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An analysis of reaction diffusion in metal–non-metal systems

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The formation of a single M_xN_y intermediate phase in a metal–non-metal system is governed by two parabolic growth regions if the metal side of the couple is finite in extent and initially unsaturated with non-metal. The first parabolic region is described by semi-infinite conditions on the metal side of the couple, while the second is according to saturated conditions. The intermediate phase reaction layer grows non-parabolically when conditions are such that the concentration profile cannot be described by either semi-infinite or saturated conditions on the metal side of the couple. Expressions have been obtained relating the growth constants to diffusion coefficients and information from an equilibrium phase diagram. The mathematical formulation of the problem was tested by application to the titanium–carbon system. The diffusion coefficient of carbon in titanium carbide was found to be in close agreement with values reported elsewhere in the literature.

1. Introduction

The kinetics of the growth of a single intermediate phase, M_xN_y, as a result of reaction diffusion between a metal, M, and a non-metal, N, can be formulated quite readily if either one of two conditions is fulfilled:

(1) the metallic phase is initially pure M or unsaturated with respect to the non-metal and also semi-infinite [1, 2]; or

(2) the metallic phase is saturated initially with the non-metal [1, 3].

One may anticipate that the rate of growth of the intermediate phase will be faster in the latter case because there is no flux of non-metal into the metallic phase. But, in both cases, the thickness of the metallic phase varies parabolically with time.

If the metallurgical history of an M–N couple covers a time range which includes both the semi-infinite and saturated cases for short and long diffusion times, respectively, then it follows that non-parabolic growth of the intermediate phase must be observable during some finite time interval. The objectives of this research were to obtain a mathematical description of the growth of the intermediate phase that includes both parabolic stages as well as the connecting non-parabolic stage and to test this analysis using data available in the literature on the growth of TiC in Ti–C couples. In this particular metal–non-metal system, the mobility of the non-metal is orders of magnitude greater than that of the metal and, therefore, the mathematical description of the growth of the TiC phase involves only the diffusivities of carbon in TiC and Ti, i.e. D_C^{TiC} and D_C^{Ti}.

2. Description and analysis of the problem

The analysis is based on the following assumptions

(1) the growth of the intermediate phase, MN, occurs by displacement of the MN/M interface. The non-metal diffuses through the MN layer to the MN/M interface where some of the non-metal reacts with M to form MN and the remainder diffuses into the metallic phase if M has not reached

saturation with respect to the non-metal throughout its extent.

(2) the concentration gradient within the intermediate phase is linear;

(3) the diffusivities of the non-metal in the intermediate phase, D_N^{MN}, and in the metal, D_N^M, are independent of concentration; and

(4) local equilibrium is maintained at the N/MN and the MN/M interfaces.

These assumptions are very reasonable and have been shown to be valid in cases of reaction diffusion involving the growth of carbide [4, 5] and silicide [6, 7] layers. The semi-infinite and saturated cases of growth will be considered first and then the more general analysis which covers both of these cases will be presented.

2.1. Case I: growth of the MN layer during the time interval within which the metal side of the couple remains semi-infinite

When an M–N couple is fabricated using pure or unsaturated M, the metal phase will be semi-infinite during the initial period of diffusion. The duration of this period depends upon the length, L, of the metal side of the couple.

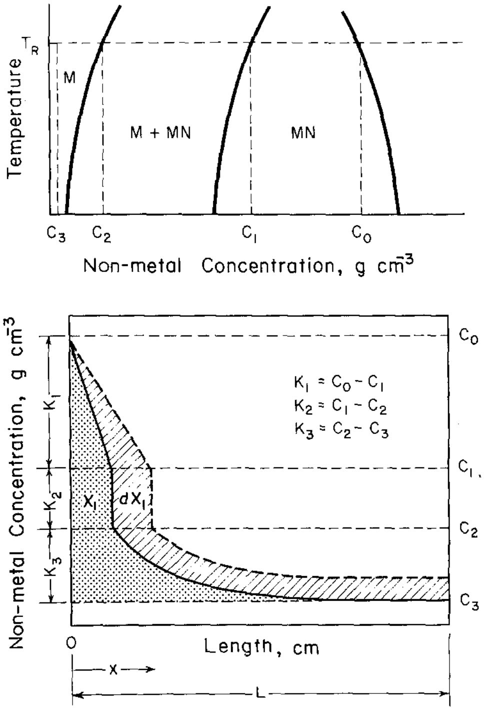

Figure 1 Relationship between the concentration–penetration diagram and the phase diagram for reaction diffusion in a metal–non-metal system.

