

## Reaction Diffusion in Binary Solid-Solid, Solid-Liquid and Solid-Gas Systems: Common and Distinctive Features

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**Abstract.** The process of reaction diffusion in binary systems, resulting in the occurrence of chemical compound layers (intermetallics, silicides, oxides, salts, etc.) at the interface between initial substances, is analysed from a physicochemical viewpoint to show that (i) under conditions of diffusion control the number of growing layers is most likely to be one or two irrespective of the number of chemical compounds on the appropriate phase diagram, (ii) major experimentally observed kinetic dependences can be obtained using a single system of differential equations, (iii) in the case of multiple growth, one inert marker is in general insufficient to decide of the main diffusing species in all the layers formed, (iv) different diffusional contributions of the components to the growth process of a chemical compound layer should not necessarily be regarded as a manifestation of the Kirkendall effect.

### Introduction

When analysing the reaction-diffusion process in binary heterogeneous systems, there is a tendency to consider different classes of chemical compounds in isolation from each other. Not only such an approach seems fruitless, but may even be misleading. Instructive examples of confusion are the linear growth kinetics and the interpretation of marker experiments with intermetallics on the one hand and with oxides (or salts) on the other. Though the linear growth of oxides is known to chemists at least since 1924 [1], many physicists and metallurgists involved into the study of intermetallics (or silicides, germanides, etc.) still tend to treat this 'abnormal' kinetic dependence as a deviation from the 'normal' parabolic one. Meanwhile, both are the two extremes following from a general kinetic law of Evans' type, and therefore may equally be expected to hold for any binary system, whatever its chemical nature, if a sufficiently wide range of compound-layer thicknesses is investigated [2]. Also, different diffusional contributions of the components to the growth process of intermetallics are often considered to be a consequence of the Kirkendall effect which in fact has no relation to growing compound layers.

Although many binary systems are multiphase, the number of compound layers growing under isothermal conditions at the phase interfaces is known to be much less than the number of chemical compounds (intermetallics, oxides, silicides, salts, etc.) on appropriate phase diagrams. For example, there are four intermetallic compounds on the Ti-Al phase diagram, while, according to F.J.J. van Loo [3], only the  $\text{TiAl}_3$  layer grows at the Ti-Al interface below the melting point of aluminium. Recent experiments by S. Wöhlert and R. Bormann [4] left no room for any doubt regarding the real absence of other titanium aluminides since even the artificially prepared  $\text{Ti}_3\text{Al}$  and TiAl layers were completely consumed in the reaction of formation of the dominant  $\text{TiAl}_3$

layer. In transition metal-aluminium binary systems the number of intermetallic compounds on the phase diagrams is three to eleven, while the number of growing layers at the transition metal-aluminium interface is one or two [5]. The  $\text{Fe}_2\text{Al}_5$  layer is known to grow between solid iron and liquid aluminium saturated [6] or undersaturated [7] with iron at  $700^\circ\text{C}$ . At this temperature, four intermetallics are stable [8]. Of a few known oxides, the  $\text{TiO}_2$  layer dominates during oxidation of titanium [9-11]. This feature is thus common to solid-solid, solid-liquid and solid-gas binary systems.

In spite of close mechanisms of layer formation, kinetic dependences observed experimentally, for example, in metal-oxygen systems are more numerous (linear, parabolic, parabolic, cubic, asymptotic, etc.) than those in metal-metal systems where in most cases the parabolic growth law is dominating. Consider briefly the reasons for these and related phenomena, starting from definitions and the mechanism of the reaction-diffusion process.

### Mechanism of reaction diffusion

By definition, chemical compound is an ordered phase of constant composition. Reaction diffusion is a physical-chemical process resulting in the occurrence of a continuous solid compound layer at the interface between initial substances. 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 the two consecutive steps:

- (1) Diffusion of atoms (ions) of the reactants across its bulk in the opposite direction;
- (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).

It should be noted that the often employed term *diffusional growth* only reflects one aspect of the layer-growth mechanism, namely, atomic diffusion. The differences in terminology are not so unimportant as it may seem at first sight.

Direct reaction between phases *A* and *B* ceases after the formation of a product layer, a few crystal-lattice units thick. Subsequently, two partial chemical reactions



and



take place at interfaces 1 and 2, causing the increase in layer thickness during  $dt$  by  $dx_{B1}$  and  $dx_{A2}$ , respectively (Fig.1). Kinetically, these are two different reactions because (i) they are separated in space and (ii) the reactants enter them in different states (as diffusing or as surface atoms). No reaction proceeds within the bulk of the growing compound layer.

It should also be emphasised that 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. For the layer to grow, it does not matter, whether the compound has any range of homogeneity or not.

### Critical thickness and growth regime of the layer

Each surface *A* atom can chemically bond a certain number of diffusing *B* atoms. For the *AB* compound, this number is equal to unity, while for the  $A_pB_q$  compound to  $q/p$ . Since the number of the *A* atoms in 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 is also finite. The *reactivity* (or

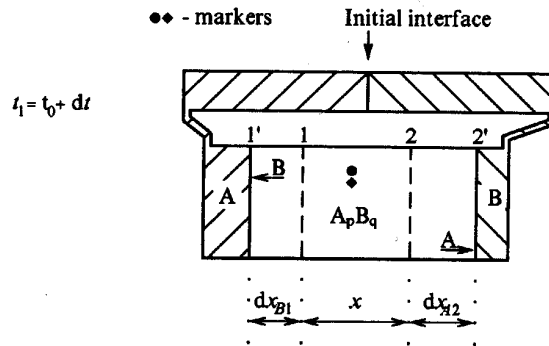


Figure 1. Schematic diagram illustrating the growth process of the  $A_p B_q$  layer.

*combining ability*) of the surface of substance  $A$  towards the  $B$  atoms is equal to the largest number of diffusing  $B$  atoms which can be combined per unit time by the surface  $A$  atoms into a compound of certain composition. While the reactivity of the  $A$  surface towards the  $B$  atoms remains constant, the flux of the  $B$  atoms across the  $A_p B_q$  layer steadily decreases from infinitely high to infinitely small values as the layer thickness increases with passing time from zero to very high values. Hence, there is a single *critical* thickness of the  $A_p B_q$  layer

$$x_{1/2}^{(B)} = \frac{k_{1B1}}{k_{0B1}} \quad (3)$$

at which these quantities are equal [2]. In Eq. 3  $k_{1B1}$  is a diffusional constant or the reaction-diffusion coefficient of the  $B$  atoms across the growing  $A_p B_q$  layer, different from the self-diffusion coefficient of component  $B$  in the same compound  $A_p B_q$  but taken alone, while  $k_{0B1}$  is a chemical constant characterising the rate of chemical transformations at interface 1.

