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Reaction diffusion in heterogeneous binary systems

Part 1 *Growth of the chemical compound layers at the interface between two elementary substances: one compound layer*

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A theory is proposed for solid-state growth of the chemical compound layers at the interface between two elementary substances one of which is solid at the given temperature while the other may be solid, liquid or gaseous. Not only the rates of diffusional transport of the reacting species through the growing layers but also the rates of chemical reactions taking place at the interfaces between the phases involved in the interaction are taken into account. This theory seems to be more consistent with the available experimental data than the existing "diffusional" theory.

1. Introduction

The improvement of existing materials as well as the development of new materials is often based on the use of a chemical reaction in which a solid reacts with a gas, a liquid or another solid to form a solid product (an oxide, an intermetallic, a salt, etc.). In spite of theoretical interest and obvious practical importance the kinetics of such reactions have so far received comparatively little attention [1–3].

A continuous, coherent layer of solid product separates the reactants from one another and therefore the rate of diffusional transport of the reacting species through the layer becomes the dominant factor determining the overall reaction rate. In such a case the layer growth usually follows the parabolic law which was first established experimentally by Tammann and was then obtained theoretically by Wagner (see [4–6]).

A recent theory developed by Wagfner [7], Kidson [8], Heumann [9], Gurov *et al.* [10], Geguzin [11] and other investigators is based upon Fick's laws (mainly upon Fick's first law) and takes no account of the rate of chemical reactions. This approach seems to be debatable in the case of a chemical compound layer. There are a number of discrepancies between the existing "diffusional" theory and the experimental data available in the literature; the main ones are the following:

1. From a "diffusional" point of view, there is no restriction on the number of compound layers growing simultaneously in a given couple. All the layers are expected to occur and grow simultaneously [10]. This is contrary to the observations. There are a number of binary systems in which up to ten compounds exist in a certain range of temperatures. However, nobody has reported the simultaneous growth, say, of five or six compound layers, the usual number being one to three and rarely four [5, 12].

2. The layer growth is often non-parabolic, especially in those cases where two or more compound layers grow simultaneously. In the initial stage the process is always non-parabolic, the layer thickness–time relationship being linear [5, 6, 12].

3. From "diffusional" considerations it follows that the layer, once formed, cannot then disappear because the smaller the thickness the greater is the layer-growth rate, that being inversely proportional to the existing layer thickness [1, 4, 5]. However, this is not the case. For example, van Loo and Rieck [13] annealed a $Ti-Ti_3Al-TiAl-TiAl_2-TiAl_3-Al$ specimen at 625° C for 15 h. As a result, the layers Ti_3Al, $TiAl$ and $TiAl_2$ vanished completely and the situation was changed to $Ti-TiAl_3-Al$. Note that all these intermetallics are thermodynamically stable at 625°C.

The neglect of a chemical reaction step appears to be the main source of discrepancies between the theory and experiment. An equation taking into account the relative influence of physical and chemical phenomena on the rate of growth of a chemical compound layer was first proposed by Evans in 1924 [14]. Evans' equation provides a suitable basis for understanding the nature of the processes taking place in multiphase binary systems. Unfortunately, there is a tendency to underestimate its importance.

The aim of the present work is, on the basis of Evans' equation and Arkharov's concept of the reaction diffusion [15–17], to attempt: (a) to reveal the role of diffusion and that of chemical reactions in determining the compound layer-growth kinetics, and (b) to develop the simplest physicochemical theory of heterogeneous kinetics in binary systems.

