

Phase Formation and Diffusion in Binary Systems: Real Facts and Misleading Views

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Keywords: Phase formation, Diffusion, Binary systems, Compound layers, Growth kinetics

Abstract

A physico-chemical consideration of the reaction-diffusion process resulting in the formation of chemical compound layers at the interface of initial substances A and B is presented to separate real facts from misleading views. The layer-growth kinetics are shown to be much more complicated than it follows from conventional diffusional views. Besides a parabolic relation, a variety of growth laws (linear, parabolic, asymptotic and others) can be observed experimentally. In the majority of multiphase binary systems, layer occurrence appears to be sequential rather than simultaneous. Under conditions of diffusion control, the number of simultaneously growing compound layers at the A – B interface cannot exceed two. Multiple layers (three or more) are formed as a result of secondary processes connected with the rupture of a diffusion couple. The latter is in most cases due to the difference in thermal expansion coefficients of couple constituents and the volume effect accompanying the process of formation of chemical compounds (intermetallics, silicides, oxides, salts, etc.). The Kirkendall effect plays a minor role, if any. With multiple-layer structures, calculation of interdiffusion or mutual-diffusion coefficients is hardly substantiated.

Introduction

Diffusion followed by interfacial interaction (reaction diffusion) results in the formation of a continuous solid compound layer A_pB_q at the interface of two mutually immiscible phases A and B , with one of them and the reaction product being solids and another may be a solid, a liquid or a gas. The consideration presented is restricted to chemical compounds. 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 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), or of more complicated (and still poorly understood) laws as in the case of intermetallics when compounds of a peculiar composition ($NiBi_3$) are formed. Though the solids contain no molecules of Al_2O_3 or $NiBi_3$ as such, the composition of the Al_2O_3 and $NiBi_3$ phases is on average described by these chemical formulae. The term “reaction diffusion” means that the layer growth is due to a continuous alternation of the two consecutive steps: (1) diffusion of atoms (ions) of the reactants across the layer bulk in the opposite direction and (2) subsequent chemical transformations (chemical reaction) taking place at the layer interfaces with the participation of diffusing atoms of one of two components and the surface atoms of another component.

With binary systems, each compound layer formed is single-phase. Consider the main features of layer-growth kinetics, which are the same for compounds of whatever chemical nature (intermetallics, silicides, oxides, salts, etc.).

Results and Discussion

Formation of single compound layer

In the general case of comparable mobilities of components A and B within the A_pB_q crystal lattice, the A_pB_q compound layer grows at the expense of two partial chemical reactions



taking place at its interfaces with initial phases (Fig. 1).

Kinetically, these are two different chemical reactions, even though the reactants are the same. Note that in any heterogeneous system that attained constant temperature-pressure conditions from below (from smaller to higher values), no reaction proceeds within the bulk of the A_pB_q layer.

If only component B is diffusing in the A_pB_q layer, the kinetic equation is [1, 2]

$$\frac{dx_{B1}}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} \quad (3)$$

where k_{0B1} is a chemical constant and k_{1B1} is a physical (diffusional) constant.

