An Approximate Solution for the Finite-extent Moving-boundary Diffusion-controlled Dissolution of Spheres

R. ASTHANA

Materials Department, University of Wisconsin-Milwaukee, Milwaukee, WI 53201 (U.S.A.)

S. K. PABI

Metallurgy Department, Indian Institute of Technology, Kharagpur 721 302 (India)

Abstract

An approximate integral profile type of analysis has been worked out for the kinetics of one-phase moving-boundary finite-extent diffusion-controlled dissolution of an array of equisized and uniformly distributed spheres. The theoretical results of the analysis are in fair agreement with the numerical spherical finite model of Tanzilli and Heckel at considerably reduced computation times.

1. Introduction

Recently, new analytical solutions have been presented for a certain class of moving-boundary phase change problems [1]. In general, however, the moving-boundary diffusion-controlled phase change problems involving multidimensional diffusion and non-linear boundary conditions at the moving interface are notoriously difficult to solve analytically, and numerical solutions are frequently resorted to [2, 3]. In addition, several mathematically approximate techniques to solve these problems have also been developed [4], and these have been applied with varying degree of success to phase change problems. Among these, Goodman's heat balance integral method (HBIM) has been successfully applied to several phase change problems with different boundary conditions [4, 5]. The basic approach of this method involves making an educated guess for the functional form of concentration (temperature) distribution in one or more independent variables, and then to integrate the governing differential equation to eliminate them from the problem. Several refinements of the original Goodman technique have been made to expand its range of applicability [6–10].

Several mathematical models for diffusion-limited dissolution have been proposed in the literature [11, 12]. Whelan [11] used a stationary interface approximation to derive the dissolution kinetics of an isolated sphere in an infinite matrix. On the contrary, Luybov and Shebelev [13] presented a moving-boundary analysis and derived series-type solutions for the dissolution of an unbounded sphere. Nolfi *et al.* [14] presented an analysis for soft impingement during dissolution of a finite array of spheres by invoking the stationary interface approximation. An evaluation of various dissolution models shows that the stationary interface model [11] is the best at low matrix supersaturation and for slow interface movement.

2. Analysis

The present treatment of soft impingement during spherical dissolution employs a diffusional analogue of Goodman's HBIM [4, 15] to derive the kinetics of finite-extent moving-interface diffusion-controlled dissolution in an array of equisized and homogeneously distributed (radial center-to-center separation $2L$) spheres of constant concentration C_p. For this situation (Fig. 1), the diffusion equation

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \tag{1}$$

with a constant diffusivity is subject to the following boundary conditions,

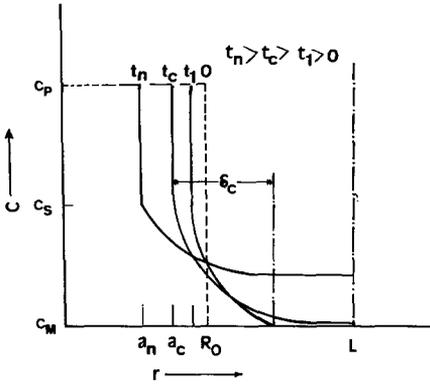$$\frac{\partial C}{\partial r} = 0 \qquad r = L \tag{2}$$

Fig. 1. Schematic diagram showing composition profiles at various times during dissolution.

$$C(r, t) = C_s \qquad r = a(t), \qquad t \geqslant 0 \qquad (3)$$

$$C(r, t) = C_p \qquad R_0 \leqslant r < a(t) \qquad (4)$$

$$D \frac{\partial C}{\partial r}\bigg|_{r=a(t)} = (C_p - C_s) \frac{da}{dt} \qquad (5)$$

where $a(t)$ denotes the moving front and C_s is the time-invariant interface concentration. These composition parameters have been normalized such that C_p is unity, C_s is a fraction between 0 and 1, and the initial unperturbed concentration C_m of the matrix is zero. By taking the total derivative of C_s with respect to time, and using conditions (1) and (5), the following moving-boundary condition is obtained in a manner similar to the one-dimensional case [15]:

$$-(C_p - C_s)\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) = \left(\frac{\partial C}{\partial r}\right)^2$$

$$r = a(t) \qquad (6)$$

Now, following Goodman [4] a cubic composition profile of the form

$$C(r, t) = C_s - A_1 \frac{r-a}{L-a} - \frac{A_2}{2}\left(\frac{r-a}{L-a}\right)^2$$

$$- \frac{A_3}{3}\left(\frac{r-a}{L-a}\right)^3 \qquad a(t) < r \leqslant L \qquad (7)$$

is assumed, where the appropriate expressions for the time-dependent coefficients A_1, A_2 and A_3 are determined by applying conditions (2), (5) and (6) to eqn. (7). $C(r, t)$ from eqn. (7) is now substituted in the following integrated form of the

diffusion equation:

$$\int_{a(t)}^{L} \frac{\partial C}{\partial t} dr = D \int_{a(t)}^{L} \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) dr \qquad (8)$$

which in view of eqn. (3) and Leibniz's rule for changing the order of integration and differentiation [16] becomes

$$\frac{d}{dt}\left\{\int_{a(t)}^{L} C(r, t) dr - 2D\right.$$

$$\times \int_{a(t)}^{L} \frac{dC}{r} + C_s \frac{da}{dt} + D\frac{\partial C}{\partial r}\bigg|_{r=L}\right\} = 0 \qquad (9)$$