2. Solid-state growth of one compound layer

Let us first consider the case where a single layer of the

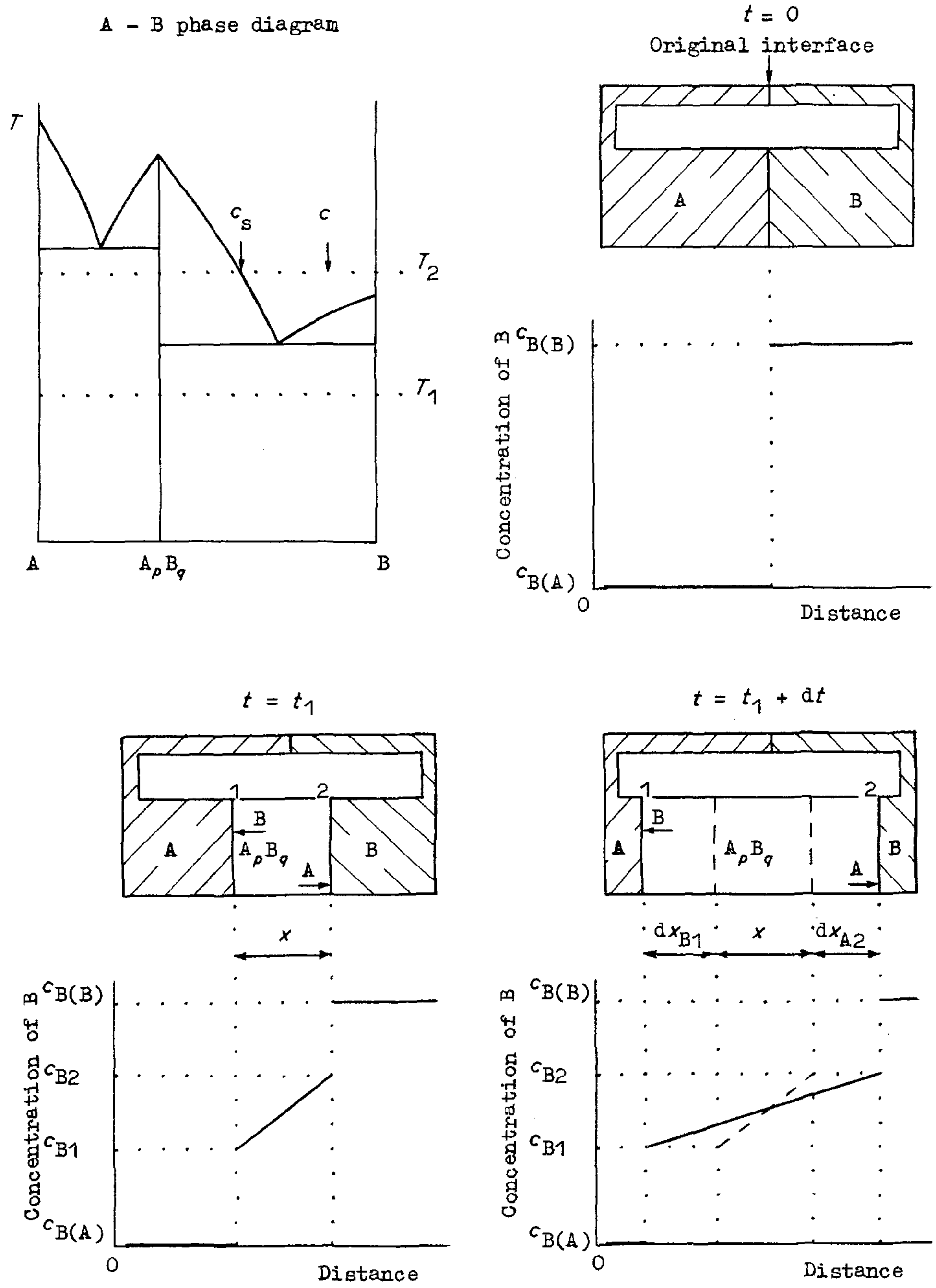

Figure 1 Schematic diagram to illustrate the growth of the A_pB_q layer between the elements A and B.

chemical compound A_pB_q, p and q being positive integers, grows between the elements A and B, Fig. 1.

2.1. Reaction diffusion model

The solid-state growth of the A_pB_q layer between the two mutually insoluble ($c_{B(A)} = 0$ and $c_{A(B)} = 0$) elementary substances A and B, say at T_1, is due to two simultaneous (parallel) processes each of which proceeds in two consecutive (alternate) steps. Firstly, the B atoms diffuse across the A_pB_q layer and then react at the A/A_pB_q interface (interface 1) with the surface A atoms according to the equation

$$q\text{B (diffusing)} + p\text{A (surface)} = \text{A}_p\text{B}_q \qquad (1)$$

Secondly, the A atoms diffuse across the layer in the opposite direction and react at the A_pB_q/B interface (interface 2) with the surface B atoms that can be described as follows

$$q\text{A (diffusing)} + q\text{B (surface)} = \text{A}_p\text{B}_q \qquad (2)$$

From the view-point of kinetics, Reactions 1 and 2 are, in general, different, while the reacting substances are the same, because the reactants A and B enter these reactions in quite different states, namely, as the diffusing or as surface atoms. The case where Reactions 1 and 2 have equal rates is therefore an exception rather than the rule.