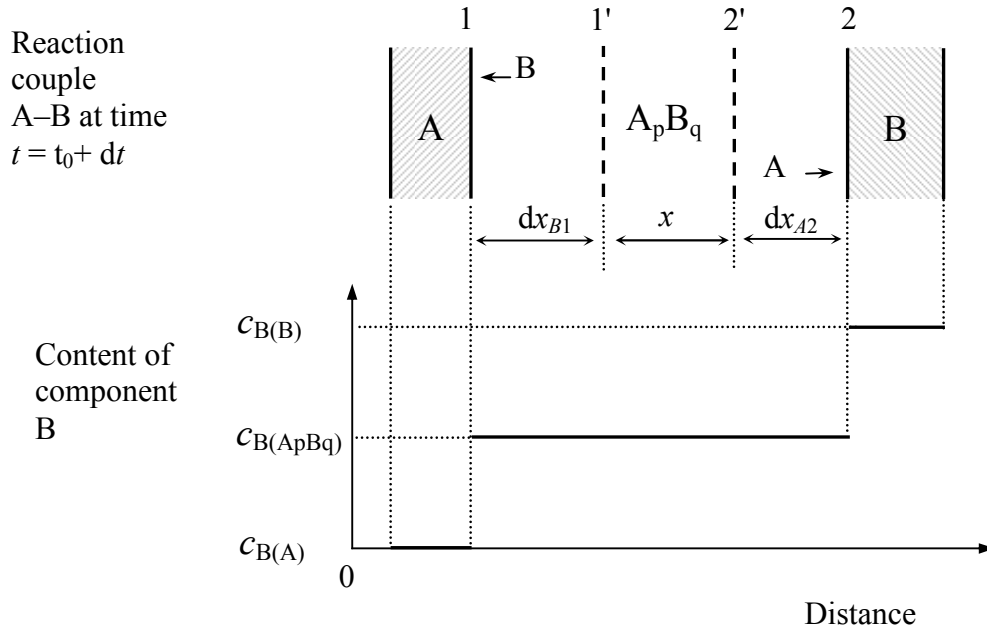


Figure 1 Schematic illustration of the growth process of the A_pB_q compound layer at the A - B interface

The layer-growth kinetics are initially linear (reaction controlled) $x = k_{0B1}t$ and then parabolic (diffusion controlled) $x^2 = 2k_{1B1}t$. An example is presented in Fig. 2 [3]. The ignorance

of the step of chemical transformations at layer interfaces results in the loss of linear growth region. Another loss, much more important, is not so obvious and will become clear later.

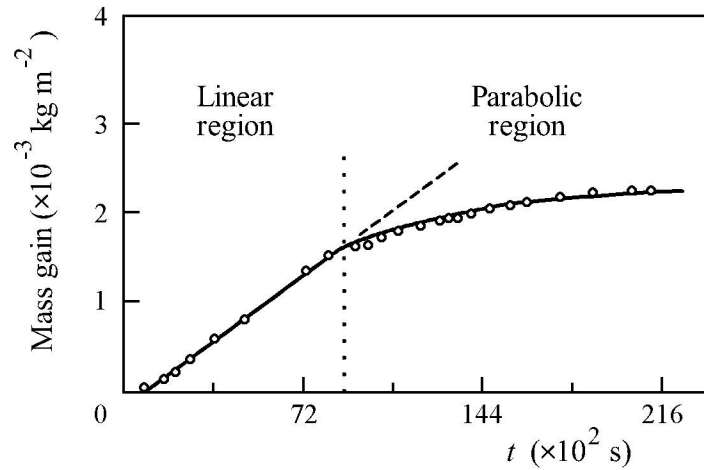


Figure 2 Sulphidation of molybdenum from the gaseous phase at 750°C and a sulphur vapour pressure of 4 Pa (0.03 mm Hg) [3]. Growth kinetics of the MoS_2 layer are initially linear and then parabolic

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 steadily 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 $x_{1/2}^{(B)} = k_{1B1} / k_{0B1}$ [2] at which these quantities are equal. 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 other chemical compounds (enriched in component A in comparison with the A_pB_q compound) of a multiphase binary system. 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 .

If both reactions 1 and 2 contribute to the layer-growth process, the kinetic equation is

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k_{0A2}}{1 + \frac{k_{0A2}x}{k_{1A2}}} \quad (4)$$

where k_{0A2} is another chemical constant and k_{1A2} is another physical (diffusional) constant.

Linear kinetics are observable with thin layers (up to 500-600 nm), while parabolic kinetics are characteristic of much thicker compound layers (1 μm or more). Examples are linear growth of CrSi_2 [4] and parabolic growth of NiBi_3 [2]. In the latter case the increase in layer thickness is due entirely to the diffusion of bismuth, as seen from marker experiments in Fig. 3. The distance between marker 3 and the Ni-NiBi₃ interface increase with passing time while that between this marker and the NiBi₃-Bi interface remains unchanged