As shown in Fig. 1, the homogeneity range of the intermediate phase, MN, is K_1, the concentration difference at the MN/M interface is K_2, and the difference between the saturation limit of the non-metal in the metal and the initial concentration of non-metal in the metal is K_3. The units of concentration of g cm^{-3}. A small displacement, dX_1, of the MN/M interface during the time increment, dt, results in the accumulation, Δ, of non-metal in the MN layer that is given by the expression

$$\Delta = \tfrac{1}{2}K_1 dX_1 + K_2 dX_1 \qquad (1)$$

and, furthermore, the conservation of non-metal requires that

$$\Delta = \tfrac{1}{2}K_1 dX_1 + K_2 dX_1 = (J_{\text{into}} - J_{\text{out}})dt \qquad (2)$$

where J_{into} is the flux of non-metal into the MN layer at $x = 0$ and J_{out} is the flux of non-metal through the MN/M interface and into the metal side of the couple.

$$J_{\text{into}} = D_N^{MN}\left(\frac{K_1}{X_1}\right) \qquad (3a)$$

and

$$J_{\text{out}} = -D_N^M\left(\frac{\partial c^M}{\partial x}\right)_{x=X_1} . \qquad (3b)$$

The concentration gradient in Equation 3b may be evaluated from the solution to Fick's second law for semi-infinite boundary conditions [8].

$$C^M = C_2 - \frac{2K_3}{\sqrt{\Pi}}\int_0^q e^{-q^2}\,dq \qquad (4a)$$

where

$$q = \frac{x}{2\sqrt{(D_N^M t)}} \qquad (4b)$$

Therefore,

$$\left(\frac{\partial C^M}{\partial x}\right)_{x=X_1} \cong \left(\frac{\partial C^M}{\partial x}\right)_{x=0} = -\frac{K_3}{\sqrt{(\Pi D_N^M t)}} \cdot (5)$$

This expression may be substituted for the gradient in Equation 3b provided that $X_1 \ll L$. This condition is normally applicable because the thickness of the reaction layer is usually very small in comparison to the length, L, of the metal side of the couple. Substitution of the flux expressions into Equation 2 yields

$$\tfrac{1}{2}K_1 \mathrm{d}X_1 + K_2 \mathrm{d}X_1 = \left[D_{\mathrm{N}}^{\mathrm{MN}}\left(\frac{K_1}{X_1}\right) - K_3\sqrt{\left(\frac{D_{\mathrm{N}}^{\mathrm{M}}}{\Pi t}\right)}\,\right]\mathrm{d}t. \qquad (6)$$

It can be shown by assuming a solution of the form $X^{\mathrm{N}} = k_\infty t$ to this equation that the growth of the MN layer is parbolic, i.e.

$$X_1^2 = k_\infty t. \qquad (7)$$

Substitution of the expression into Equation 6 yields the following expression for the growth constant.

$$k_\infty = \left\{-\left(\frac{K_3}{\tfrac{1}{2}K_1 + K_2}\right)\sqrt{\left(\frac{D_{\mathrm{N}}^{\mathrm{M}}}{\Pi}\right)} + \sqrt{\left[\left(\frac{K_3}{\tfrac{1}{2}K_1 + K_2}\right)^2 \frac{D_{\mathrm{N}}^{\mathrm{M}}}{\Pi} + \frac{2D_{\mathrm{N}}^{\mathrm{MN}}K_1}{(\tfrac{1}{2}K_1 + K_2)}\right]}\right\}^2 \qquad (8)$$

2.2. Case II: growth of the MN layer when the metal side of the couple is saturated initially with non-metal

For this case, one may simply repeat the above analysis but with $J_{\mathrm{out}} = 0$ and $K_3 = 0$. The growth of the intermediate phase again is parabolic, i.e.

$$X_1^2 = k_{\mathrm{s}} t \qquad (9)$$

where

$$k_{\mathrm{s}} = \frac{2D_{\mathrm{N}}^{\mathrm{MN}}K_1}{\tfrac{1}{2}K_1 + K_2}\,. \qquad (10)$$

This growth constant also may be determined directly from Equation 8 by the substitution of $K_3 = 0$.