Both processes involve two consecutive steps [15–17]: (a) diffusion of atoms through the layer; (b) chemical reaction with the participation of these atoms taking place at the interface between the layer and either A or B. The processes involving these two steps are usually called the reaction or chemical diffusion [15–17].

2.2. Assumptions

The consideration below is based upon the following assumptions:

1. the concentrations of components A and B in the

layer at boundaries 1 and 2 are equal to the limits of the A_pB_q homogeneity range;

2. a change in concentration with distance within the A_pB_q layer is linear (see Fig. 1);

3. during growth, both the boundary concentrations and a linear concentration distribution remain almost unchanged.

It should be noted that these assumptions are usually made to treat the growth kinetics of compound layers [7, 9, 14]. If these assumptions are satisfied then

$$\frac{\partial c_B}{\partial t} \approx 0 \tag{3}$$

Equation 3 expresses the condition of a quasistationary concentration distribution when the concentrations of A and B within the A_pB_q layer depend only on position, x, and are independent of time, t [4]. It is obvious that this condition is undoubtedly satisfied in the case of stoichiometric compounds having no ranges of homogeneity. This approximation seems to be fairly justified in the case of chemical compounds with narrow ranges of homogeneity (compared to the average content of a given component in a compound) and is confirmed by electron probe microanalysis (see, for example, [18]). It is the formation of these chemical compounds which will be treated here.

2.3. One process in the A–B system

Let Reaction 1 be the only reaction in the A–B system. This is the case when the diffusion of A within the A_pB_q layer is negligible compared to that of B.

In an initial stage of the interaction, the A_pB_q layer thickness is small and therefore the diffusional path is very short. Hence, a number of B atoms is able to reach the A/A_pB_q interface. The overall rate of Reaction 1 is, therefore, limited only by the reactivity of the A surface. The reactivity of the surface of the substance A (or its combining ability) is the largest number of the diffusing B atoms which can be combined by the surface A atoms into the A_pB_q compound per unit time. It is clear that the reactivity of the A surface towards B atoms remains unchanged during the whole course of Reaction 1. This is the reaction regime of growth of the A_pB_q layer when the growth rate is determined only by the rate of chemical reaction at the A/A_pB_q interface, the transport of B atoms across the layer being very fast (in the limit, instantaneous). In such a case, the layer-growth rate is constant; thus

$$\left(\frac{dx}{dt}\right)_{\text{reaction regime}} = k_{0B1} \tag{4}$$

where x is the thickness of the A_pB_q layer (m); t the time (sec); k_{0B1} the rate constant of the layer growth under conditions of reaction control (chemical constant, m sec^{-1}). In the subscript 0B1, zero indicates the reaction regime of growth of the layer, B shows that it is the B atoms which diffuse towards the reaction site and 1 shows where chemical reactions take place (at interface 1).

It is obvious that the reaction regime of growth of the A_pB_q layer is one of the two extremes. Another extreme is the diffusional regime of its growth when the rate of Reaction 1 is limited only by the rate of diffusional transport of B atoms across the layer, the further chemical reaction with the participation of these atoms being very fast. This is obviously the case if the A_pB_q layer is fairly thick. This "diffusional" case can easily be treated using Fick's first law

$$j_B = -D_B\frac{\partial c_B}{\partial x} \tag{5}$$

where j_B is the flux of the diffusing B atoms across the A_pB_q layer towards interface 1 (mol m^{-2}sec^{-1}); D_B the diffusion coefficient of B into the A_pB_q lattice (m^{2}sec^{-1}); c_B the concentration of component B within the compound layer (mol m^{-3}).

