

Analytical treatment of diffusional growth kinetics of two intermetallic-compound layers

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Intermetallic compounds are known to form continuous layers at phase interfaces in the course of many technological processes such as hot-dip protective coating of solid surfaces with metals, soldering, welding of dissimilar metals and alloys, sintering in the presence of the liquid phase, making very-large-scale-integrated circuits, etc. [1–4]. The diffusional growth kinetics of intermetallic layers are usually treated using parabolic equations of the type $x^2 = 2kt$, where x is the layer thickness, k is the layer growth-rate constant and t is the time [5–7]. For sufficiently thick layers, such equations produce quite a satisfactory fit to the experimental data.

However, growth kinetics of the A_pB_q and A_rB_s layers at the diffusional stage of their formation at the interface between simple substances A and B (Fig. 1) are somewhat more complicated and described by a system of two non-linear equations [8]

$$\frac{dx}{dt} = \frac{k_A}{x} - \frac{rg}{p} \frac{k_B}{y} \quad (1a)$$

$$\frac{dy}{dt} = \frac{k_B}{y} - \frac{q}{sg} \frac{k_A}{x} \quad (1b)$$

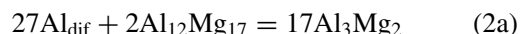
where x is the A_pB_q layer thickness, y is the A_rB_s layer thickness, k_A is the A_pB_q layer growth-rate constant, k_B is the A_rB_s layer growth-rate constant and g is the ratio of the molar volumes of the A_pB_q and A_rB_s compounds.

As shown in Fig. 1, under conditions of diffusion control the A_pB_q layer grows at the expense of diffusion of the A atoms across its bulk and their subsequent reaction with the A_rB_s compound. As a result, its thickness increases during dt by dx_{A2} . The A_rB_s layer grows at the expense of diffusion of the B atoms across its bulk and their further reaction with the A_pB_q compound. During the same time dt , its thickness increases by dy_{B2} . Since the A_pB_q and A_rB_s compounds are consumed in the formation of each other, the thickness of the A_pB_q layer simultaneously decreases by dx_{-} , while that of the A_rB_s layer by dy_{-} . The net change of the A_pB_q layer thickness during dt is the difference between dx_{A2} and dx_{-} , while that of the A_rB_s layer thickness is the difference

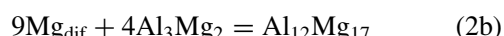
between dy_{B2} and dy_{-} . Therefore, Equations 1a and 1b contain two terms on their right-hand parts.

Both layers thicken at their common interface 2. Hence, the distance from an inert marker inside the A_pB_q layer to this interface increases with passing time, whereas that from the marker to interface 1 remains unchanged. Again, the distance from an inert marker inside the A_rB_s layer to interface 2 increases with time, whereas that from the marker to interface 3 remains the same.

An obvious criterion for the applicability of the system of Equations 1 is the constancy of k_A and k_B over a given range of time. For the sake of illustration, the experimental data on the growth kinetics of the $Al_3Mg_2(A_pB_q)$ and $Al_{12}Mg_{17}(A_rB_s)$ layers by Tanguet Njiokep *et al.* [9] can be used. Both intermetallic-compound layers were found to grow simultaneously at the interface between aluminum and magnesium. Their formation is likely to be due to partial chemical reactions



and



taking place at their common interface.

A plot of layer thickness against annealing time of Al–Mg diffusion couples at a temperature of 400 °C, according to the data of Tanguet Njiokep *et al.*, as shown in Fig. 2. The parabolic constant k is $1.57 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for the Al_3Mg_2 compound and $1.63 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ for the $Al_{12}Mg_{17}$ compound. From these, smoother layer thickness–time dependences, $x - t$ and $y - t$, were calculated. Then, the data thus obtained were treated using the system of Equations 1. The value of g was estimated from the densities of the Al_3Mg_2 and $Al_{12}Mg_{17}$ compounds [10, 11] as 0.94. The values of k_A and k_B were found to be $3.40 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ and $9.37 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, respectively (Table I). These remain unchanged in the 3.0×10^4 – 2.6×10^6 s time range.