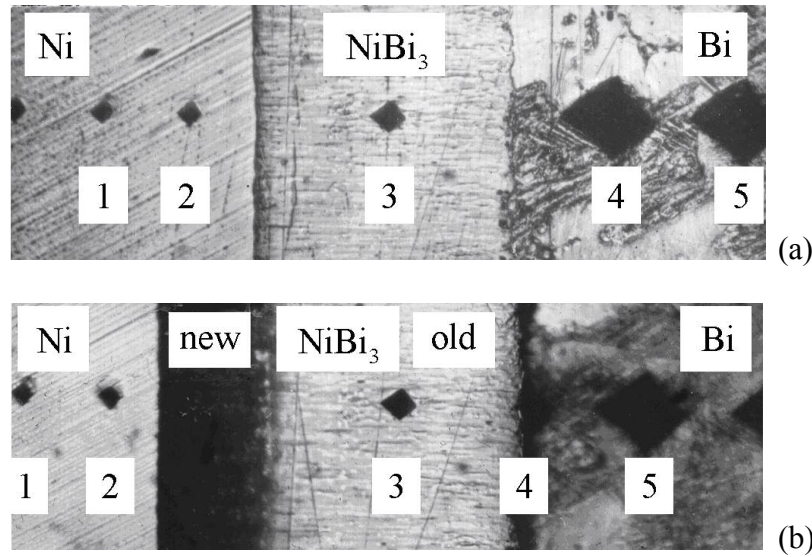


Figure 3 Optical micrographs of the Ni–Bi transition zone before (a) and after (b) the third anneal at 200°C. (a) annealed two times 18×10^4 s + 18×10^4 s (50 h + 50 h). Microhardness indentations were put onto the electropolished surface of the cross-section after the second anneal at a load of 0.196 N (20 g). (b) same place after the third anneal for 36×10^4 s (100 h) in the as-received condition

Since the consumption of bismuth (in terms of thickness) is ten times greater than that of nickel, the NiBi_3 layer displaces as a whole relative to the initial Ni–Bi interface into the side of bismuth. Note that the position of any growing compound layer relative to an initial interface between reacting phases is only dependent on the stoichiometry of that compound and therefore provides no information about the main diffusing species in the layer bulk.

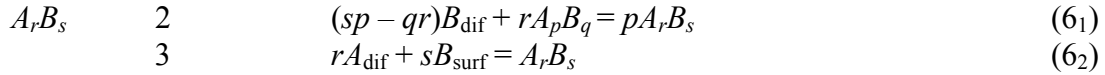
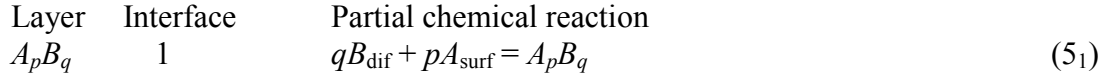
Different diffusional contributions of the components to the layer-growth process are often considered to be a consequence of the Kirkendall effect. In fact, however, the Kirkendall effect is unobservable with growing compound layers (for more detail, see Ref. [2]).

For a given component, a relation between the layer growth-rate constant k_1 and the diffusion coefficient D is found from the equation $k_1 = D(c_1 - c_2)/c_{\text{average}}$, where c_1 and c_2 are the concentrations of vacancies of this component at layer interfaces. At a reacting interface, the concentration of vacancies is numerically equal to the content of a given component in a compound. At the opposite interface, it is zero (ideal case, thermal vacancies are neglected). Hence, for compounds without any range of homogeneity, $k_1 = D$, whereas for compounds with a (narrow) range of homogeneity, $k_1 \approx D$. It should be noted that if the difference $c_1 - c_2$ is considered to be equal to the homogeneity range a compound, as in many works, then the values of D obtained are infinitely high in the former case and too high in the latter. Clearly, it is hardly possible physically.

Unlike self-diffusion coefficients which tend to increase with increasing degree of deficiency of any compound, reaction-diffusion coefficients (diffusional constants) decrease with increasing degree of deficiency of that compound [2], so that the greater the degree of deficiency of the compound, the less is the growth rate of its layer in the A – B couple. For any compound layer to grow, no native defects or a range of homogeneity are necessary because the number of defects (vacancies) formed at layer interfaces in the course of reaction far exceeds their equilibrium number.

