

Interfacial Interaction and Diffusion in Binary Systems

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Keywords: Interfacial Interaction, Diffusion, Binary systems, Compound layers, Growth kinetics, Sequence of occurrence.

Abstract. A physico-chemical consideration of the interfacial interaction and diffusion resulting in the formation of chemical compound layers at the interface of initial substances A and B is presented. The layer-growth kinetics are shown to be much more complicated than it follows from conventional diffusional views neglecting interfacial reactions. 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 and more) can only form as a result of secondary processes connected with the rupture of a diffusion couple. In such cases, great care is necessary when calculating diffusion coefficients to avoid obtaining their physically meaningless values.

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 [1]. The term „reaction diffusion“ indicates that the layer growth is due to two alternating 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 (oxides, intermetallics, silicides, salts, etc.).

Formation of one 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 (Fig. 1):

$$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q, \quad (1)$$

$$pA_{\text{dif}} + qB_{\text{surf}} = A_pB_q. \quad (2)$$

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.

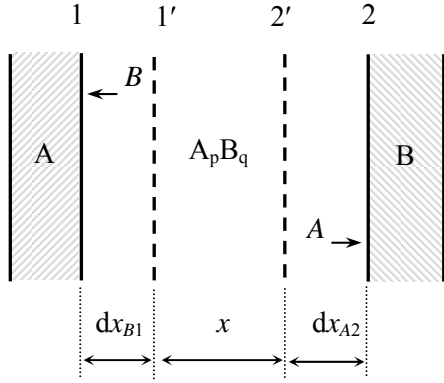


Fig. 1. Scheme of the growth process of the $A_p B_q$ compound layer at the A–B interface.

The layer-growth kinetics are initially linear (reaction controlled) $x = k_{0B1}t$ and then parabolic (diffusion controlled) $x^2 = 2k_{1B1}t$. 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.

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 infinitely high values. Hence, there is a single *critical* thickness of the $A_p B_q$ layer $x_{1/2}^{(B)} = k_{1B1} / k_{0B1}$ [1] 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 $A_p B_q$ 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 $A_p B_q$ 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 $A_p B_q$ 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.

If both reactions (1) and (2) contribute to the layer formation, 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_{1A2} is another physical (diffusional) constant and k_{0A2} is another chemical 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 [3] and parabolic growth of NiBi_3 [1]. In the latter case the increase in layer thickness is due entirely to the diffusion of bismuth. 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 provides no information about the main diffusing species.

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 inobservable with growing compound layers (for more detail, see Ref. [1]).

Two compound layers

Direct chemical reaction between substances A and B ceases after the formation of compound layers $A_p B_q$ and $A_r B_s$ 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 (Fig. 2):

Layer	Interface	Partial chemical reaction	
A_pB_q	1	$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q$,	(5 ₁)
	2	$(sp - qr)A_{\text{dif}} + qA_rB_s = sA_pB_q$,	(5 ₂)
A_rB_s	2	$(sp - qr)B_{\text{dif}} + rA_pB_q = pA_rB_s$,	(6 ₁)
	3	$rA_{\text{dif}} + sB_{\text{surf}} = A_rB_s$.	(6 ₂)

These reactions cause the changes in thickness of appropriate layers, as shown in Fig. 2.

The layer-growth kinetics are described by a system of two equations of the form [1]:

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

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

In this system, all k_1 are physical (diffusional) constants, all k_0 are chemical 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.

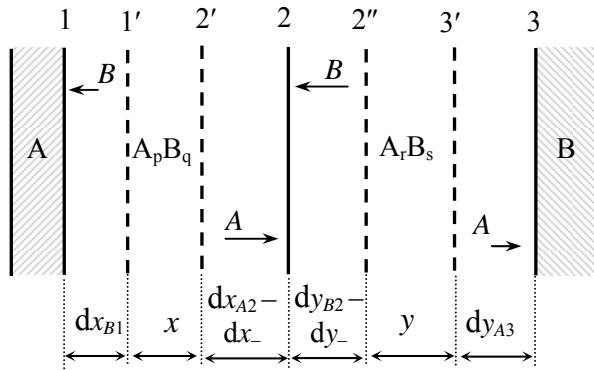


Fig. 2. Reaction controlled growth of two compound layers.

The sequential occurrence of the layers 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

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

at which the rate of its consumption in the formation of the A_pB_q layer (reaction (5₂)) becomes equal to the 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 [4].

Initially ($k_0 \ll k_1/x$, etc.), the layer-growth kinetics are again linear. Then, a variety of growth laws may be observed, and finally the layer growth becomes close to parabolic [1]. The diffusional (parabolic) growth is due to reactions (5₂) and (6₁), as shown in Fig. 3.