Carrying out the integrations indicated above by making use of eqn. (7), and simplifying the resulting equation after some lengthy but straightforward algebra, yields the following equation for the finite-extent spherical dissolution kinetics:

$$\frac{dz}{da} = -\frac{\phi_2(a)Z^2 + \phi_3(a)Z + \phi_4(a)}{2Z + \phi_1(a)} \qquad (10)$$

$$Z = \frac{da}{dt} \qquad (11)$$

$$\phi_1(a) = \frac{3D(4L + a)}{F(a)(2L + a)(L - a)} \qquad (12)$$

$$\phi_2(a) = \frac{1.5}{a(L-a)F(a)}\left[1.3(4a - L) - \frac{2}{(2L+a)^2}\right.$$

$$\times \left\{(a+L)^3 - (a-L)^3 - \frac{L^3}{2}\right.$$

$$+ 2aL(3a - 2L)\Big\}\Big] \qquad (13)$$

$$\phi_3(a) = \frac{3D}{F(a)(L-a)^2}\left[\frac{2(L-5a)}{a} - \frac{1}{(2L+a)^2}\right.$$

$$\times \{(6L + 5a)(2L + a) - 4(a - L)^2$$

$$- 3a(L - 2a)\}\Big] \qquad (14)$$

$$\phi_4(a) = \frac{12D^2}{(L-a)^3 F(a)}\left(\frac{3a}{2L+a} - \frac{C_s}{1-C_s}\right) \qquad (15)$$

$$F(a) = \frac{1.5(L + a)}{(2L + a)} - 1 \qquad (16)$$

We now define the initial conditions for solving

eqn. (10) as the interface position $a(t_c)$ and velocity $Z(t_c)$ at some critical time t_c such that $t < t_c$ represents the infinite-field (isolated particle) situation and $t \geqslant t_c$ denotes the finite-extent dissolution situation. The concept of a critical time t_c is understood by introducing the idea of penetration depth $\delta(t)$ (the depth of the perturbed composition profile in the matrix), such that $t = t_c$ corresponds to the diffusion field overlap in the array, so that $a(t) + \delta(t) = L$ at $t = t_c$. The transition in kinetics at $t = t_c$ is assumed to be smooth and continuous. The boundary conditions for dissolution at times $t < t_c$ are given by eqns. (5) and (6), whereas eqn. (2) is replaced by

$$\frac{\partial C}{\partial r} = 0 \qquad r = a(t) + \delta(t) \qquad (17)$$

$$C(r, t) = C_m \qquad r = a(t) + \delta(t) \qquad (18)$$

By introducing a new variable u defined as $u = Cr$, the governing field equation is transformed to its one-dimensional form

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial r^2} \qquad (19)$$

Similarly eqns. (3), (5), (6), (17) and (18) are transformed to

$$u(a, t) = C_s \qquad t \geqslant 0 \qquad (20)$$

$$D\left(a\frac{\partial u}{\partial r} - u\right) = a^2 \frac{\mathrm{d}a}{\mathrm{d}t}(C_p - C_s) \qquad r = a(t) \quad (21)$$

$$-(C_p - C_s)a \frac{\partial^2 u}{\partial r^2} = \left(\frac{\partial u}{\partial r} - \frac{u}{a}\right)^2 \qquad r = a(t) \quad (22)$$

$$u(a + \delta, t) = 0 \qquad (23)$$

$$\frac{\partial u}{\partial r} = 0 \qquad r = a(t) + \delta(t) \qquad (24)$$

The mass balance integral for times $t < t_c$ becomes

$$\int_{a(t)}^{a(t) + \delta(t)} \frac{\partial u}{\partial t}\,\mathrm{d}r = D \int_{a(t)}^{a(t) + \delta(t)} \frac{\partial^2 u}{\partial r^2}\,\mathrm{d}r$$

which simplifies to

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\{\int_{a(t)}^{a(t) + \delta(t)} u(r, t)\,\mathrm{d}r + aC_s \frac{\mathrm{d}a}{\mathrm{d}t} + D\frac{\partial u}{\partial r}\bigg|_{r = a(t)}\right\} = 0 \qquad (25)$$

The variable u is now represented by the following third-degree polynomial:

$$u = \frac{2aC_s}{\delta^2}\{r - (a + \delta)\}^2 + \frac{aC_s}{\delta^3}\{r - (a + \delta)\}^3 \qquad (26)$$