Two compound layers

Direct chemical reaction between 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 layer interfaces:



These reactions cause the changes in thickness of appropriate layers, as shown in Fig. 4. The layer-growth kinetics are described by a system of two equations of the form [2]:

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + \frac{k_{0B1}x}{k_{1B1}}} + \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}} - \frac{rg}{p} \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}} \quad (7_1)$$

$$\frac{dy}{dt} = \frac{k'_{0B2}}{1 + \frac{k'_{0B2}y}{k'_{1B2}}} + \frac{k_{0A3}}{1 + \frac{k_{0A3}y}{k_{1A3}}} - \frac{q}{sg} \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x}{k'_{1A2}}} \quad (7_2)$$

In this system, all k_0 are chemical constants, all k_1 are physical (diffusional) constants, and g is the ratio of the A_pB_q and A_rB_s molar volumes. The first two terms of each of these equations describe the rates of growth of an appropriate compound layer at its two interfaces, while the third term reflects the rate of consumption of this layer in the process of formation of an adjacent compound layer.

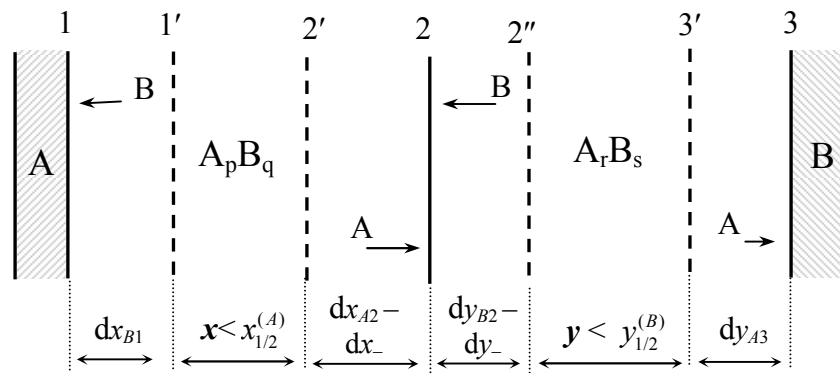


Figure 4 Reaction controlled growth of two compound layers. Note that the flux of the B atoms across the A_rB_s layer is greater than that across the A_pB_q layer, as indicated by arrows of different length, because both layers consume this type of atoms exclusively from substance B. Similarly, the flux of the A atoms across the A_pB_q layer is greater than that across the A_rB_s layer because both layers consume this type of atoms exclusively from substance A. Each faraway layer can only consume those diffusing atoms which have not been consumed by its neighbor located closer to a source of given atoms

The sequential occurrence of compound layers in any binary system is seen to be more likely because the probability of the case where dx/dt and dy/dt are positive is less than the probability of the case where they have different signs. If the A_pB_q layer has formed first, the next layer A_rB_s occurs after the first reaches a thickness, x_{\min} , defined by the equation

$$k'_{0B2} + k_{0A3} = \frac{q}{sg} \frac{k'_{0A2}}{1 + \frac{k'_{0A2}x_{\min}}{k'_{1A2}}} \quad (8)$$

At $x = x_{\min}$, the rate of consumption of the A_rB_s layer in the formation of the A_pB_q layer (reaction 5₂) becomes equal to its growth rate due to reactions 6₁ and 6₂. An example is the Pd–Al diffusion couple in which the PdAl₃ layer starts to grow after the Pd₂Al₃ layer has reached a thickness of 5.7 μm at 386 °C [5].

With two compounds, the layer-growth kinetics are again linear initially ($k_0 \ll k_1/x$, etc.). Then, a variety of growth laws can be observed (paralinear [6], asymptotic and others), and finally the layer growth becomes close to parabolic [2]. The diffusional growth is due to reactions 5₂ and 6₁, as shown in Fig. 5.

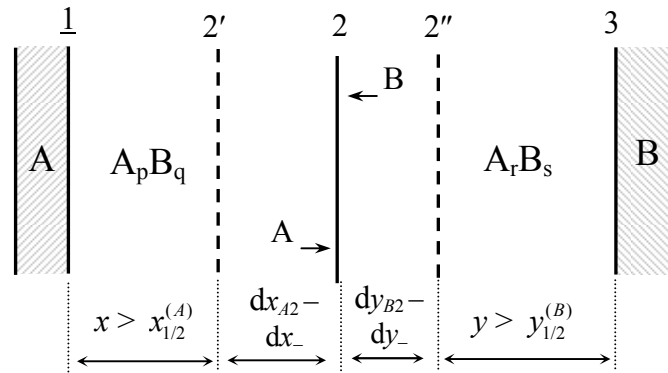


Figure 5 Diffusion controlled growth of two compound layers. Both layers only thicken at their common interface 2. No chemical reactions take place at interfaces 1 and 3 in view of the lack of appropriate diffusing atoms