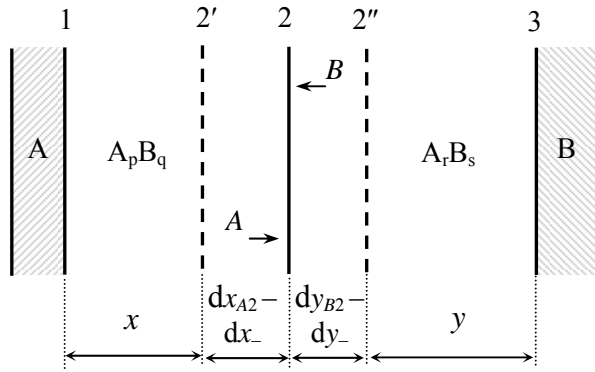


Fig. 3. Diffusion controlled growth of two compound layers.

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

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

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

An example of diffusional growth kinetics is the formation of the Al_3Mg_2 and $\text{Al}_{12}\text{Mg}_{17}$ layers in the Al–Mg diffusion couple [5]. Appropriate constants (reaction-diffusion coefficients) found from the system of equations (12) are $4.49 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for the Al_3Mg_2 layer and $9.41 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ for the $\text{Al}_{12}\text{Mg}_{17}$ layer [6].

Multiple compound layers

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 and the more so *grew* between elementary substances A and B are very rare compared to the cases where one or two layers were formed [1].

Consider a reaction couple with three chemical compound layers A_pB_q , A_rB_s and A_lB_n (Fig. 4). Partial chemical reactions taking place at phase interfaces are as follows.

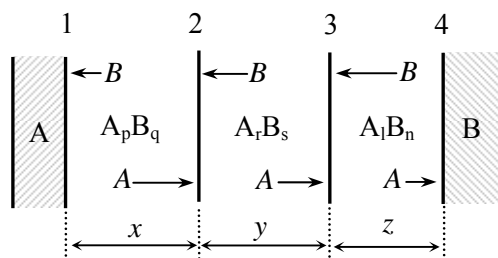


Fig. 4. Reaction controlled growth of three compound layers.

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. 5).

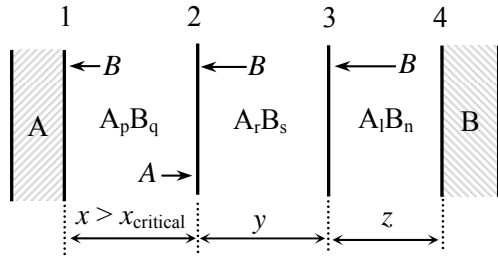


Fig. 5. Diffusion controlled growth of the A_pB_q layer. A atoms are not available for the A_rB_s and A_lB_n layers to grow.

The same applies to the diffusion of component B. At some moment of time, the flux of B atoms across the A_lB_n layer becomes too small to supply these atoms for the faraway layers A_rB_s and A_pB_q , which hence stop growing at the expense of diffusion of component B (Fig. 6).

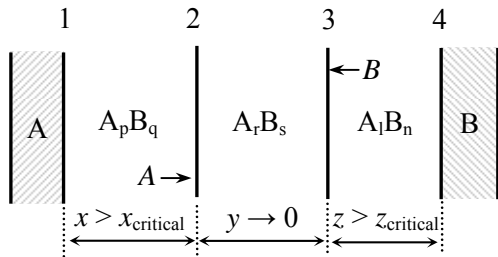


Fig. 6. Diffusion controlled growth of the A_pB_q and A_lB_n layers. A and B atoms are not available for the A_rB_s layer to grow.

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. Hence, 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 [7, 8]. Nonetheless, many workers ignore it till now. Meanwhile, it is quite obvious and can readily be understood, if chemical processes at the 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 [9]. 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: $T_{m(Ti)} = 1943$ K, $T_{m(Al)} = 933$ K, $r_{Ti} = 0.146$ nm, $r_{Al} = 0.143$ nm [10]).

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: $T_{m(Mg)} = 924$ K, $T_{m(Al)} = 933$ K, $r_{Mg} = 0.160$ nm, $r_{Al} = 0.143$ 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 (Fe_2Al_5 in Fe-Al , not FeAl_3 or Fe_2Al_7). Note that if those directions are blocked up with atoms of other elements (Ni in Fe_2Al_5), a compound enriched in a low-melting component is formed (FeAl_3 or Fe_2Al_7).

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 (NiZn_{3-6} 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 may 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 [1]. Examples are $\text{Ti-Ti}_3\text{Al-TiAl-TiAl}_2\text{-TiAl}_3\text{-Al}$ [11], $\text{Ti-Ti}_3\text{Al-Al}$ and Ti-TiAl-Al [12] samples, in which all initially existing layers have been consumed completely in the course of formation of the TiAl_3 layer during isothermal annealing.

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 [1], 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 the layer interfaces in the course of reaction far exceeds their equilibrium number.

Summary

The layer-growth kinetics are generally rather complicated, not simply parabolic. In multiphase binary systems, layer occurrence is sequential rather than simultaneous. Under conditions of diffusion control, the number of growing compound layers at the $A-B$ interface cannot exceed two. Two layers never grow at the expense of diffusion of the same component. Multiple layers (three and more) can only form as a result of secondary processes.

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