If the concentration distribution is linear, then (see Fig. 1)

$$-\frac{\partial c_B}{\partial x} = \frac{c_{B2} - c_{B1}}{x} \tag{6}$$

Hence,

$$j_B = D_B\frac{c_{B2} - c_{B1}}{x} \tag{7}$$

If the chemical reaction is instantaneous then all the B atoms passing across the layer per unit time are combined by the surface A atoms into the A_pB_q compound at interface 1. This results is an increase in thickness of the layer by dx. Therefore, the flux, j_B, can alternatively be expressed as follows

$$j_B = c_{B1}\left(\frac{dx}{dt}\right)_{\text{diffusional regime}} \tag{8}$$

By equating Equations 7 and 8, one obtains

$$\left(\frac{dx}{\partial t}\right)_{\text{diffusional regime}} \frac{D_B(c_{B2} - c_{B1})}{c_{B1}x} \tag{9}$$

In this equation

$$k_{1B1} = \frac{D_B(c_{B2} - c_{B1})}{c_{B1}} \tag{10}$$

is the rate constant of the layer growth under conditions of diffusional control (physical constant, m^{2}sec^{-1}). In the subscript 1B1 the first 1 indicates the diffusional regime of the layer growth and the other indexes have the former meaning.

It should be noted that the definitions of the reaction and diffusional regimes given above are "practical" ones. The more precise theoretical definitions will be given below.

It should be emphasized that equations such as Equations 9 and 10 were first proposed to calculate the diffusion coefficients in growing intermetallic layers by Heumann [9].

In general, the growth rate of the A_pB_q layer depends on both the rate of diffusion and the rate of chemical reaction since each of these two processes always proceeds at a finite rate. Therefore, Equations 4 and 9 are the limiting cases of a general relationship which can formally be found by summating the reciprocals; thus

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + (k_{0B1}x/k_{1B1})} \tag{11}$$

Integration of Equation 11 at the initial condition $x = 0$ at $t = 0$ yields

$$r = \frac{x^2}{2k_{1B1}} + \frac{x}{k_{0B1}} \quad (12)$$

The equations of this type were first obtained by Evans [14]. It is seen that if $k_{0B1} \ll k_{1B1}/x$ then Equation 11 transforms into Equation 4. Therefore, for small x Equation 12 becomes

$$x = k_{0B1}t \quad (13)$$

Hence, the reaction constant k_{0B1} can be found as the slope of the initial straight portion of the experimental thickness–time dependence plotted in x–t coordinates.

On the other hand, if $k_{0B1} \gg k_{1B1}/x$ then Equation 11 reduces to Equation 9. Accordingly, for large x Equation 12 simplifies to

$$x^2 = 2k_{1B1}t \quad (14)$$

The diffusional constant k_{1B1} can therefore be found as the slope of the straight portion of the same data, but plotted in x^2–t coordinates. Another way to find k_{1B1} is by calculation using known values of D_B, c_{B1} and c_{B2} (Equation 10).

Note that the reactivity of the A surface towards B atoms remains constant, the substance A being uniform from a macroscopic view-point, whereas the flux of these atoms through the A_pB_q layer gradually decreases as the layer thickens. Hence, there exists a single value, $x_{1/2}^{(B)}$, of the layer thickness at which these quantities are equal. The flux is expressed by Equation 7 while the reactivity is

$$j_B = c_{B1}\left(\frac{dx}{dt}\right)_{\text{reaction regime}} = c_{B1}k_{0B1} \quad (15)$$

Thus,

$$x_{1/2}^{(B)} = \frac{k_{1B1}}{k_{0B1}} \quad (16)$$

At $x < x_{1/2}^{(B)}$ the rate of reaction at the A surface is less than the flux of B atoms through the A_pB_q layer and therefore there is an "excess" of these atoms which can be used by the layers of other chemical compounds (enriched in component A compared to A_pB_q). On the other hand, at $x > x_{1/2}^{(B)}$ there is a deficit of B atoms because the rate of reaction at the A surface is greater than the flux of B atoms through the layer. On reaching interface 1, each B atom will therefore be combined into the A_pB_q compound. No B atom is thus available for the growth of other layers enriched in component A.