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  $A_p B_q$  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  $A_p B_q$  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  $A_p B_q$  layer. Therefore, on reaching interface 1, each  $B$  atom is combined at this interface into the  $A_p B_q$  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  $A_p B_q$  can grow at the expense of diffusion of component  $B$ . This almost obvious result following in a natural way from the physicochemical considerations [2] is crucial for understanding the mechanism of formation of multiple compound layers. Note that it remained overlooked until 1982 [12].

It should be emphasised that in the examined case of growth of a single layer of the  $A_p B_q$  compound, there is only the *possibility* of formation of an 'excess' of the  $B$  atoms at  $x < x_{1/2}^{(B)}$ , and not this 'excess' as such in the form of a build-up of those atoms at interface 1. In the solid, there is simply no space for this to take place there. Therefore, the word *excess* was placed within quotation marks 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  $A_p B_q$  layer itself, which could otherwise have grown at much higher rates.

The thickness,  $x_{1/2}^{(B)}$ , of the  $A_p B_q$  layer is referred to as *critical* because the growth conditions for the layers of other compounds of a given multiphase system become indeed critical at  $x > x_{1/2}^{(B)}$

because all of them lose a source of the  $B$  atoms (actually, only substance  $B$  is such a source) and their growth at the expense of diffusion of the  $B$  atoms is stopped. This problem will be examined in more detail when analysing the process of simultaneous formation of two and multiple chemical compound layers.

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

If components  $A$  and  $B$  have comparable mobilities in the  $A_pB_q$  lattice, then reactions 1 and 2 proceed simultaneously at close rates. 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 partial reactions 1 and 2 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 words *chemical interaction* and *chemical transformations*. Note that, to avoid any confusion with terminology, it would be more correct to speak of *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 with regard to component B* at  $x < x_{1/2}^{(B)}$  or *diffusion control with regard to this component* at  $x > x_{1/2}^{(B)}$ .

Obviously, in addition to  $x_{1/2}^{(B)}$  there is another critical value

$$x_{1/2}^{(A)} = \frac{k_{1A2}}{k_{0A2}} \quad (4)$$

of the thickness of the  $A_pB_q$  layer at which all the  $A$  atoms capable of reaching interface 2 by a given moment of time are combined at this interface by the surface  $B$  atoms into the  $A_pB_q$  compound. In Eq. 4  $k_{1A2}$  is another diffusional constant or the reaction-diffusion coefficient of the  $A$  atoms across the growing the  $A_pB_q$  layer, different from the self-diffusion coefficient of component  $A$  in the same compound  $A_pB_q$  but taken alone, while  $k_{0A2}$  is another chemical constant characterising the rate of chemical transformations at interface 2.

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

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 can once again be divided into the two regions: reaction controlled with regard to component  $A$  at  $0 < x < x_{1/2}^{(A)}$  and diffusion controlled

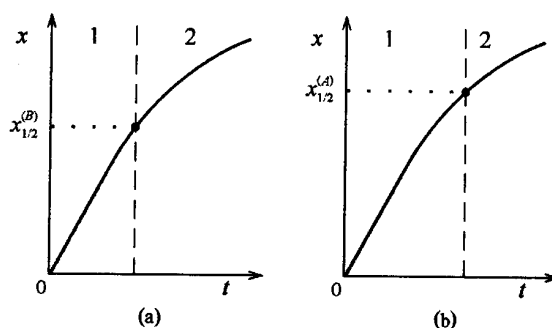


Figure 2. Schematic diagram to explain the theoretical definition of the concept of the growth regime of the  $A_p B_q$  layer with regard to components A and B.

(a): 1, region of reaction (or, most 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.

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. 2). Hence, during some time (at  $x_{1/2}^{(B)} < x < x_{1/2}^{(A)}$ ) the  $A_p B_q$  layer grows in the reaction controlled regime with regard to component A and in the diffusion controlled regime with regard to component B.

### Layer-growth kinetics

**One compound.** Kinetic equation expressing the growth rate of the  $A_p B_q$  layer as a result of diffusion of the B atoms and subsequent reaction 1 can readily be found using the following assumptions ( postulates) [2,12]:

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

$$dt = dt_{\text{dif}}^{(B)} + dt_{\text{chem}}^{(B)}. \quad (5)$$

(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  $A_p B_q$  layer and its existing total thickness  $x$ :

$$dt_{\text{dif}}^{(B)} = \frac{x}{k_{1B1}} dx_{B1}. \quad (6)$$

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

$$dt_{\text{chem}}^{(B)} = \frac{1}{k_{0B1}} dx_{B1} \quad (7)$$

Note that  $dt_{\text{chem}}^{(B)}$  is proportional to  $x^0$ , while  $dt^{(B)}$  is proportional to  $x^1$ .

Basic assumptions 1 to 3 were put forward [12] as a result of analysis, firstly, of the reaction-diffusion mechanism described in detail by V.I. Arkharov [13,14] and, secondly, of a linear-parabolic equation derived for the first time by U.R. Evans from somewhat different considerations [1]. It should be noted that similar assumptions were used earlier by B.Ya. Pines [15,16] who, in deriving differential forms of kinetic equations, summed up the duration of 'external' and 'internal' diffusion. The physicist B.Ya.Pines appeared to be unaware of chemical studies of U.R. Evans. He never cited them and probably discovered independently the kinetic equation which had already been known for a long time, at least to chemists.