2.3. Case III: growth of the MN layer when the metal side is initially unsaturated with the non-metal and also of finite length

In this situation, the initial growth of the intermediate phase will be parabolic with the growth constant, k_∞, given by Equation 8 and the final stage of growth also will be parabolic but with a growth constant, k_{s}, given by Equation 10. Therefore, a period of non-parabolic growth must exist between the initial and final parabolic stages of growth which occur at different rates.

In order to described mathematically the complete range of growth behaviour, the concentration gradient of the non-metal in the metal at $x = X_1$ (i.e. the MN/M interface) must be obtained from the solution to Fick's second law subject to the following boundary conditions:

$$C_{X_1,t} = C_2 \text{ for } t \geqslant 0 \qquad (11\mathrm{a})$$

$$C_{x,0} = C_3 \text{ for } X_1 \leqslant x \leqslant L \qquad (11\mathrm{b})$$

$$\left(\frac{\partial C}{\partial x}\right)_{\mathrm{L},t} = 0. \qquad (11\mathrm{c})$$

Again utilizing the reasonable condition that $X_1 \ll L$, the solution is

$$C^{\mathrm{M}} = C_2 - \frac{4K_3}{\Pi}\sum_{n=1}^{\infty}\frac{1}{(2n-1)}\sin\left[\frac{(2n-1)\Pi x}{2L}\right]\exp\left[-\frac{(2n-1)^2\Pi^2 D_{\mathrm{N}}^{\mathrm{M}}t}{4L^2}\right] \qquad (12)$$

and, therefore, the concentration gradient in the metal at the MN/M interface is

$$\left(\frac{\partial C^{\mathrm{M}}}{\partial x}\right)_{x=X_1} \cong \left(\frac{\partial C^{\mathrm{M}}}{\partial x}\right)_{x=0}$$

$$= -\frac{2K_3}{L}\sum_{n=1}^{\infty}\exp\left[-\frac{(2n-1)^2\Pi^2 D_{\mathrm{N}}^{\mathrm{M}}t}{4L^2}\right] \qquad (13)$$

Substitution of Equations 3a and b into Equation 2 yields the differential equation governing the growth of the intermediate phase subject to the boundary conditions stated above.

$$\tfrac{1}{2}K_1 \mathrm{d}X_1 + K_2 \mathrm{d}X_1 = \left[D_{\mathrm{N}}^{\mathrm{MN}}\left(\frac{K_1}{X_1}\right) - \frac{2K_3 D_{\mathrm{N}}^{\mathrm{M}}}{L}\left\{\sum_{n=1}^{\infty}\exp\left[-\frac{(2n-1)^2\Pi^2 D_{\mathrm{N}}^{\mathrm{M}}t}{4L^2}\right]\right\}\right]\mathrm{d}t \qquad (14)$$

It should be noted that this equation describes case II layer growth when $K_3 = 0$ and, also because of its more general nature, describes layer growth under case I as well. A closed form solution to this equation cannot be obtained because of the mathematical singularity at the origin ($X_1 = 0$, $t = 0$). Consequently, numerical methods, the details of which will be described below, must be used to obtain a solution. Depending upon the information which is avialable, Equation 14 may be used in a variety of ways. For example, if $D_{\mathrm{N}}^{\mathrm{MN}}$ and $D_{\mathrm{N}}^{\mathrm{M}}$ are known, the time required to produce a layer of a given thickness may be calculated. On the other hand, if only one diffusion coefficient is known and some X_1 versus

t data are available, the magnitude of the unknown diffusion coefficient may be determined. The latter approach was utilized in this research.