Equations 11 and 12 can easily be interpreted in terms of time. Indeed, Equation 11 can be rewritten as follows

$$dt = \left(\frac{x}{k_{1B1}} + \frac{1}{k_{0B1}}\right)dx \quad (17)$$

The quantity on the left-hand side of Equation 17 is the "differential" time, dt, necessary for the A_pB_q layer to grow from x to $x + dx$. Hence, the first term on the right-hand side is the time for diffusion of the reacting atoms to the reaction site

$$dt_{\text{diffusion}} = \frac{x}{k_{1B1}}dx \quad (18)$$

and the second is the time for subsequent chemical transformations with the participation of these atoms

$$dt_{\text{reaction}} = \frac{1}{k_{0B1}}dx \quad (19)$$

Note that the critical thickness, $x_{1/2}^{(B)}$, of the A_pB_q layer can be found from Equation 17 by putting $dt_{\text{diffusion}} = dt_{\text{reaction}}$. This equality means that half of the "differential" time is spent on the transport of atoms and another half is spent on the subsequent chemical reaction.

2.4. General case: Reactions 1 and 2 proceed simultaneously

In general, Reactions 1 and 2 take place simultaneously. The growth of the A_pB_q layer to the left from the original A–B interface is due to Reaction 1 while its growth to the right is due to Reaction 2 (see Fig. 1). Let dt be the time necessary for the A_pB_q layer to grow from x to $x + dx_{B1}$ at interface 1 and from x to $x + dx_{A2}$ at interface 2. Then taking into account the results of Section 2.3 one obtains

$$dt = \left(\frac{x}{k_{1B1}} + \frac{1}{k_{0B1}}\right)dx_{B1} \quad (20)$$

and

$$dt = \left(\frac{x}{k_{1A2}} + \frac{1}{k_{0A2}}\right)dx_{A2} \quad (21)$$

where k_{0A2} is a chemical constant and k_{1A2} is a physical (diffusional) constant; the latter is a function of D_A, the diffusion coefficient of A in the A_pB_q lattice, and of c_{A1} and c_{A2}, the boundary concentrations of A into the layer:

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

Reactions 1 and 2 are considered to be independent of one another for the two following reasons: (a) they are separated in space; (b) the fluxes, j_A and j_B, of components A and B across the growing A_pB_q layer appear to be independent of each other. This is due to the fact that in the lattice of a chemical compound each component forms its own sublattice [4]. In this sublattice all atoms as well as all sites are structurally equivalent. Again, the vacancies are continuously created in the sublattices as Reactions 1 and 2 proceed, namely, the vacancies in the B sublattice due to Reaction 1 appear at boundary 1 whereas the appearance of vacancies in the A sublattice at boundary 2 is due to Reaction 2. The vacancies formed are filled by the atom-by-atom movements. In such a way the B atoms are transferred from interface 2 to interface 1 while the A atoms are transferred in the opposite direction. The most essential point is that each kind of atoms moves in its own sublattice, thus not hindering the movement of another kind of atoms.

From Equations 20 and 21 it follows

$$\frac{dx_{B1}}{dt} = \frac{k_{0B1}}{1 + (k_{0B1}x/k_{1B1})} \tag{23}$$

and

$$\frac{dx_{A2}}{dt} = \frac{k_{0A2}}{1 + (k_{0A2}x/k_{1A2})} \tag{24}$$

A general equation describing the A_pB_q layer growth between the A and B phases is the sum of Equations 23 and 24; thus

$$\frac{dx}{dt} = \frac{k_{0B1}}{1 + (k_{0B1}x/k_{1B1})} + \frac{k_{0A2}}{1 + (k_{0A2}x/k_{1A2})} \tag{25}$$

The solution to this equation is

$$R_1x^2 + R_2x - R_3 \ln(1 + R_4x) = t, \tag{26}$$

where

$$R_1 = \frac{1}{2(k_{1B1} + k_{1A2})}$$

$$R_2 = \frac{k_{1B1}^2 k_{0A2} + k_{0B1}k_{1A2}^2}{k_{0B1}k_{0A2}(k_{1B1} + k_{1A2})^2}$$

$$R_3 = \frac{k_{1B1}k_{1A2}(k_{0B1}k_{1A2} - k_{1B1}k_{0A2})^2}{k_{0B1}^2 k_{0A2}^2(k_{1B1} + k_{1A2})^3}$$

$$R_4 = \frac{k_{0B1}k_{0A2}(k_{1B1} + k_{1A2})}{k_{1B1}k_{1A2}(k_{0B1} + k_{0A2})}$$