At the late diffusional stage of growth ($k_0 \gg k_1/x$, etc.), the system of equations 7 assumes the form

$$\frac{dx}{dt} = \frac{k'_{1A2}}{x} - \frac{rg}{p} \frac{k'_{1B2}}{y} \quad (9_1)$$

$$\frac{dy}{dt} = \frac{k'_{1B2}}{y} - \frac{q}{sg} \frac{k'_{1A2}}{x} \quad (9_2)$$

Growth kinetics of the Al₃Mg₂ and Al₁₂Mg₁₇ layers in the Al–Mg diffusion couple [7] can be described by this system of equations. Appropriate constants k (reaction-diffusion coefficients) are $4.49 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for the Al₃Mg₂ layer and $9.41 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ for the Al₁₂Mg₁₇

layer at at 950 °C [2, 8]. Another example is the formation of iron boride layers (Fig. 6) at the interface between a Fe-10% Cr alloy and amorphous boron [9]. In this case, the value of k at 950 °C is $9.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for the FeB layer and $15.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for the Fe₂B layer.

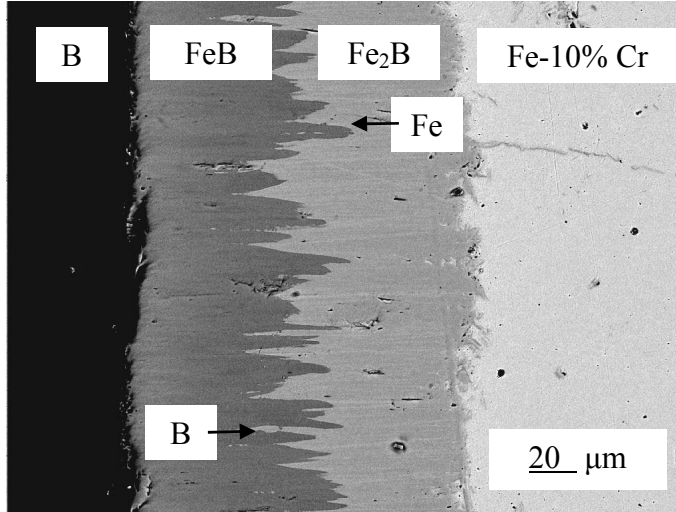


Figure 6 Backscattered electron image of boride layers at the interface of a Fe-10% Cr alloy and amorphous boron. Boriding conditions: temperature 950 °C, reaction time 21600 s (6 h)

Schematic illustration of the similarity and difference in the growth mechanism of one and two compound layers at the interface of reactants A and B is presented in Fig. 7.

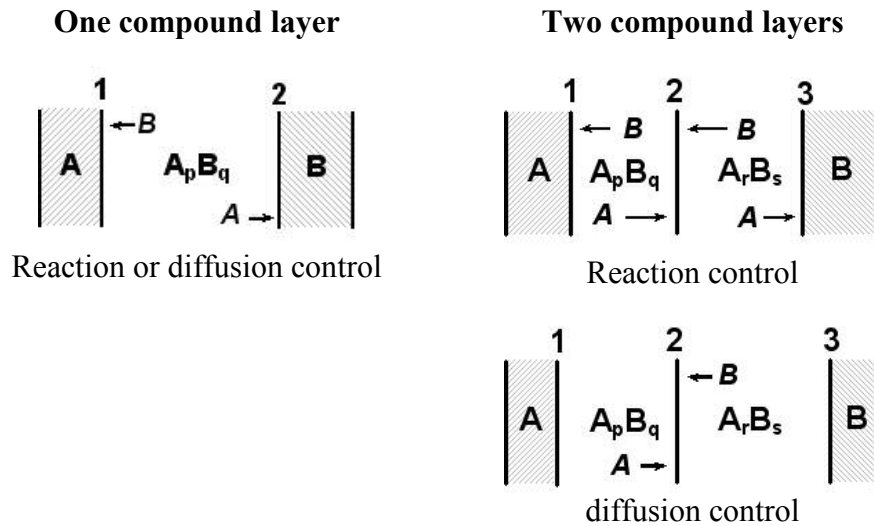


Figure 7 Schematic diagram to illustrate the similarity and difference in the growth mechanism of one and two compound layers at the A-B interface

Whatever the growth regime (reaction or diffusion controlled), one compound layer can grow at the expense of diffusion of both components across its bulk. With two compounds, this is only possible under conditions of reaction control. Under conditions of diffusion control, only one component is diffusing in each layer. Therefore, for chemical compounds the concept of mutual diffusion loses any physical meaning.