3. Results and discussion

The following discussion is concerned mainly with the numerical solution of Equation 14 and its application to the prediction of the kinetics of layer growth in metal–non-metal systems. The efficacy of the analysis was established using data available in the literature on the Ti–C system.

The kinetics of the growth of the intermediate phase TiC in Ti–graphite couples have been investigated experimentally by Vansant and Phelps [9]. These researchers assumed that the layer growth was parabolic and employed an analytical approach suggested by Wagner to obtain values of the diffusion coefficient of carbon in titanium carbide, i.e. $D_{\mathrm{C}}^{\mathrm{TiC}}$. The primary objective of this research was to re-analyse the experimental data of Vansant and Phelps using Equation 14 which does not involve an assumption relative to the kinetics of layer growth, e.g. parabolic behaviour.

The numerical solution of Equation 14 is facilitated by rewriting the equation in finite difference form,

$$X_1 \Delta X_1 = \left[W_1 D_{\mathrm{N}}^{\mathrm{MN}} - W_2 D_{\mathrm{N}}^{\mathrm{M}} X_1 \sum \mathrm{e}^{-\beta_n t} \right] \Delta t \qquad (15)$$

where

$$W_1 = \frac{K_1}{\frac{1}{2}K_1 + K_2}, \qquad (16)$$

$$W_2 = \frac{2K_3}{(\frac{1}{2}K_1 + K_2)L}, \qquad (17)$$

and

$$\beta_n = \frac{(2n-1)^2 \Pi^2 D_{\mathrm{N}}^{\mathrm{M}}}{4L^2}. \qquad (18)$$

Using the growth data of Vansant and Phelps, the values of $D_{\mathrm{C}}^{\mathrm{Ti}}$ determined by Wagner *et al.* [10] and the solubility limits reported by Cadoff and Nielsen [11] and Brukl [12], values of $D_{\mathrm{C}}^{\mathrm{TiC}}$ were obtained from Equation 15 using a computer program which consisted of the following steps:

(1) A set of experimental values of X_1 and t, a value of $D_{\mathrm{C}}^{\mathrm{Ti}}$ corresponding to the reaction temperature and an assumed value of $D_{\mathrm{C}}^{\mathrm{TiC}}$ were substituted into Equation 15.

(2) Using time increments, Δt, of 0.05 h, computed sets of X_1, t data were generated for the times $t - \Delta t$, $t - 2\Delta t$, etc. The correctness of the assumed value of $D_{\mathrm{C}}^{\mathrm{TiC}}$ was judged by the extent to which the computed value of X_1 at $t = 0.05$ h deviated from zero.

(3) Steps 1 and 2 were repeated until a value of $D_{\mathrm{C}}^{\mathrm{TiC}}$ which yielded a value X_1 less than or equal to 5×10^{-5} cm at $t = 0.05$ h was selected. Reference is made at this point to the fact that the origin ($X_1 = 0$, $t = 0$) cannot be used in the computation because of the mathematical singularity in Equation 15).

(4) The value of $D_{\mathrm{C}}^{\mathrm{TiC}}$ obtainted in step 3 was used to generate layer growth data from $t = 0.05$ h to 100 h.

TABLE I Comparison of numerically computed values of $D_{\mathrm{C}}^{\mathrm{TiC}}$ with the values obtained by Vansant and Phelps [9]