Note that there exists another critical value, $x_{1/2}^{(A)} = k_{1A2}/k_{0A2}$, at which the reactivity of the B surface towards A atoms and the flux of A atoms through the A_pB_q layer are equal. The existence of the critical thicknesses, $x_{1/2}^{(A)}$ and $x_{1/2}^{(B)}$, provides a basis for the theoretical definitions of the reaction and diffusional regimes of growth of the A_pB_q layer. That is, the regime of growth of the layer is reaction controlled with regard to component B if $x < x_{1/2}^{(B)}$ ($dt_{\text{reaction}} > dt_{\text{diffusion}}$, see Equations 17 to 19) and is diffusional with regard to this component if $x > x_{1/2}^{(B)}$ ($dt_{\text{reaction}} < dt_{\text{diffusion}}$). Again, the regime is reaction with regard to component A if $x < x_{1/2}^{(A)}$ and is diffusional if $x > x_{1/2}^{(A)}$. In general,

$$x_{1/2}^{(A)} \neq x_{1/2}^{(B)}$$

This is the only reason for the complex look of Equation 26. If $k_{0B1} = k_{0A2}$ and $k_{1B1} = k_{1A2}$ then Equations 25 and 26 become, respectively,

$$\frac{dx}{dt} = \frac{2k_{0B1}}{1 + (k_{0B1}x/k_{1B1})} \tag{27}$$

and

$$t = \frac{x^2}{4k_{1B1}} + \frac{x}{2k_{0B1}} \tag{28}$$

For small x, Equation 28 reduces to

$$x = 2k_{0B1}t, \tag{29}$$

whereas for large x it becomes

$$x^2 = 4k_{1B1}t. \tag{30}$$

This is the case when the contributions of both components to the layer growth are equal (compare Equations 29 and 30 with Equations 13 and 14). In general, these contributions are different. Nevertheless, an initial portion of the thickness–time relationship is always a straight line. Indeed, if $k_{0B1} \ll k_{1B1}/x$ and $k_{0A2} \ll k_{1A2}/x$ (or, alternatively, $x \ll x_{1/2}^{(B)}$ and $x \ll x_{1/2}^{(A)}$) then

$$\frac{dx}{dt} = k_{0B1} + k_{0A2} \tag{31}$$

and therefore

$$x = (k_{0B1} + k_{0A2})t \tag{32}$$

Again, for fairly large x the conditions $k_{0B1} \gg k_{1B1}/x$ and $k_{0A2} \gg k_{1A2}/x$ ($x \gg x_{1/2}^{(B)}$ and $x \gg x_{1/2}^{(A)}$) are satisfied; thus

$$\frac{dx}{dt} = \frac{k_{1B1} + k_{1A2}}{x} \tag{33}$$

and

$$x^2 = 2(k_{1B1} + k_{1A2})t. \tag{34}$$

Therefore, this long-time portion of the x–t relationship is parabolic.

3. The effect of dissolution on the growth of the A_pB_q layer

Let A be a solid and B a liquid, say at T_2, see Fig. 1. If the liquid is undersaturated with A then the dissolution of the layer occurs simultaneously with its growth. The overall change in thickness of the layer is therefore the difference between the rate of growth of the layer and the rate of its dissolution.

3.1. Dissolution of the layer

The rate of dissolution of the layer is described by the equation [19–21]

$$\left(\frac{dx}{dt}\right)_{\text{dissolution}} = b \exp(-at), \tag{35}$$

where $a = ks/v$, $b = c_sk/\varrho_{A_pB_q}\varphi$; k being the dissolution rate constant (m sec^{-1}), s the specimen surface area (m^2), v the volume of the liquid (m^3), c_s the saturation concentration of A in B (kg m^{-3}), $\varrho_{A_pB_q}$ the density of A_pB_q, and φ the content of A in A_pB_q in the mass fraction.

It is assumed that the compound A_pB_q decomposes during dissolution, i.e. $A_pB_q \rightarrow pA + qB$. The dissolution-rate constant, k, can be found from the Nernst–Shchukarev equation

$$c = c_s[1 - \exp(-at)], \tag{36}$$

describing a change in concentration, c, of A in B with time, t (for details see [19–21]).