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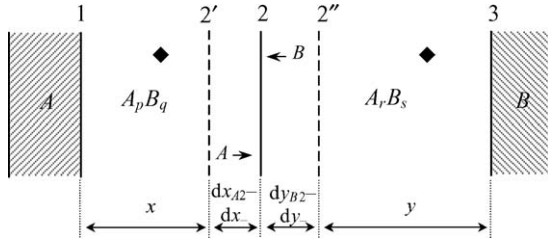


Figure 1 Schematic diagram to illustrate the growth process of two intermetallic-compound layers under conditions of diffusion control. Only component A is diffusing across the $A_p B_q$ layer, while only component B is diffusing across the $A_r B_s$ layer. Both layers thicken at their common interface 2. No reactions take place at interfaces 1 and 3 in view of the lack of appropriate diffusing atoms. The symbol \blacklozenge designates an inert marker.

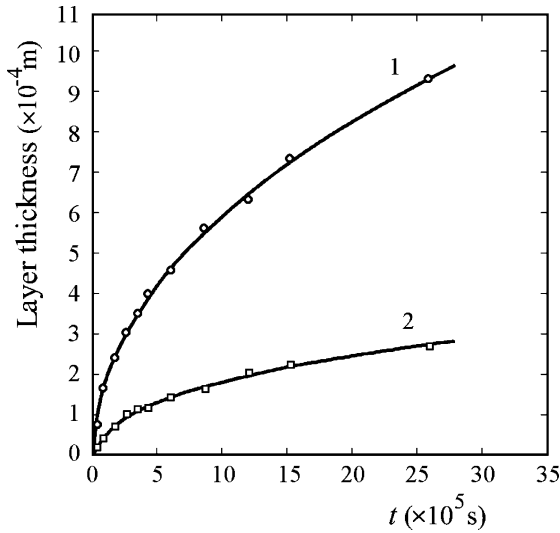


Figure 2 Plots of layer thickness against annealing time of Al–Mg diffusion couples at 400 °C according to the data of Tanguép Njiokep *et al.* [9]. 1, Al_3Mg_2 ; 2, $Al_{12}Mg_{17}$.

Hence, in the case under consideration both the parabolic relations and the system of Equations 1 adequately describe the layer growth kinetics. It should be noted, however, that generally the growth kinetics of two compound layers are not strictly parabolic. Moreover, from the system of Equations 1 it follows that

TABLE I Calculations of diffusional constants k_A and k_B for the Al_3Mg_2 ($A_p B_q$) and $Al_{12}Mg_{17}$ ($A_r B_s$) intermetallic-compound layers using the smoothed experimental data of Tanguép Njiokep *et al.* [9]

t ($\times 10^3$ s)	x ($\times 10^{-4}$ m)	y ($\times 10^{-4}$ m)	k_A ($\times 10^{-13}$ m ² s ⁻¹)	k_B ($\times 10^{-14}$ m ² s ⁻¹)
30	0.97	0.31	3.40	9.37
75	1.54	0.49	3.40	9.37
170	2.31	0.74	3.40	9.37
255	2.83	0.91	3.40	9.37
340	3.27	1.05	3.40	9.37
425	3.66	1.18	3.40	9.37
600	4.34	1.40	3.40	9.37
865	5.21	1.68	3.40	9.37
1205	6.15	1.98	3.40	9.37
1525	6.92	2.23	3.40	9.37
2596	9.03	2.91	3.40	9.37

Calculated values: $k_A = 3.40 \times 10^{-13}$ m² s⁻¹, $k_B = 9.37 \times 10^{-14}$ m² s⁻¹.

one of them can shrink, while the other will grow. This happens if their initial thicknesses, x_0 and y_0 , are such that, for example, the derivative $(dx/dt)_{t=t_0}$ is negative and the derivative $(dy/dt)_{t=t_0}$ is positive. Then, the thickness of the $A_p B_q$ layer will decrease, while the thickness of the $A_r B_s$ layer will increase until the x/y ratio falls into the range defined by the inequality

$$\frac{q}{sg} \frac{k_A}{k_B} < \frac{x}{y} < \frac{p}{rg} \frac{k_A}{k_B}. \quad (3)$$

Subsequently, both layers will grow simultaneously.