Couple number	Reaction conditions		TiC layer thickness × 10^4 (cm)	$D_{\mathrm{C}}^{\mathrm{TiC}}$ (cm^2 h^{-1})	
	Temp. (°C)	Time (h)		[9]*	Equation 15
1	1090	4	1.0	4.14×10^{-8}	2.92×10^{-8}
2	1288	2	12.7	7.52×10^{-7}	1.16×10^{-6}
3	1288	4	18.0	7.52×10^{-7}	8.36×10^{-7}
4	1288	4	15.4	7.52×10^{-7}	6.24×10^{-7}
5	1288	4	10.2	7.52×10^{-7}	2.95×10^{-7}
6	1288	8	26.4	7.52×10^{-7}	7.65×10^{-7}
7	1305	8	29.5	9.33×10^{-7}	9.33×10^{-7}
8	1488	1	24.9	7.28×10^{-6}	6.00×10^{-6}
9	1488	2	37.6	7.28×10^{-6}	6.02×10^{-6}
10	1488	2	37.0	7.28×10^{-6}	5.84×10^{-6}
11	1488	2	28.2	7.28×10^{-6}	3.43×10^{-6}
12	1488	4	61.5	7.28×10^{-6}	7.56×10^{-6}
13	1488	8	85.0	7.28×10^{-6}	7.02×10^{-6}
14	1488	10	89.2	7.28×10^{-6}	6.15×10^{-6}
15	1505	4	68.6	8.62×10^{-6}	9.35×10^{-6}
16	1505	4	60.5	8.62×10^{-6}	7.29×10^{-6}

*Calculated from $D_{\mathrm{C}}^{\mathrm{TiC}} = 360 \exp(-62\,000/RT)$ cm^2 h^{-1}.

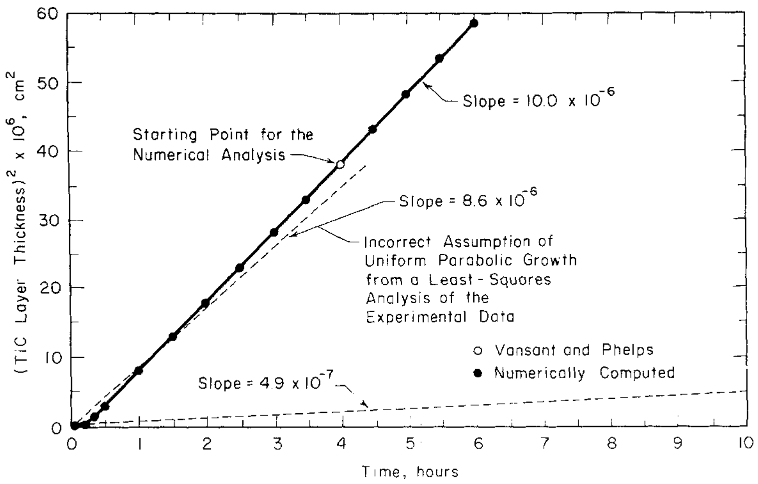

Figure 2 Titanium carbide reaction layer growth behaviour predicted by Equation 15 at 1488° C from experimental data obtained by Vansant and Phelps [9].

(5) Another set of data (X_1, t, D_C^{Ti}) was selected and the above process repeated.

A comparison of the values of D_C^{TiC} obtained by this technique with those reported by Vansant and Phelps is presented in Table I. The agreement is quite good, the expressions for the temperature dependence of D_C^{TiC} being

$$D_C^{TiC} = 360 \exp\left(-\frac{62\,000}{RT}\right) \text{cm}^2\,\text{h}^{-1} \quad [9] \tag{16a}$$

and

$$D_C^{TiC} = 1010 \exp\left(-\frac{65\,500}{RT}\right) \text{cm}^2\,\text{h}^{-1} \quad \text{(this work).} \tag{16b}$$

Fig. 2 illustrates the numerically computed growth behaviour of a TiC layer at 1488° C. The data points were obtained by starting the numerical solution of Equation 15 at the data point reported by Vansant and Phelps for couple 12 (Table I). Note that the growth of the intermediate phase is suggestive of both case I and case II conditions. The region of case II parabolic growth, i.e. metal side of the couple saturated with non-metal, is particularly evident. The growth constant as calculated for this region by the numerical analysis is $k_s = 10 \times 10^{-6}$ cm² h⁻¹m which agrees exactly with the theoretical value predicted by Equation 10. The region of case I parabolic growth, i.e. metal side of the couple is semi-infinite, is not as evident as the case II region because of the short length (0.254 cm) of the metal side of the couple. A reference line for parabolic growth subject to case I conditions is superposed on Fig. 2; the slope, $k_\infty = 4.9 \times 10^{-7}$ cm² h⁻¹, of this line was calculated from Equation 8. Although case I growth is not distincly delineated in Fig. 2, it is apparent that layer growth is not uniformly parabolic. Similar patterns of growth behaviour were noted for the other sets of data points obtained by Vansant and Phelps (Table I). If one assumes that the growth of the TiC layer is uniformly parabolic from the origin (dashed line in Fig. 2), then an incorrect value of the growth constant is obtained. Thus, Vansant and Phelps, who utilized this procedure, obtained a value of 8.6×10^{-6} cm² h⁻¹ for k_s at 1488° C whereas the present numerical approach yields a value of 10×10^{-6} cm² h⁻¹ and, consequently, by use of Equation 10, a more accurate value of D_C^{TiC}.