Combining Eq. 5, 6 and 7 yields

$$dt = \left( \frac{x}{k_{1B1}} + \frac{1}{k_{0B1}} \right) dx_{B1} \quad (8)$$

or

$$\frac{dx_{B1}}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} \quad (9)$$

Since chemical reactions 1 and 2 are considered as independent of one another, similar expressions hold also for component A:

$$dt = \left( \frac{x}{k_{1A2}} + \frac{1}{k_{0A2}} \right) dx_{A2} \quad (10)$$

and

$$\frac{dx_{A2}}{dt} = \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} \quad (11)$$

Summation of the right-hand sides of Eq. 9 and 11 yields the following 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 reactions 1 and 2:

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} \quad (12)$$

It should be emphasised that, although it is possible to distinguish much more consecutive steps in the reaction-diffusion process, they can be divided into two groups on the basis of their dependence on  $dx$  and  $x$ :

(1) The steps which depend on  $dx$  but are independent of  $x$ . These were united under the term *chemical transformations* (synonyms: chemical reaction or interaction, interfacial reaction or interaction).

(2) The steps which depend on both  $dx$  and  $x$ , with the only representative being the diffusion of atoms or ions across a growing chemical compound layer.

Therefore, Eq. 8 and 10 contain only two terms on their right-hand sides. An equation of type 9 was first proposed by U.R. Evans in 1924 [1], while of type 12 by B. Ya. Pines in 1959 [16].

From Eq. 12 it follows that initial growth of the  $A_pB_q$  layer is linear (at  $x\zeta x_{1/2}^{(B)}$  and  $x\zeta x_{1/2}^{(A)}$ ), while then there is a gradual transition to the parabolic growth (at  $x\Omega x_{1/2}^{(B)}$  and  $x\Omega x_{1/2}^{(A)}$ ). The higher the temperature, the narrower in time is the region of linear growth, typical of layer thicknesses from a few tens to a few hundreds of nanometres [17,18]. Ignorance of the step of chemical transformations results in the 'loss' of linear growth region.

Note that for a compound layer to grow, both components should not necessarily diffuse across its bulk simultaneously. As the formation of chemical compounds is characteristic of the elements strongly differing by their atomic radii and melting points, diffusion of one component may be expected to predominate. For example, bismuth is known to be the only diffusant in the  $\text{NiBi}_3$  layer growing between Ni and Bi [19]. Shown in Fig. 3a 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 electrolytically polished after annealing, the  $\text{NiBi}_3$  layer is quite homogeneous in appearance. Then, it was annealed for the third time at 200°C for 100 h (200 h in total). Figure 3b shows its microstructure in the as-received condition (without any polishing). The newly-grown  $\text{NiBi}_3$  phase is much darker than the old one and therefore is easily distinguishable.

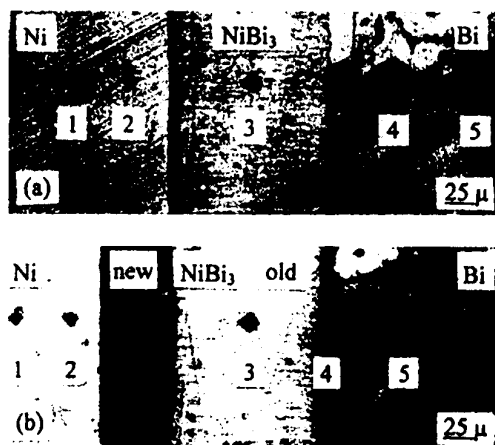


Figure 3. Optical micrographs of the Ni-Bi transition zone before (a) and after (b) the third anneal. Temperature 200°C.

(a) annealed two times (50h + 50 h). Microhardness indentations were put onto the electropolished surface of the cross-section after the second anneal at a load of 0.196 N (20 g).

(b) the same place after the third anneal for 100 h in the as-received condition.

Before the third anneal, microhardness indentation markers were put onto the electropolished cross-section surface in the Ni phase (five markers, about 50  $\mu\text{m}$  apart), in the middle of the  $\text{NiBi}_3$  layer (one marker) and in the Bi phase (five markers, about 75  $\mu\text{m}$  apart). Only part of them are shown in Fig. 3.

After the third anneal, the distance between the marker 3 and the Ni- $\text{NiBi}_3$  interface increased from 76 to 137  $\mu\text{m}$ , whereas the distance between this marker and the  $\text{NiBi}_3$ -Bi interface remained unchanged (70  $\mu\text{m}$ ). Marker 4 almost disappeared as a result of consumption of the Bi phase. The

distance between the markers 3 and 5 decreased by 61  $\mu\text{m}$  (from 202 to 141  $\mu\text{m}$ ). In terms of thickness, the consumption of nickel (around 6  $\mu\text{m}$ ) is seen to be much less than that of bismuth (61  $\mu\text{m}$ ). These values agree with the stoichiometry of the  $\text{NiBi}_3$  intermetallic compound, as it must be from a chemical viewpoint. Indeed,

$$\frac{x_{\text{Ni}}}{x_{\text{Bi}}} = \frac{c_{\text{Ni}}\rho_{\text{Bi}}}{c_{\text{Bi}}\rho_{\text{Ni}}} \quad (13)$$

where  $x$ ,  $c$  and  $\rho$  are respectively the thickness consumed, the content in  $\text{NiBi}_3$  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  $\rho_{\text{Bi}} = 9.8 \times 10^3 \text{ kg m}^{-3}$ , Eq. 13 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  $\text{NiBi}_3$  layer mostly displaces as a whole into the side of bismuth, though its increase takes place entirely at the opposite side (near nickel).

**Two compounds.** When considering the process of layer formation, it is necessary first of all to write down partial chemical reactions taking place at the interfaces of reacting phases (Fig. 3):

Layer	Interface	Reaction	
$A_pB_q$	1	$qB_{\text{diff}} + pA_{\text{surf}} = A_pB_q$ ,	(14 <sub>1</sub> )
	2	$(sp - qr)A_{\text{diff}} + qA_rB_s = sA_pB_q$ ,	(14 <sub>2</sub> )
$A_rB_s$	2	$(sp - qr)B_{\text{diff}} + rA_pB_q = pA_rB_s$ ,	(15 <sub>1</sub> )
	3	$rA_{\text{diff}} + sB_{\text{surf}} = A_rB_s$ .	(15 <sub>2</sub> )

In the general case of comparable mobilities of both components, the growth rates of two compound layers between  $A$  and  $B$  phases are described by the system of differential equations [2]:

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} - \frac{rg}{p} \frac{k_{0B2}}{1 + \frac{k_{0B2}y}{k_{1B2}}}, \quad (16_1)$$

$$\frac{dy}{dt} = \frac{k_{0B2}}{1 + \frac{k_{0B2}y}{k_{1B2}}} + \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}} - \frac{q}{sg} \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}}, \quad (16_2)$$

where  $x$  and  $y$  are thicknesses of the layers at time  $t$ , all  $k_0$  are chemical constants, all  $k_1$  are diffusional constants equal to reaction-diffusion coefficients of appropriate elements in the layer bulks ( $k_1 = D_{\text{rd}}$ ) and  $g$  is the ratio of molar volumes of the compounds. From this system, it follows that the sequential formation of the layers is more probable than their simultaneous occurrence at the  $A$ - $B$  interface. It is also clear that the sequence of their appearance is determined by the *rate of chemical transformations* at the interfaces, and not by the *rate of diffusion* of the elements  $A$  and  $B$  across the layer bulks. Simply speaking, at small  $t$  these 'bulks' are too negligible in order that diffusion across them could play a noticeable role in determining the overall rate of the compound growth process.

Initially, the layer growth is linear. After the first occurred layer has reached a minimally necessary thickness, the second starts to grow. Their growth kinetics change with passing time from linear to parabolic or cubic. Asymptotic and parabolic laws are also possible [2]. The distinctive feature of metal-metal and metal-gas systems is that in the former ones in most cases only parabolic growth was observed, whereas in the latter a variety of growth laws was revealed experimentally [1,9-11]. This is due to the different sensitivity of experimental methods used, and

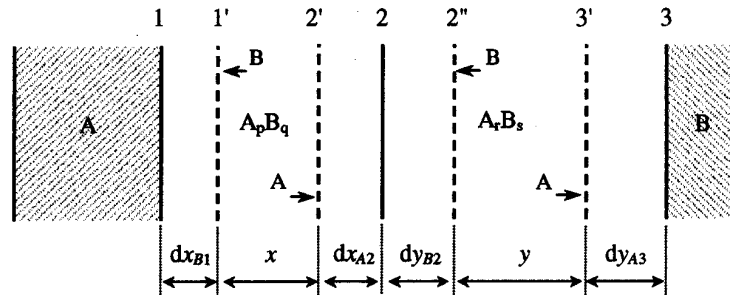


Figure 4. Schematic diagram illustrating the growth process of two compound layers at the expense of diffusion of both components.

not to some significant difference in the mechanism of layer formation. Simply, metal-gas systems were studied over much wider periods of time using more sensitive techniques than the metallic ones.

Note that under conditions of diffusion control ( $x > x_{1/2}^{(A)}$  and  $y > y_{1/2}^{(B)}$ ), each layer grows at the expense of diffusion of *one* component (Fig. 5). Therefore, their growth can by no means be regarded as a result of *mutual* diffusion of the components *A* and *B* since reactions 14<sub>1</sub> and 15<sub>2</sub> do not proceed in view of the lack of appropriate diffusing atoms.

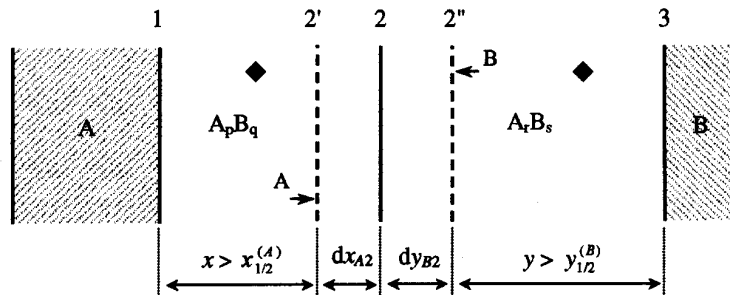


Figure 5. Schematic diagram illustrating the growth process of two compound layers under conditions of diffusion control ( $x > x_{1/2}^{(A)}$  and  $y > y_{1/2}^{(B)}$ ). Only component *A* is diffusing in the  $A_pB_q$  layer, while only component *B* is diffusing in the  $A_rB_s$  layer. Both layers thicken at their common interface 2. No reactions take place at interfaces 1 and 3. The symbol  $\blacklozenge$  designates an inert marker.

Indeed, the source of diffusing *A* atoms for both layers to grow is actually phase *A*, while the source of diffusing *B* atoms is phase *B*. The growing layers themselves readily supply these atoms to each other until the rates of atomic diffusion across their bulks are sufficient to compensate their loss in appropriate chemical reactions at the phase interfaces. Clearly, only the remaining *A* atoms, which has diffused across the bulk of the  $A_pB_q$  layer but has not reacted with the  $A_rB_s$  'molecules' at interface 2 via reaction 14<sub>2</sub>, are able to diffuse further across the bulk of the  $A_rB_s$  layer and then to enter reaction 15<sub>2</sub> at interface 3. Similarly, only the remaining *B* atoms, which has diffused across the bulk of the  $A_rB_s$  layer but has not reacted with the  $A_pB_q$  'molecules' at interface 2 via reaction 15<sub>1</sub>, are able to diffuse further across the bulk of the  $A_pB_q$  layer and then to enter reaction 14<sub>1</sub> at

interface 3. At  $x > x_{1/2}^{(A)}$  and  $y > y_{1/2}^{(B)}$  all the diffusing atoms are combined into appropriate compounds at interface 2. Thus, interface 2 becomes a natural barrier to their further diffusion. This *chemically* obvious conclusion is lost as a result of ignorance of the step of chemical transformations, and mutual diffusion of both components in both growing layers becomes 'possible'. The latter *incorrect* conclusion is usually drawn if diffusion is a more slow process than reaction itself. In fact, rapid reaction rapidly consumes diffusing atoms, and it remains nothing for other reactions than to stop.