Thus, the $y - x$ phase plane [12–14] is divided into three regions, as shown in Fig. 3. In regions I and III the thickness of one of the layers increases and that of the other decreases. In region II the thickness of both layers increases.

Region I is separated from region II by the nodal line 1

$$y = \frac{sgk_B}{qk_A} x. \quad (4)$$

To obtain this equation, it suffices to put $dx/dt = 0$ in Equation 1a. The nodal line 2 between the regions II and III is the straight line

$$y = \frac{rgk_B}{pk_A} x, \quad (5)$$

which is obtained from Equation 1b by putting $dy/dt = 0$.

If the initial thicknesses of the $A_p B_q$ and $A_r B_s$ layers correspond to any point in region I, then with passing time the $A_p B_q$ layer will grow, whereas the $A_r B_s$ layer will shrink until the phase trajectory indicating the direction of growth enters region II, in which both layers will grow. If these thicknesses correspond to any point in region III, then the $A_r B_s$ layer will grow, whereas the $A_p B_q$ layer will shrink again until the phase trajectory enters region II where both layers will grow. If the initial

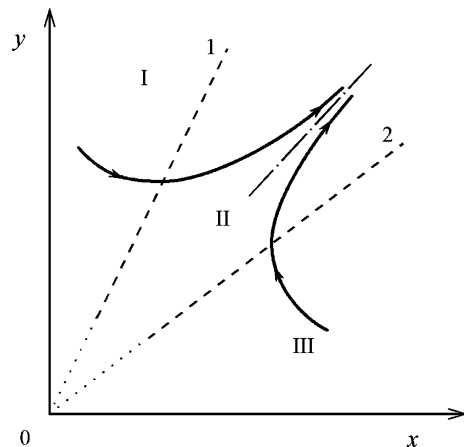


Figure 3 The $y - x$ phase plane in the diffusional stage of formation of two compound layers. The nodal lines 1 and 2 separate the phase plane into three regions. In regions I and III the thickness of one of the layers increases, while that of the other decreases. In region II both layers grow simultaneously. The arrows at phase trajectories indicate the direction of variation of the layer thicknesses with increasing time.

TABLE II Calculations of diffusional constants k_A and k_B for the Al_3Mg_2 (A_pB_q) and $Al_{12}Mg_{17}$ (A_rB_s) intermetallic-compound layers using the initial experimental data of Tanguiep Njiokep *et al.* [9]

t ($\times 10^3$ s)	x ($\times 10^{-4}$ m)	y ($\times 10^{-4}$ m)	k_A ($\times 10^{-13}$ m ² s ⁻¹)	k_B ($\times 10^{-14}$ m ² s ⁻¹)
30	0.58	0.03		
75	1.58	0.18	5.06	4.71
170	2.43	0.53	4.70	9.32
255	3.08	0.88	4.84	12.10
340	3.63	0.98	4.40	9.26
425	4.13	1.03	4.11	8.42
600	4.78	1.33	4.13	9.77
865	5.93	1.53	4.27	9.38
1205	6.73	1.98	4.40	11.20
1525	7.88	2.23	4.53	10.50
2596	10.00	2.73		

Average calculated values: $k_A = 4.49 \times 10^{-13}$ m² s⁻¹, $k_B = 9.41 \times 10^{-14}$ m² s⁻¹.

thicknesses of the A_pB_q and A_rB_s layers correspond to any point in region II, then the A_pB_q and A_rB_s layers will grow simultaneously from the very beginning of isothermal annealing of an $A - A_pB_q - A_rB_s - B$ specimen.

Both trajectories are seen to asymptotically tend with increasing time to a straight line corresponding to a constant ratio of the layer thicknesses. Whenever these are sufficiently close to this line, the parabolic growth law becomes a good approximation for both layers and therefore can be employed to treat the experimental kinetic data.