Multiple compound layers

Using the ideas of preceding sections, it is not difficult to analyze qualitatively the process of multiple-layer formation. 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 an appropriate phase diagram. The cases where three or more compound layers of a multiphase binary system were present between elementary substances A and B are very rare compared to the cases where one or two layers were formed (see [2]). Consider a reaction couple with three chemical compound layers A_pB_q , A_rB_s and A_lB_n (Fig. 8).

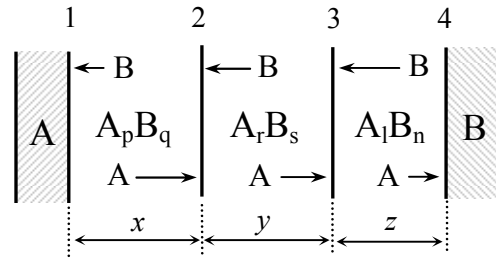


Figure 8 Reaction controlled growth of three compound layers. The B atoms which have crossed the A_lB_n layer from interface 4 to interface 3 but have not been consumed in the formation of this layer at interface 3 are consumed in the formation of the A_rB_s and A_pB_q layers at interfaces 2 and 1, respectively. The A atoms which have crossed the A_pB_q layer from interface 1 to interface 2 but have not been consumed in the formation of this layer at interface 2 are consumed in the formation of the A_rB_s and A_lB_n layers at interfaces 3 and 4, respectively. The fluxes of atoms of both kinds are sufficient for all three layers to grow simultaneously.

Partial chemical reactions taking place at phase interfaces are as follows.

Layer	Interface	Partial chemical reaction
A_pB_q	1	$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q,$ (10 ₁)
	2	$(sp - qr)A_{\text{dif}} + qA_rB_s = sA_pB_q,$ (10 ₂)
A_rB_s	2	$(sp - qr)B_{\text{dif}} + rA_pB_q = pA_rB_s,$ (11 ₁)
	3	$(rn - ls)A_{\text{dif}} + sA_lB_n = nA_rB_s,$ (11 ₂)
A_lB_n	3	$(rn - ls)B_{\text{dif}} + lA_rB_s = rA_lB_n,$ (12 ₁)
	4	$lA_{\text{dif}} + nB_{\text{surf}} = A_lB_n.$ (12 ₂)

Suppose that with passing time the growth of the A_pB_q layer became diffusion controlled with regard to component A . It means that all the diffusing A atoms are combined into the A_pB_q compound at interface 2 (reaction (10₂)). Since the only source of A atoms for all the layers is substance A , the faraway layers A_rB_s and A_lB_n stop growing at the expense of diffusion of component A (Fig. 9).

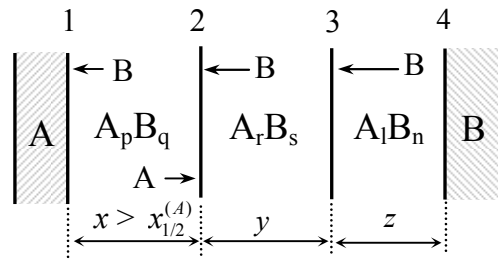


Figure 9 Diffusion controlled growth of the $A_p B_q$ layer with regard to component A . The A atoms are not available for the $A_r B_s$ and $A_l B_n$ layers to grow

The same applies to the diffusion of component B . At some moment of time, the flux of B atoms across the $A_l B_n$ layer becomes too small to supply these atoms for the faraway layers $A_r B_s$ and $A_p B_q$, which hence stop growing at the expense of diffusion of component B (Fig. 10).