**Multiple compounds.** In the case of three compounds, appropriate partial chemical reactions resulting in the increases of layer thicknesses at the interfaces of reacting phases (Fig. 5) are

Layer	Interface	Reaction	
$A_pB_q$	1	$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q$ ,	(17 <sub>1</sub> )
	2	$(sp - qr)A_{\text{dif}} + qA_rB_s = sA_pB_q$ ,	(17 <sub>2</sub> )
$A_rB_s$	2	$(sp - qr)B_{\text{dif}} + rA_pB_q = pA_rB_s$ ,	(18 <sub>1</sub> )
	3	$(rn - ls)A_{\text{dif}} + sA_lB_n = nA_rB_s$ ,	(18 <sub>2</sub> )
$A_lB_n$	3	$(rn - ls)B_{\text{dif}} + lA_rB_s = rA_lB_n$ ,	(19 <sub>1</sub> )
	4	$lA_{\text{dif}} + nB_{\text{surf}} = A_lB_n$ .	(19 <sub>2</sub> )

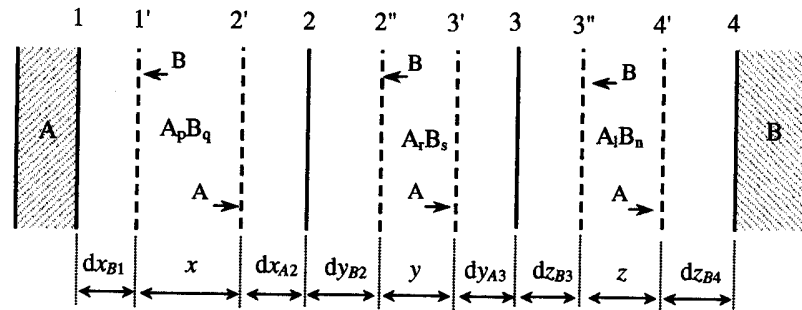


Figure 6. Schematic diagram illustrating the growth process of three compound layers at the expense of diffusion of both components.

The system of differential equations describing the growth rates of three compound layers between A and B phases is [2]

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} - \frac{rg_1}{p} \frac{k_{0B2}}{1 + \frac{k_{0B2}y}{k_{1B2}}}, \quad (20_1)$$

$$\frac{dy}{dt} = \frac{k_{1B1}}{k_{0B2}} + \frac{k_{1A2}}{k_{0A3}} - \frac{q}{sg_1} \frac{k_{1B2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} - \frac{lg_2}{r} \frac{k_{0B3}}{1 + \frac{k_{0B3}z}{k_{1B3}}}, \quad (20_2)$$

$$\frac{dz}{dt} = \frac{k_{1B2}}{k_{0B3}} + \frac{k_{1A3}}{k_{0A4}} - \frac{s}{ng_2} \frac{k_{1A2}}{1 + \frac{k_{0A3}y}{k_{1A3}}}, \quad (20_3)$$

where  $g_1$  is the ratio of molar volumes of  $A_pB_q$  and  $A_rB_s$ , while  $g_2$  is that of  $A_rB_s$  and  $A_lB_n$ . Note that a simplification in designations of some chemical and diffusional constants (insignificant for further considerations) was made when writing down the systems 16 and 20.

Initial layer growth is again linear. Their simultaneous occurrence at the A-B interface is highly unlikely since the probability of the case where all three derivatives  $dx/dt$ ,  $dy/dt$  and  $dz/dt$  are positive (+,+,+) is evidently much less than the probability of the case where these derivatives have different signs (+,-,-; -,+,-; -,+,-; +,+,-; +,-,+; -,+,+). Rather, in any binary system the layers must occur sequentially, in accordance with experimental observations. Under conditions of diffusion control the number of *simultaneously growing* layers can hardly be expected to exceed two (Fig.7).

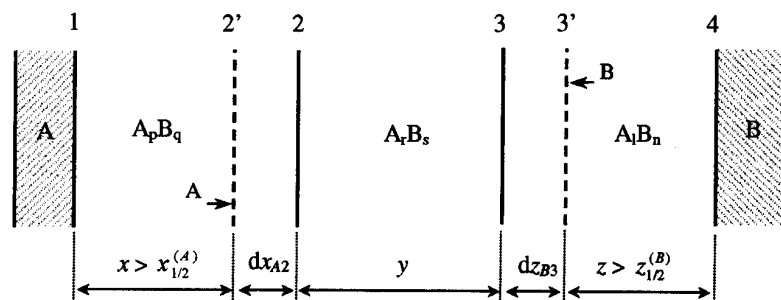


Figure 7. Schematic diagram illustrating the reaction-diffusion process in the case where the  $A_pB_q$  and  $A_lB_n$  layers grow under conditions of diffusion control ( $x > x_{1/2}^{(A)}$  and  $z > z_{1/2}^{(B)}$ ). The  $A_rB_s$  layer has no diffusing atoms to grow and is consumed until full disappearance.

Indeed, at  $x > x_{1/2}^{(A)}$  all the A atoms diffusing across the bulk of the  $A_pB_q$  layer are spent in the formation of the  $A_pB_q$  compound at interface 2 via reaction 17<sub>2</sub>, while at  $z > z_{1/2}^{(B)}$  all the B atoms diffusing across the bulk of the  $A_lB_n$  layer are spent in the formation of the  $A_lB_n$  compound at interface 3 via reaction 19<sub>1</sub>. Reactions 17<sub>1</sub>, 18<sub>1</sub>, 18<sub>2</sub> and 19<sub>2</sub> do not proceed in view of the lack of appropriate diffusing atoms. Therefore, at  $x \gg x_{1/2}^{(A)}$  and  $z \gg z_{1/2}^{(B)}$  the system 20 is simplified to

$$\frac{dx}{dt} = \frac{k_{1A2}}{x}, \quad (21_1)$$

$$\frac{dy}{dt} = -\frac{q}{sg_1} \frac{k_{1A2}}{x} - \frac{lg_2}{r} \frac{k_{1B3}}{z}, \quad (21_2)$$

$$\frac{dz}{dt} = \frac{k_{1B3}}{z}. \quad (21_3)$$

Thus, the  $A_pB_q$  and  $A_lB_n$  layers will grow parabolically at the expense of the  $A_rB_s$  layer. This system is clearly very suitable to determine the diffusional constants  $k_{1A2}$  and  $k_{1B3}$  which, by their physical meaning, are respectively the reaction-diffusion coefficient of the A atoms in the  $A_pB_q$  lattice and the reaction-diffusion coefficient of the B atoms in the  $A_lB_n$  lattice.

