of intermetallics with other gaseous phases.

This example shows once again how important it is to consider the entire system in question on the whole, not dividing it into a number of individual parts which are supposed to be in local equilibrium with each other, as is often assumed. The latter approach is in most cases like the step-by-step approach to an absurd final result, though each of those steps may seem rather substantiated.

The growth kinetics of compound layers during the oxidation of zirconium aluminides have been described in detail by M. Paljevič [494-496]. Since relatively thick layers were investigated, increase of the mass of a solid specimen with passing time followed a parabolic law.

According to the studies of M.A. Nicolet [490] and F.M. d'Heurle *et al.* [493], oxidation of transition-metal silicides, like that of silicon, obeys a linear-parabolic relation. Note that if the diffusion of oxygen atoms across the SiO₂ layer is the rate-determining step, the parabolic regions of oxidation of silicon and silicides should be characterised by the same growth-rate constant. If not, then either the experiments were carried out under considerably differing conditions or the structure of the SiO₂ layer was different with various silicides. On the contrary, the linear-rate constant must clearly depend upon the chemical composition of silicides, as indeed observed experimentally [490, 493].

5.7: Reaction-diffusion kinetics in solid-liquid and solid-gas systems: short conclusions

1. If the chemical compound is formed under conditions of simultaneous dissolution in the liquid phase or evaporation into the gaseous phase, then its layer does not occur at the *A–B* interface until the rate of dissolution or evaporation becomes equal to the sum of the rates of chemical transformations (chemical reactions as such) taking place at the layer interfaces with initial substances *A* and *B*.

2. If the rate of layer formation is limited by the rate of diffusion of the atoms of reacting substances across its bulk, it is impossible to prevent the occurrence of this layer between *A* and *B* by any reasonable increasing the dissolution or evaporation rate. What is only possible is a considerable reduction of its thickness.

3. If the chemical compound layer dissolves or evaporates under isothermal conditions at a constant rate, its thickness reaches with passing time a certain highest value and then remains almost unchanged. Subsequently, the layer of constant (maximal) thickness moves as a whole into the bulk of phase *A* until this phase is consumed completely.

4. At a considerable solubility of solid A in liquid B , formal search for the so-called layer-growth laws by means of mathematical treatment of the experimental data using linear, parabolic, logarithmic or other dependences does not seem to be reasonable. Each of the “laws” thus obtained holds only under particular (in most cases, unspecified) dissolution conditions. It is therefore sufficient to slightly change those conditions, and the “law” will also change. The same applies to the case of formation of the layer of a volatile chemical compound.

5. At finite values of the surface area of a solid and the volume of a liquid, the dissolution rate of the solid in the liquid phase decreases with passing time from its highest value to zero (when the saturation concentration is reached). The greater the surface area of the solid and the less the volume of the liquid, the quicker the saturation of the liquid by the dissolving substance is attained. With increasing degree of saturation, the influence of dissolution on the growth kinetics of a chemical compound layer gradually weakens and hence the layer thickness-time dependence asymptotically approaches that which would be observed in the case of a saturated solution of A in B .

6. Partial (soft) oxidation of a chemical compound is likely to result in the formation of the layers of two other compounds, one of which is an oxide and another is the other chemical compound of a given binary system, enriched in a non-oxidising element.

Concluding Remarks

The consideration of the reaction-diffusion process in binary heterogeneous systems, carried out in this book, is actually based upon two simple and obvious assumptions:

- (1) About the quasi-stationary distribution of the concentration of the components in all phases involved into the interaction.
- (2) About the summation of the time of lattice diffusion and that of subsequent chemical transformations in the solid-state growth of chemical compound layers.

When combined with the very fundamental concepts and laws of chemistry and physics, these allow the kinetic dependences most often observed experimentally to be derived from a single theoretical viewpoint. Clearly, not all the details of the experimental dependences may be unambiguously interpreted on the basis of the proposed relations because in analysing the mathematical equations attention was only paid to apparent limiting cases. This reduces the number of dependences which could be obtained from the same premises without additional assumptions.

Nevertheless, in this book the number of the theoretically substantiated kinetic equations, for the experimentalist to use in practice, appears to exceed that resulting from purely diffusional considerations. Whether the experimentalist will be pleased with such an abundance of equations is another question. Still, for many researchers in the field it is so tempting to employ a single parabolic relation and then to discuss in detail the reasons for (unavoidable and predictable) deviations from its course. Note that, unlike diffusional considerations where each interface is assumed to move according to the square root of the time, in the framework of the physico-chemical approach the layer-growth kinetics are not predetermined beforehand by any additional assumptions, except basic ones, but immediately follow in a natural way from the proposed mechanism of the reaction-diffusion process.