During the natural course of the process of formation of the A_pB_q and A_rB_s layers between elementary substances A and B , when an $A - B$ specimen is given to itself at constant temperature and pressure, a correct ratio of their thicknesses is established automatically. However, if an $A - A_pB_q - A_rB_s - B$ specimen was prepared artificially, this ratio can hardly be expected to be correct. During its subsequent isothermal annealing, one of the intermetallic-compound layers will inevitably shrink and may even disappear completely.

For comparisons, the constants k_A and k_B were also calculated directly using initial experimental values of layer thicknesses listed in Table II. These were read from a graph, as shown in Fig. 2, because tabulated values are lacking in the work of Tanguiep Njiokep *et al.* The derivatives, dx/dt and dy/dt , at each value of time were found by the numerical three-point method. The average value of k_A was determined to be 4.49×10^{-13} m² s⁻¹ and that of k_B 9.41×10^{-14} m² s⁻¹. Comparing these with the previous values $k_A = 3.40 \times 10^{-13}$ m² s⁻¹ and $k_B = 9.37 \times 10^{-14}$ m² s⁻¹, it may be concluded that both sets of the constants k_A and

k_B agree fairly well, providing evidence for the validity of the analytical treatment proposed.

As seen in Table II, the results of calculations using the system of Equations 1 are strongly dependent upon the accuracy of measuring layer thicknesses, especially in the initial abruptly ascending portion of any layer thickness-time dependence. Approximations of experimental data with any suitable analytical functions are therefore advisable to obtain more accurate values of k_A and k_B .

Physically, the value of k_A thus obtained is the reaction-diffusion coefficient, D_{Al} , of aluminum atoms in the Al_3Mg_2 compound lattice, whereas the value of k_B is the reaction-diffusion coefficient, D_{Mg} , of magnesium atoms in the $Al_{12}Mg_{17}$ compound lattice. Note that reaction-diffusion coefficients are always much greater than appropriate self-diffusion coefficients [15].

Acknowledgment

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References

1. "Composite Materials," "Interfaces in Metal Matrix Composites," edited by A. G. Metcalfe (Academic Press, New York, 1974) Vol. I.
2. "Thin Films—Interdiffusion and Reactions," edited by J. M. Poate, K. N. Tu and J. W. Mayer (Wiley, New York, 1978).
3. "Proizvodstvo bimetallicheskih trub i prutkov," edited by V. Ya. Ostrenko (Metallurgiya, Moskwa, 1986).
4. S. M. GUREVICH, "Spravochnik po svarke tsvetnykh metallov" (Naukova Dumka, Kiev, 1990).
5. W. SEITH, "Diffusion in Metallen" (Springer, Berlin, 1955).
6. K. HAUFFE, "Reaktionen in und an festen Stoffen" (Springer, Berlin, 1955).
7. K. P. GUROV, B. A. KARTASHKIN and YU. E. UGASTE, "Vzaimnaya diffuziya v mnogofaznykh metallicheskih sistemakh" (Nauka, Moskwa, 1981).
8. V. I. DYBKOV, "Reaction Diffusion and Solid State Chemical Kinetics" (The IPMS Publications, Kyiv, 2002).
9. E. M. TANGUEP NJIOKEP, M. SALAMON and H. MEHRER, *Defect and Diffusion Forum* **194–199** (2001) 1581.
10. N. N. MATYUSHENKO, "Kristallicheskie struktury dvoynykh soedineniy" (Metallurgiya, Moskwa, 1969).
11. L. F. MONDOLFO, "Aluminium Alloys: Structure and Properties" (Butterworths, London, 1976).
12. V. I. SMIRNOV, "Kurs vysshey matematiki" (Nauka, Moskwa, 1967) Vol. 2.
13. L. S. PONTRYAGIN, "Obykvennyye differentsial'nye uravneniya" (Nauka, Moskwa, 1982).
14. W. C. JOHNSON and G. MARTIN, *Solid State Phenomena* **3–4** (1988) 247.
15. V. I. DYBKOV, *J. Mater. Sci. Lett.* **13** (1994) 770.

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