Simultaneous presence of thick ( $> 1 \mu$ ) multiple layers is most likely a result of secondary causes, to be revealed in each particular case. First of all, cracking of the reaction couples due to thermal expansion and volume effect must be mentioned. Also, additional layers may occur during cooling a reaction couple from experiment temperature down to room temperature. Couples with

close coefficients of thermal expansion of their constituents like Ni and Bi are a rare exception [19]. These withstand a few successive anneals without cracking. Unfortunately, the great majority of reaction couples like the Ni-Zn [20] or Co-Zn [21] ones crack along layer interfaces even in the course of their first anneal. Actually, the initial couple thus splits into two new independent couples, in each of which again up to two compound layers may occur. This produces a hardly tractable microstructure of the transition zone between reacting phases and supports the myth about the simultaneous *growth* of multiple compounds. Also, in solid-liquid and solid-gas systems the cracked layers lose their protective qualities against further liquid or gas attack, and it becomes not so easy to unambiguously interpret experimental results. Even similar systems may behave differently. For example, according to J. Brandstötter and W. Lengauer [22], compact transition metal boride layers occur at the solid-gas interface sequentially, whereas more permeable transition metal nitride layers were found by W. Lengauer [23] to form simultaneously.

The situation with predicting the sequence of layer formation in multiphase binary systems is still far from being satisfactory. Proposed empirical rules [24-28] give the predictions for a certain class of compounds at a probability of 75 to 90 % but fail to predict possible exceptions. This considerably lowers their value since any researcher or technologist is clearly interested in knowing the sequence of occurrence of compound layers in a *particular* reaction couple.

### **Phase diagram and compound-layer formation between A and B phases**

In the case of binary systems with one chemical compound, there is a full correspondence between what is seen at the A-B interface and the appropriate A-B equilibrium phase diagram. 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 the available 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 a binary system with two compounds a full correspondence between the microstructure of the A-B transition zone and the appropriate A-B equilibrium phase diagram can in principle be achieved at prolonged anneals. The only obstacle for this may be a very great difference in growth rates of the 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 is close to linear.

In a binary system with three or more compounds no full correspondence between the microstructure of the A-B transition zone and the appropriate A-B equilibrium phase diagram can be achieved, whatever the annealing time. Part of compounds will inevitably be missing, not simply too thin to be observed. Therefore, to confidently judge of the structure of the A-B equilibrium phase diagram from 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 some their compounds.

### **Reaction- and self-diffusion coefficients**

A relation between the reaction-diffusion coefficient of the A atoms across the bulk of any growing compound layer (see Fig.1) and the diffusional constant is

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$$D_A = \frac{(c_{A1} + c_{A2})}{2(c_{A1} - c_{A2})} k_{1A2}. \quad (22)$$

According to T. Heumann [29], the quantity  $(c_{A1} + c_{A2})/2$  is the average content of component  $A$  in a chemical compound, whereas the difference of its contents at the layer interfaces 1 and 2  $\Delta c_A = c_{A1} - c_{A2} = HR$  represents the range of homogeneity of the compound at a given temperature.

It is usually assumed that  $\Delta c_A$  is the driving force for the process of formation of a chemical compound layer and  $j_A \sim \Delta c_A$ . However, if this were the case, the layers of chemical compounds without any homogeneity range like  $\text{NiBi}_3$  or  $\text{Al}_2\text{O}_3$  would not grow at all. Indeed, at  $\Delta c_A \rightarrow 0$ , Eq. 22 produces infinitely high values of the diffusion coefficient ( $D_A \rightarrow \infty$ ). Physically, this is clearly impossible. Since wide ranges of homogeneity are not characteristic of chemical compounds, this equation either gives unrealistic values of diffusion coefficients of the components in growing layers of chemical compounds having narrow ranges of homogeneity ( $\text{Fe}_2\text{Al}_5$ ,  $\text{Fe}_{3-8}\text{O}_4$ ) or cannot be employed at all in the case of compounds without any homogeneity range ( $\text{NiBi}_3$ ,  $\text{Al}_2\text{O}_3$ ). The introduction of the so-called integrated diffusion coefficient [30] can hardly be regarded as a satisfactory solution to this problem.

The problem 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  $A_pB_q$  layer is the difference in concentration of vacancies of component  $A$  at the layer interfaces. Then, the value of  $c_{A1}$  in the denominator of Eq. 22 is *numerically* equal to the content of  $A$  in  $A_pB_q$ , while  $c_{A2}$  is practically zero. Consequently, this equation yields  $D_A = k_{1A2}$ . Therefore, the diffusional constant  $k_{1A2}$  is identified with the *reaction-diffusion* coefficient,  $D_A$ , of component  $A$  in the lattice of any chemical compound. The same clearly also applies to component  $B$ , with  $D_B = k_{1B1}$ .

The concentration gradient of components  $A$  and  $B$  in any growing layer is established only in the case of existence of a considerable homogeneity range of a given compound. The establishment of this gradient is a *consequence* of the reaction-diffusion process, not the *reason* for this process to proceed, as is usually believed. For its layer to grow, a chemical compound should not necessarily have any range of homogeneity.

In the case where both components  $A$  and  $B$  are sufficiently mobile in the  $A_pB_q$  lattice, two rows (planes) of vacancies (one row of  $A$  vacancies and one row of  $B$  vacancies) are formed as a result of the occurrence of chemical reactions at the interfaces of this layer with initial phases. During layer growth, the rows of  $A$  and  $B$  vacancies periodically move across its bulk in opposite directions. It should be stressed that the vacancies formed cannot be distributed uniformly within the bulk of a chemical compound layer. These exceed in amount all permissible equilibrium limits. Their existence is only possible in *growing* compound layers.

For the same component of the same compound  $A_pB_q$ , the value of the self-diffusion coefficient found by means of radioactive tracers is much less than the value of the appropriate reaction-diffusion coefficient determined from the  $A_pB_q$  layer growth kinetics at the  $A$ - $B$  interface, with the difference reaching a few orders of magnitude. However, these become identical or at least close when normalised to the same vacancy concentration,  $c_v$ , using the relation  $(D/c_v) = \text{const}$  [2, 31].

### Interpretation of marker experiments and Kirkendall effect

In general, any marker only indicates the diffusing species in that compound layer, in which it is embedded or with which it borders. From Fig. 5 it must be clear that even in the case of two compound layers it is necessary to have markers inside both layers to *directly* decide of the diffusing species in their bulks. Indeed, the fact that the distance between a marker inside the  $A_pB_q$  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 diffusant in this layer and nothing more, though component  $B$  is often

regarded to be the main diffusant in *both* layers. The latter conclusion is erroneous. In fact, the very presence of the  $A_pB_q$  layer growing under conditions of diffusion control provides *indirect* evidence that component *A* is the *only* diffusant in this layer.