If the compound A_pB_q dissolves without decomposition then $b = c_skV_{A_pB_q}$, $V_{A_pB_q}$ being the molar volume of A_pB_q (m^3 mol^{-1}). Note that in this case c and c_s are the concentrations of A_pB_q into the liquid.

3.2. Growth of the layer under conditions of its simultaneous dissolution

For simplicity, consider the case where both components equally contribute to the layer growth, i.e. $k_{0B1} = k_{0A2}$ and $k_{1B1} = k_{1A2}$. Then Equation 25

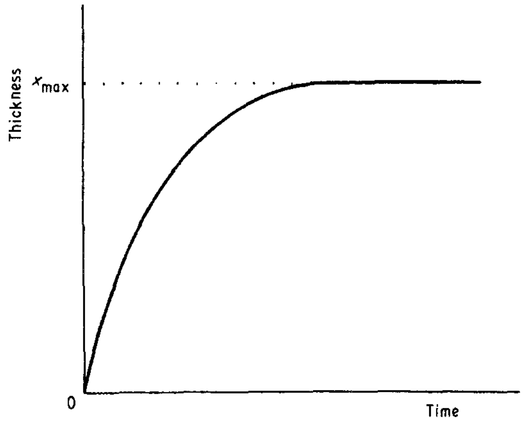

Figure 2 Growth of the A_pB_q layer under conditions of its simultaneous dissolution into the liquid at a constant rate.

becomes

$$\frac{dx}{dt} = \frac{k_0}{1 + (k_0x/k_1)} \qquad (37)$$

where $k_0 = k_{0B1} + k_{0A2} = 2k_{0B1}$, $k_1 = k_{1B1} = k_{1A2}$. Subtracting Equation 35 from Equation 37 yields an equation describing the rate of growth of the layer under conditions of its simultaneous dissolution

$$\frac{dx}{dt} = \frac{k_0}{1 + (k_0x/k_1)} - b \exp(-at) \qquad (38)$$

If s/v tends to zero then $\exp(-at)$ is close to unity. In such a case, the rate of dissolution of the layer is almost constant; therefore,

$$\frac{dx}{dt} = \frac{k_0}{1 + (k_0x/k_1)} - b \qquad (39)$$

The solution to this equation is

$$-\frac{k_1}{b^2}\ln\left[1 - \frac{k_0bx}{k_1(k_0 - b)}\right] - \frac{x}{b} = t \qquad (40)$$

From Equation 40 it follows that the layer thickness tends asymptotically to a maximum value (see Fig. 2) which can easily be found from Equation 39 by putting $dx/dt = 0$; thus

$$x_{max} = k_1(k_0 - b)/k_0b. \qquad (41)$$

It is seen that if $k_0 > b$ then the A_pB_q layer grows between the A and B phases from the very beginning of the interaction. However, if $k_0 < b$ the layer cannot grow because the rate of its dissolution exceeds the growth rate. In general, the dissolution rate decreases with time from b to 0. Therefore the time, t_0, is achieved when

$$k_0 \geqslant b \exp(-at_0) \qquad (42)$$

and the A_pB_q layer will grow between the A and B phases only after some delay.

4. Solid–gas system

If the reaction product is non-volatile, there is almost no difference between the solid–gas, solid–liquid and solid–solid interaction. However, if the product is volatile, the effect of evaporation on the layer growth should be taken into account.

4.1. Evaporation of the layer

The rate of evaporation of the layer is described by an equation analogous to Equation 35 [21]:

$$\left(\frac{dx}{dt}\right)_{\text{evaporation}} = b \exp(-at) \qquad (43)$$

where $a = ks/v$, $b = c_skV_{A_pB_q}$; k being the evaporation-rate constant (m sec^{-1}), c_s the equilibrium concentration of A_pB_q into the diffusion boundary layer at the A_pB_q/B interface (mol m^{-3}), and $V_{A_pB_q}$ the molar volume of A_pB_q (m^{3}mol^{-1}).