Of possible directions of further experimental work, the following are worth mentioning.

- (1) Systematic accumulation of experimental data on the reaction kinetics for a variety of chemical compounds under well defined conditions. It should be recognised that, in spite of a number of investigations that have been and are being carried out in the field, the available experimental data bear an odd character. In most cases, their juxtaposition and joint theoretical treatment for the verification of theoretical views are hardly possible. Moreover, much of the available experimental data is not suitable for quantitative treatment at all.
- (2) Thorough experimental verification of basic kinetic equations in order to support or reject the existing theoretical views. This applies, for example, to equations of the type (1.64) and (1.65). Although the possibility of growth of the layers of chemical compounds

without any homogeneity range is no longer questionable, a relationship between the reaction-diffusion coefficient of a component in the growing compound and the self-diffusion coefficient of the same component in the non-growing one is still debatable. It may prove that equations (1.64) and (1.65) are only the landmarks indicating the way to a solution of this problem rather than the solution itself.

The main obstacle to performing systematic detailed studies likely to provide an insight into the underlying chemical and physical phenomena appears to be the economical pressure for a marketable product, device or technology to pay for research work. Unfortunately, most scientific foundations refuse to support pure science, though often readily finance projects without any serious substantiation, containing (mainly unrealistic) promises to make a revolution in production or technology. The present scattered and poorly coordinated approach can scarcely yield scientific results of considerable value. Rather, these are likely to be incommensurably small when juxtaposed to expenditures, but it usually becomes clear after the money allocated has already been spent successfully. In many cases, it (*i.e.* spending money) happens to be the only success of the whole work.

As to theory, attention is to be directed towards

- (i) establishing the relationships or at least correlations between the values of chemical and physical (diffusional) constants on the one hand, and the physical and chemical properties of the components *A* and *B* and their compounds on the other;
- (ii) mathematical analysis of kinetic dependences, especially in the vicinity of the critical values of the layer thicknesses.

It should be emphasised that of primary interest for both theory and practice is the investigation of the very beginning of interaction of initial substances, including the linear region of growth of compound layers, which has still been explored insufficiently well.

I hope that the reader has understood how unreasonable it is to ignore any of the two steps of the reaction-diffusion process (either reaction or diffusion). Irrespective of the educational background, any researcher must realise that only chemistry, physics and mathematics, taken together, are likely to result in a correct consideration of solid-state chemical kinetics.

It may well happen that the physicist is not very keen on chemistry and therefore tends to underestimate the significance of Proust's law of definite proportions and Dalton's law of multiple proportions. Similarly, the chemist might have attended the lectures on physics not too often and is therefore unaware of Fick's laws. However, it is not a sufficient reason for the former to ignore the step of reaction or for the latter to do the same with the step of diffusion. Though much of the literature on the reaction-diffusion kinetics consists of controversy in favour of one or the other of two most fundamental linear and parabolic relations (more often, in favour of a parabolic relation), the truth, as always, appears to lie somewhere in between. Depending on experimental conditions, the demarcation zone between those laws may displace either towards reaction or towards diffusion, but, unlike some "superfluous" compound layers, it never disappears.

Attention must also be paid to secondary and accompanying effects as well, but of course not at the expense of ignorance of the main features of the reaction-diffusion process. Continuous interplay of theory and experiment is essential in order that not to conduct fruitless experiments and not to put forward misleading theories.

It appears relevant to note that many researchers tend to exaggerate the significance of thermodynamic predictions concerning the direction of the reaction-diffusion process. In fact, however, those only bear a likelihood character. Thermodynamics never say yes, rather may be. Even if the free energy of formation of one compound from its constituents is -200 kJ mol^{-1} , while that of the other is -20 kJ mol^{-1} , it does not necessarily mean, as often (tacitly or directly) assumed, that the former will occur first and the more so that its growth rate must be ten times greater than that of the latter. As exemplified with the growth rate of a compound layer in various diffusion couples of the same multiphase binary system, the opposite may well take place.

Too categorical judgments must be avoided even in the case of a positive change in the free energy of formation of a compound. Account is to be taken of other chemical reactions proceeding simultaneously, because it may happen that the loss of energy in one of them is offset by its gain in the other(s), thus making the former possible.

Finally, it remains to me to express my hope that the reader has convinced that, starting from physico-chemical views, it is indeed possible to derive a self-consistent and rather adequate description of the compound layer-growth kinetics observed experimentally. At least, most probable types of the layer thickness-time dependence can readily be predicted. Also, in some cases (unfortunately, their number is as yet very limited) it is even possible to evaluate the parameters of theoretical equations governing the process of layer growth. Perhaps, this book will stimulate further work in this direction.

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