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, in many cases this does not seem to be sufficiently substantiated.

The Kirkendall effect was described in 1939-1947. Its final formulation was presented in a paper published by E. Kirkendall in collaboration with his student Alice Smigelskas in 1947 [32] (see also Refs 33 and 34). 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 [35].

The Kirkendall effect arises from different values of the self-diffusion 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 the one side as have entered the other. If  $D_A = D_B$ , its position coincides with the initial interface between phases *A* and *B*. If not, it displaces into the side of a faster diffusant (for more detail, see Refs 33 and 34). Note that Kirkendall's discovery only relates to disordered phases. It was indeed a discovery since at that time most researchers considered the relation  $D_A = D_B$  to hold for any solid solution of substitutional type. Kirkendall's experiments showed that this is not the case.

At the times 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 relation. In particular, this is so in the case of formation of chemical compound layers at the interface of elementary substances.

The fact that the components of a *chemical compound* diffuse in its growing layer at *different* speeds became known far before the appearance of the works of E. Kirkendall. 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 1930's (see Ref. 34). 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 diffusant in growing layers of  $\alpha$ -Ag<sub>2</sub>S. 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*. The reasons for this are obvious. Firstly, formation of chemical compounds is typical of the elements strongly differing by their physical-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 allows some degree of disorder, each component is free to move in its own sublattice. There are therefore no reasonable grounds to think that the speeds of such a movement are equal for both components of any chemical compound including intermetallics. Note that in this respect solid solutions of interstitial type stand closer to chemical compounds than to substitutional solid solutions.

It is evident that different diffusional contributions of nickel and bismuth to the growth process of the NiBi<sub>3</sub> layer are by no means 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 compound must be taken in the form of two its pieces differing by their chemical composition. With intermetallics like CoTi, NiAl, ReAl<sub>4</sub>, MoIr<sub>3</sub>, etc., having wide ranges of homogeneity (a few atomic per cent), such experiments are quite feasible. These would enable revealing the Kirkendall effect, if sufficiently pronounced, the calculation of the integrated diffusion coefficient and the establishment of its concentration dependence. It should be noted that, from a physico-chemical viewpoint, application of Wagner's concept of the integrated diffusion coefficient and Darken's equations to *growing*

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*compound layers* seems somewhat artificial, while in the case of compounds without any range of homogeneity physically meaningless. No real Matano's interface in fact exists in such cases. Though widely employed, for example, to growing intermetallic compound layers, Matano's analysis thus produces *fictional* diffusion coefficients.

### Peculiarities of the reaction-diffusion process in solid-liquid and solid-gas systems

In distinction to solid-solid systems, in solid-liquid and solid-gas systems the effect of dissolution or evaporation on the layer growth kinetics must be taken into account. In both cases, the most general equation describing the layer growth rate is [2]

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} - b \exp(-at), \quad (23)$$

where  $a = kS/v$ ,  $b = c_s kV_{A_p B_q}$ ,  $k$  is the dissolution (evaporation) rate constant,  $S$  is the solid specimen surface area,  $v$  is the volume of the liquid or gaseous phase and  $V$  is the molar volume of the  $A_p B_q$  compound.

At  $k_{0B1} + k_{0A2} < b$ , the  $A_p B_q$  layer will not occur between  $A$  and  $B$  phases since its growth rate is less than the rate of dissolution or evaporation ( $dx/dt < 0$ ). With passing time, the rate of dissolution or evaporation decreases from  $b$  to 0. Therefore, at a certain moment of time the  $A_p B_q$  layer occurs at the  $A$ - $B$  interface.

If the rate,  $b$ , of dissolution or evaporation is maintained constant, the  $A_p B_q$  layer thickness asymptotically reaches the maximally possible value

$$x_{\max} = \frac{k_1(k_0 - b)}{k_0 b} \quad (24)$$

and then remains practically unchanged. In this equation, simplified designations of the constants were employed [2]. During further interaction of  $A$  and  $B$  phases, the  $A_p B_q$  layer of constant thickness  $x_{\max}$  displaces as a whole into the bulk of solid phase  $A$ . If  $B$  is a gas, the mass of the solid specimen first increases, while then decreases and becomes less than the initial value, as is the case with tungsten, on the surface of which volatile oxides are known to form [36].

If  $k_0 \gg b$ , then

$$x_{\max} = \frac{k_1}{b}. \quad (25)$$

This equation allows a rough (but useful in practice) estimation of the layer thickness to be made under conditions of simultaneous dissolution of a solid in a liquid. Examples include welding, brazing, protective coating, liquid-metal cooling of atomic power reactors, and so on.

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**Seeger:** What you told us sounds nice and simple, but I wonder whether the simplicity is a direct consequence of the one-dimensional geometry you assumed. As you emphasized yourself, in chemical reactions there may be large changes in the specific volume. For non-planar geometries, e.g. the 3-D growth from small nuclei, this means either participation and diffusion of a third "constituent" (either vacancies or interstitials) or the setting-up of intense stresses, which then should be taken into account. What can you say about these questions?

**A:** Only planar couples are considered and the consideration started with the formation of a continuous layer along the interface between initial phases. The influence of stresses is ignored, though it is obviously an idealization. Changes in volume of a reaction system are automatically taken into account through the equations of chemical reactions.

**Gusak:** Do you agree that the driving force of phase layer growth is the gradient of chemical potential across the layer?

**A:** The driving force is the difference in chemical potentials of the components in initial phases and this difference exists until the full consumption of at least one of the initial phases.

**Referee comments: (F.J.J. Van Loo)**

I think it is worthwhile to insert a comment on the interesting paper of Dr. Dybkov. His views on the growth of chemical compound layers are now widely spread through his book [Ref.2] and through this paper which has been presented to a large audience of scientists interested in diffusion.

I very much like the way the author has treated diffusion and reaction in the early stage of the process. His contribution to that field is important and the scientific community owes him a lot for this.