It is assumed that the product evaporates without decomposition:

$$(A_pB_q)_{\text{solid}} \rightarrow (A_pB_q)_{\text{gas}} \qquad (44)$$

4.2. The effect of evaporation on the rate of the layer growth

The most convenient method of investigation of the solid–gas interaction is a continuous thermogravimetric one (see, for example, [12]). If the reaction product is non-volatile, a change in the specimen mass reflects a change in the layer thickness because these quantities are proportional. If the product is volatile, this change is due to two factors acting in opposite directions, namely, the growth of the A_pB_q layer results in an increase whereas the evaporation of A_pB_q results in a decrease of the specimen mass. Experiments are usually performed in large volumes of gaseous phase and therefore the condition $s/v \approx 0$ is almost always satisfied. Hence, the thickness of the A_pB_q layer at the A/B interface tends with time to a limiting value defined by Equation 41. On the other hand, the amount (thickness) of the A_pB_q evaporated increases linearly as the rate of evaporation remains constant and equals b (see Equation 43). A typical curve is shown schematically in Fig. 3. It is seen that a mass loss may be observed instead of a mass gain if the duration of the experiment is long. Such a dependence was obtained, for example, during oxidation of molybdenum, tungsten and other metals whose oxygen-rich oxides are volatile at elevated temperatures [5, 12, 22, 23].

If $k_0 < b$, the A_pB_q layer cannot grow at the A/B interface. Reactions 1 and 2 proceed, of course, but all the product evaporates.

5. Discussion

From Equations 12 and 17 to 21 it follows that the portion of the time required for the chemical transformations gradually decreases as the layer thickens and at last at large thicknesses it becomes negligible compared to the portion necessary for the diffusion of atoms. In this stage of the interaction, the overall rates of Reactions 1 and 2 are determined practically only by the rates of diffusion of the reacting atoms. This is the "reason" for the neglect of a chemical reaction step as such. In the case of a single layer such a neglect does not result in a serious error as the initial linear stage of the layer growth is observable only with the help of very sensitive experimental techniques. However, this is not the case for multiphase layers where the neglect of a chemical reaction step leads to qualitative errors.

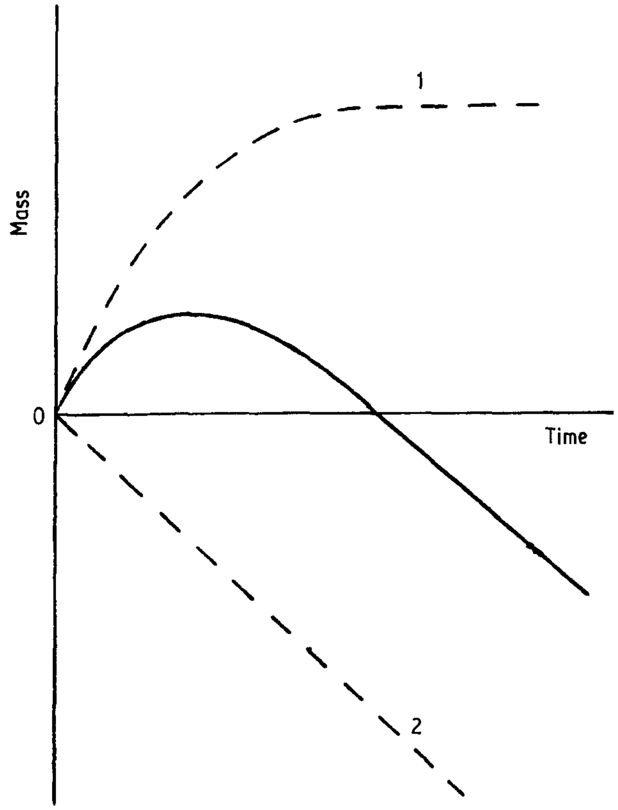

Figure 3 Change in mass of a specimen in the case of a volatile reaction product (solid line): 1, mass of the solid product layer at the solid–gas interface; 2, mass of the gaseous reaction product.

6. Conclusions

1. Growth of the A_pB_q compound layer between the elements A and B is due to two simultaneous processes.

2. Each of these two processes occurs in two consecutive (alternate) steps: (a) diffusion of atoms; (b) chemical reactions with the participation of these atoms.

3. In general, an initial portion of the layer thickness–time relationship in linear but there is then a gradual transition from a straight line to a parabola.

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