In order to reveal more clearly the non-parabolic transition between case I and case II conditions, the thickness of the layer as a function of time was numerically computed using Equation 15 for various values of the length, L, of the metal side of the couple. It was assumed that at $t = 0.05$ h growth is subject to case I conditions; this assumption permitted a corresponding value of X_1 to be calculated. The results of these calculations are shown in Fig. 3 for the lengths $L = 0.254$, 1.0 and 2.0 cm, respectively. When $L = 0.254$, the agreement between the experimental data and the computed curves is excellent. Thus, the numerical computation of growth data from Equation 15 based on the initial assumption of case I parabolic growth at $t = 0.05$ h is apparently justified. A comparison of the growth curves in Fig. 3 shows that the major effects of increasing the length, L, of the metal side of the couple are to lengthen the time interval over which the transition from case I

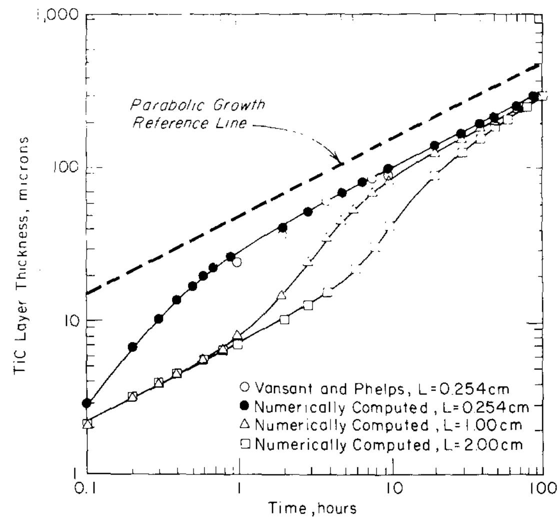

Figure 3 Titanium carbide reaction layer growth behaviour predicted by Equation 15 at 1488° C for various values of L.

to case II growth occurs and also the time interval of case I growth. Clearly, the assumption of uniform parabolic growth is not warranted and will result in an erroneous value of the growth constant. If the metal is not saturated with the non-metal initially, the growth of the intermediate phase is characterized by two parbolic stages and an intermediate transition stage.

A transition time was arbitrarily established from X_1^2 versus t plots at the point of intersection of the extrapolations of the slopes describing semi-infinite and saturated growth regions. A plot of the transition time thus defined as a function of the square of the length of the metal side of the couple for six values of L ranging from 0.254 to 2.0 cm is linear. Such a plot may be useful in selecting a diffusion time for predominantly case I or case II growth for a given length of the metal side of the couple.

4. Conclusion

The growth of an intermediate phase, M_xN_y, in an M–N diffusion couple will be parabolic if either (1) the metal side of the couple is pure or unsaturated with the non-metal and also semi-infinite or (2) the metal is initially saturated with the non-metal. The kinetics of growth are different for the two cases. If the metal side of an M–N couple is of finite length and initially not saturated with non-metal, then both parbolic stages will be observed and a non-parabolic intermediate stage will be observed as well. A mathematical analysis which describes the complete range of layer growth is presented and its application to the growth of TiC in Ti-graphite couples is discussed in detail. Values of the diffusion coefficient of carbon in TiC are obtained using this analysis and they compare extremely well with data previously reported in the literature.

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