My concern relates to the extension of these ideas to the case of longer annealing times, and situations where the rate-limiting step is diffusion, and the growth kinetics are parabolic. I respectfully disagree with several statements made by the author. His formalism yields a process description that conflicts with the underlying thermodynamics. The formalism predicts specific experimental consequences that are in conflict with the results of careful studies. I feel that I can best serve the scientific community by summarising the relevant thermodynamic principles and listing their kinetic consequences. This thermokinetic approach provides an alternative framework for interpreting the formation of multiple reaction layers. It is my hope that such a commentary will clarify the sources of conflict, stimulate debate, and focus the attention of researchers on the underlying assumptions that lead to such very different views of reaction layer formation.

1. In a binary system where only one phase is stable between the pure end-members this phase will be formed in a diffusion couple. In quasi-thermodynamic equilibrium (diffusion-controlled process) the thermodynamic potential will be continuous at the interfaces, and the driving force for diffusion is the thermodynamic potential gradient over the phase. It is of no importance whether a measurable homogeneity range exists over this phase: the distinction between a "chemical compound" and whatever intermetallic phase with a smaller or larger homogeneity range is not essential. In all cases a thermodynamic driving force will be present.
2. If more phases are stable in a system, then in principle all these phases can form and grow simultaneously proportional with the square root of time. The driving force is again the thermodynamic potential gradient across each layer. It is true that in some cases the diffusion coefficients in a phase are very low, so that it takes very long annealing times to reach a critical thickness for that phase. Using the concept of the integrated diffusion coefficient, it is easy to predict the layer widths of all phases in a couple between pure end-members. The necessary data can be found from incremental couples in which only one phase grows between its neighbouring phases. It turns out that a factor of  $10^4$  difference in layer width between various phases is not unusual. The occurrence of many layers growing simultaneously proportional with the square root of time has very often been confirmed in very carefully performed experiments.
3. When e.g. two or three phases grow simultaneously in a diffusion couple, it is very well possible that one component is very much faster than the other in all layers. That can easily be verified in experiments in which only one phase grows between its neighbours from the position of the markers present originally at the contact interface. Also in terms of reaction equations at the interfaces no problem arises.
4. The relation between the intrinsic diffusion coefficient, tracer diffusion coefficient, integrated diffusion coefficient and the thermodynamics of a system has been shown

theoretically as well as experimentally. There is no ambiguity in these relations [see e.g. "Reactive Phase Formation in the Ni-Si system" Ph-D-thesis by J. Gülpen, Eindhoven 1995]. Markers originally placed in the contact interface are found back in a multiphase couple either at some interface or within a growing layer. If experimentally it is shown that these markers stay at the same composition and move parabolically with time, then from their position the ratio of the intrinsic diffusion coefficients at that composition can be found. In fact, all calculations made for a solid solution, using the Matano- or Kirkendall frame of reference, can be made equally well for a multiphase diffusion couple. The presence of interfaces does not change these calculations in any way. [The Kirkendall frame of reference is defined by the position of inert markers, originally placed throughout the whole reaction zone; their velocity with respect to the laboratory-fixed or Matano frame of reference is given by the sum of the intrinsic volume fluxes of both components. Most often these markers are only put at the contact interface, and, therefore, only at that composition a statement can be made about the ratio of the intrinsic diffusion coefficients.]

5. A last remark about the experimental details. Under the right experimental conditions different expansion coefficients or volume effects cannot account for the presence of relatively thick ( $> 1 \mu\text{m}$ ) phases which should be absent during annealing. In a quenching procedure the couple can break if you don't use the right type of furnace or lose the contact pressure. But even then, the couple halves can separately be analysed and linked together without serious problems. On the contrary, if no contact pressure is used during annealing, phases might be absent which should be present because they are consumed by competing phases if the supply from one source is hindered, e.g. by a crack. The competing phase is, in such a case, thicker than predicted by calculations based on a non-disturbed supply.

#### Reply of the author:

The comment by Professor F.J.J.van Loo to my paper seems to be useful to researchers in the field. Nature hides its secrets and therefore not always what seems obvious to the authors of theoretical and experimental works is indeed correct and valid. This leads to the difference in interpretation of the same experimental data.

First of all, I would like to emphasise that my theoretical views are, to a considerable extent, a result of reading excellent works by F.J.J.van Loo himself. Just his result about the disappearance of artificially prepared aluminide layers between titanium and aluminium, except  $\text{TiAl}_3$ , made me doubt that the compound-layer formation is simultaneous and parabolic. Therefore, if my views happen to be wrong, it is partly also his fault. As yet, however, I don't see serious reasons to change these views expressed in my previous works and in this paper. Using the opportunity, it appears relevant to draw the attention of readers to the following points.

1. In most known cases of multiple layer formation in binary systems, at least one of the layers shrank, indicative of the loss of contact between the phases. Also, the layers were cracked, non-flat or discontinuous. Precise measuring their thickness could hardly be possible. This gives rise to an ambiguity. On the contrary, when the layers were compact, flat and continuous, multiple parabolic growth was never observed, if quenching was applied.

2. In the case of two and more compound layers, the concept of the integrated diffusion coefficient is meaningless because the theoretical background, on which its derivation is based, has nothing in common with the real mechanism of formation of these layers. In any of two layers growing under conditions of diffusion control only one component is diffusing across its bulk. The growth process of each layer is thus characterized by a single diffusion

coefficient. In such circumstances, the integrated diffusion coefficient becomes a fictitious characteristic like to the average temperature of patients over the hospital.

Under pressure all things are known to go badly. Diffusion experiments are no exception. Any pressure does not prevent a reaction couple from cracking due to thermal expansion and volume effect. Its application only masks this phenomenon.

3. Greater care is necessary in interpretation of marker experiments. From a physicochemical viewpoint, even in the case of two compounds one marker is insufficient to directly judge of the diffusing species in both layers.

4. It is necessary to distinguish between the formation of chemical compounds, interstitial and substitutional solid solutions. Restrictions in regards to the number of growing compound layers are due to partial chemical reactions taking place at the layer interfaces. In solid solutions, there are no reactions at interfaces and therefore no restrictions on the number of simultaneously growing layers. Also, no restriction can clearly exist, if the compound formation is diffusionless.

These and related questions will be considered in more detail in my forthcoming book "Reaction diffusion and solid-state chemical kinetics", to be published in 2002.