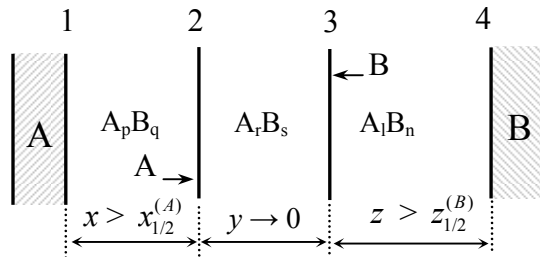


Figure 10 Diffusion controlled growth of the $A_p B_q$ and $A_l B_n$ layers. The A and B atoms are not available for the $A_r B_s$ layer to grow. This layer must disappear with passing time

Thus, in any couple A – B only two compound layers can grow under conditions of diffusion control: one layer at the expense of diffusion of component A and another at the expense of diffusion of component B . Two compact compound layers can never grow at the expense of diffusion of the same component. Again, calculation of coefficients of mutual diffusion does not seem substantiated.

This conclusion confirmed by the available experimental data was drawn more than twenty years ago [10, 11]. Nonetheless, many workers ignore it till now. Meanwhile, it is quite obvious and can readily be understood, if chemical processes at phase interfaces are taken into account. If not, the linear growth region is again lost and no restrictions concerning the number of growing compound layers occur.

Since the formation of chemical compounds is typical of the elements strongly differing by their physico-chemical properties, not always even two compound layers occur, as is the case with many aluminium-transition metal binary systems [12]. If diffusion of one of two components (A or B) prevails in all the compounds of a binary system, one layer is formed in the A – B couple. If the rates of diffusion of both components in the compounds are comparable, two layers will grow.

The main factors affecting the mobility of atoms and hence the sequence of compound-layer formation are (i) melting points, $T_{m(A)}$ and $T_{m(B)}$, of components A and B , (ii) atomic radii, r_A and r_B , of those components, and (iii) crystal structures of the compounds. If the difference in

melting points of components A and B is large and $r_A \approx r_B$, a compound enriched in a low-melting component may be expected to occur and grow first at the A - B interface (TiAl₃ in Ti-Al: $T_{m(\text{Ti})} = 1943$ K, $T_{m(\text{Al})} = 933$ K, $r_{\text{Ti}} = 0.146$ nm, $r_{\text{Al}} = 0.143$ nm [13]).

If the difference in atomic radii of components A and B is large and $T_{m(A)} \approx T_{m(B)}$, a compound enriched in a component of smaller atomic radius may be expected to grow faster in the A - B couple (Mg₂Al₃ in Mg-Al: $T_{m(\text{Mg})} = 924$ K, $T_{m(\text{Al})} = 933$ K, $r_{\text{Mg}} = 0.160$ nm, $r_{\text{Al}} = 0.143$ nm).

A compound with the crystal structure providing preferable directions of diffusion of atoms may be expected to occur and grow first at the A - B interface (Fe₂Al₅ in Fe-Al, not FeAl₃ or Fe₂Al₇). Note that if those directions are blocked up with atoms of other elements (Ni in Fe₂Al₅), a compound enriched in a low-melting component is formed (FeAl₃ or Fe₂Al₇).

As the layer growth takes place in diffusion couples under highly non-equilibrium conditions, formation of compounds with crystal structures of low symmetry is preferable. Different portions of the same compound layer may even possess different structures (NiZn₃₋₆ in Ni-Zn), with fresh portions having more low symmetry than those formed earlier.

If the formation of multiple layers is observed in a particular diffusion couple, it is in all probability due to the loss of its integrity. Sooner or later, any diffusion couple cracks as a result of (i) thermal expansion and (ii) volume effect due to the difference in volumes of reactants and products of any reaction, thereby giving rise to new diffusion couples in which additional compound layers can readily occur.

In artificially prepared couples, compound layers (even two) will never grow simultaneously because it is practically impossible to ensure the correct ratio of their thicknesses [2]. Examples are Ti-Ti₃Al-TiAl-TiAl₂-TiAl₃-Al [14], Ti-Ti₃Al-Al and Ti-TiAl-Al [15] samples, in which all initially existing layers are consumed completely in the course of formation of the TiAl₃ layer during isothermal annealing.

Schematic illustration of the similarity and difference in the growth mechanism of one, two and three compound layers at the interface of reactants A and B is presented in Fig. 11.

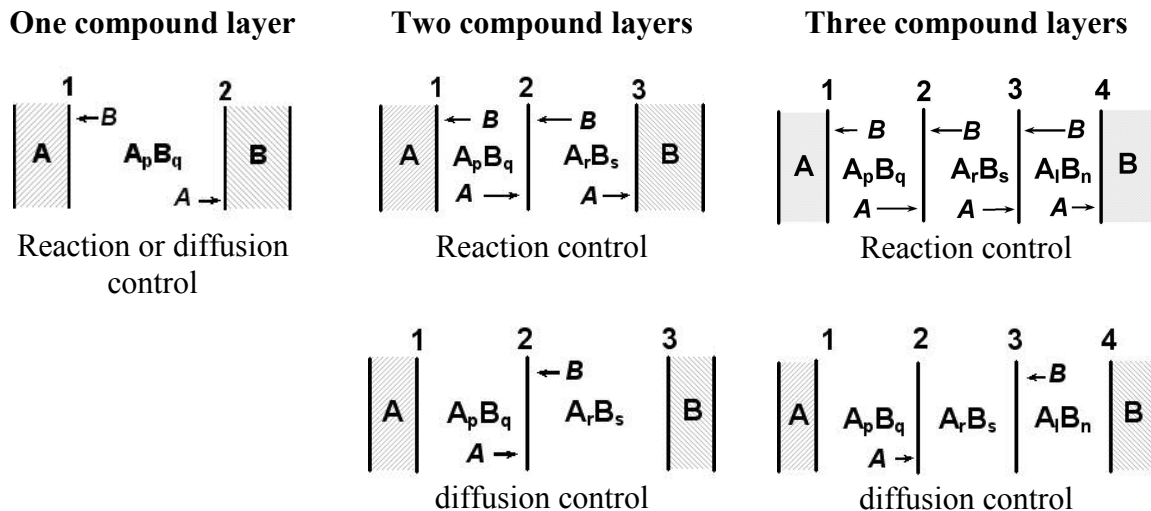


Figure 11 Schematic diagram to illustrate the similarity and difference in the growth mechanism of one, two and three compound layers at the A - B interface

Two compound layers can grow simultaneously. Three layers can only occur under conditions of reaction control, but it is highly unlikely. Under conditions of diffusion control, one of three layers becomes superfluous. Two first occurred layers continue to grow until one of the reactants is exhausted. Then, the next compound layer occurs in a new diffusion couple, and so on, until the equilibrium state, with at most two phases left, is established.

Summary

From the present consideration, it follows that most of widespread conventional views need a serious modification. A short summary is provided below.

Number of compound layers	Conventional views	Modified views
One	<ol style="list-style-type: none"> 1. Layer-growth kinetics are parabolic 2. The wider the homogeneity range of a compound, the greater is the growth rate of its layer 3. The driving force of the layer growth is the difference in the concentrations of a given component at layer interfaces 	<ol style="list-style-type: none"> 1. Layer-growth kinetics are linear-parabolic 2. The layer-growth rate is practically independent of the width of the homogeneity range of a compound 3. The driving force of the layer growth is the difference in the concentrations of vacancies of a given component at layer interfaces
Two	<ol style="list-style-type: none"> 1. Layer-growth kinetics are parabolic 2. Layer formation is simultaneous 3. The layer growth is a result of mutual diffusion of both components 	<ol style="list-style-type: none"> 1. A variety of layer thickness-time dependences (linear, parabolic, asymptotic, parabolic and others) is possible 2. Sequential layer formation is more likely 3. Mutual diffusion is only possible under conditions of reaction control. Under conditions of diffusion control, only one component from an adjacent initial phase is diffusing in each layer
Three or more	<ol style="list-style-type: none"> 1. Layer-growth kinetics are parabolic 2. Layer formation is simultaneous 3. The layer growth is a result of mutual diffusion of both components 	<ol style="list-style-type: none"> 1. Layer-growth kinetics are complicated and generally cannot be adequately represented by any simple mathematical relation 2. Layer formation is sequential. Formation of multiple-layer microstructures is a result of secondary reactions taking place after the rupture of an initial diffusion couple 3. With chemical compounds, the concept of mutual diffusion has no physical meaning because under conditions of diffusion control three or more layers cannot grow simultaneously

Acknowledgments

This investigation was supported in part by the US Civilian Research and Development Foundation grant No. UKE2-2698-KV-06.

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