Equation (26) simultaneously satisfies the conditions (20), (23) and (24). Substitution of u from eqn. (26) above into eqn. (25) yields a differential equation in $\mathrm{d}\delta/\mathrm{d}t$, $\mathrm{d}a/\mathrm{d}t$, $a(t)$ and $\delta(t)$. A relationship between $a(t)$ and $\delta(t)$ is now obtained by using the moving-boundary condition, eqn. (22), in conjunction with eqn. (26), and this is used to eliminate $a(t)$ from the previous equation. Similarly, the term $\mathrm{d}a/\mathrm{d}t$ is eliminated using eqn. (26) in conjunction with the condition (21). The above manipulation yields a first-order non-linear differential equation in $\mathrm{d}\delta/\mathrm{d}t$ and $\delta(t)$ which could be variable separated and integrated together with the initial condition $\delta(t) = 0$, at $t = 0$, to give the kinetics of penetration layer growth. Finally, in a manner similar to the planar HBIM analysis [15] the expression for $\delta(t)$ is substituted in the mass balance, eqn. (21), to derive a differential equation in $a(t)$ and t. Integration of this equation together with the initial condition $a(t) = R_0$, at $t = 0$, yields a short-time weak solution for the dissolution kinetics of an isolated sphere in an infinite matrix. This solution is

$$a(t) = R_0 - \beta(Dt)^{1/2} \qquad (27)$$

where

$$\beta = \frac{2}{K}\left(1 + \frac{1}{K_1}\right)\left(\frac{2}{\alpha}\right)^{1/2}$$

$$K_1 = -\frac{1 + K^{1/2}}{1 - K}$$

$$K = \frac{2(1 - C_s)}{C_s}$$

$$\alpha = 2.4 + \frac{2}{K}\left(2.4 + \frac{1}{K_1}\right)\left(1 + \frac{1}{K_1}\right)$$

Now making use of the expressions derived for $a(t)$ and $\delta(t)$ and noting that $a(t) + \delta(t) = L$ at $t = t_c$, the critical time for diffusion layer overlap is obtained as

$$t_c = \frac{(L - R_0)^2}{D((2\alpha)^{1/2} - \beta)^2} \qquad (28)$$

In dimensionless form this becomes

$$\left(\frac{Dt_c}{R_0^2}\right) = \frac{(1/C_A^{1/3} - 1)^2}{\{(2\alpha)^{1/2} - \beta\}^2} \qquad (29)$$

where $C_A = (R_0/L)^3$ is the initial volume fraction of the second phase. The two initial conditions required to solve eqn. (10) are obtained by substituting eqn. (28) for t_c in the expressions for $a(t)$ and da/dt that are obtained from eqn. (27). This yields

$$a(t_c) = R_0 - \frac{\beta(L - R_0)}{(2\alpha)^{1/2} - \beta} \qquad (30)$$

$$\left.\frac{da}{dt}\right|_{t_c} = Z(t_c) = -\frac{\beta D\{(2\alpha)^{1/2} - \beta\}}{2(L - R_0)} \qquad (31)$$

3. Results and discussion

Since a closed-form solution cannot be obtained for eqn. (10) in terms of elementary functions, the latter was solved by a numerical predictor–corrector method with the initial conditions (30) and (31). The dissolution kinetics of $CuAl_2$ precipitates in the well-characterized Al–4.5wt.%Cu alloy, calculated by using the present method are in good qualitative agreement with the spherical finite model of Tanzilli and Heckel (TH) [2] as shown in the dimensionless plots in Fig. 2. Also shown in Fig. 2 are experimental data on solution kinetics of $CuAl_2$ particles at two different temperatures from that in ref. 17. The computation times for the present method are almost two orders of magnitude smaller than the finite-difference TH model. The

present procedure therefore represents a method for quick estimation of solution kinetics at some expense to exactness.

Figure 3 compares the infinite geometry theoretical dissolution kinetics of plates calculated using HBIM from ref. 15 and of spheres calculated from eqn. (27), in terms of dimensionless thickness and time parameters. The faster dissolution kinetics of spheres compared with plates noted from Fig. 3 are obviously due to existence in the former of multidimensional fluxes as well as of a progressively shrinking area of the receding interface. This is also confirmed from the plots of normalized critical time vs. interface concentration C_s for both spheres and plates (Fig. 4). At a constant volume fraction of second phase, the diffusion fields overlap earlier (i.e. smaller t_c) in a periodic array of spheres than in a uniform

Fig. 3. Theoretical plots of normalized particle radius (or half-thickness) vs. dimensionless dissolution time for the infinite extent ($t < t_c$) dissolution of spheres and plates based on integral profile analysis.
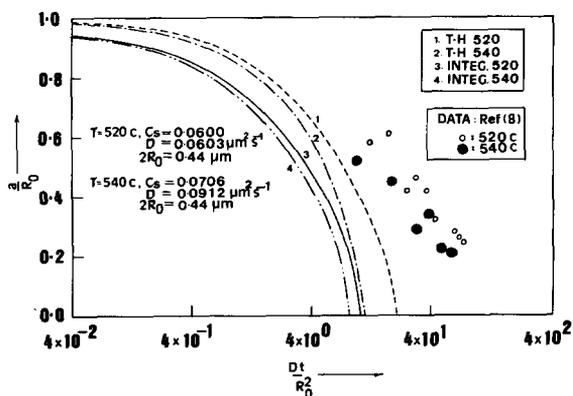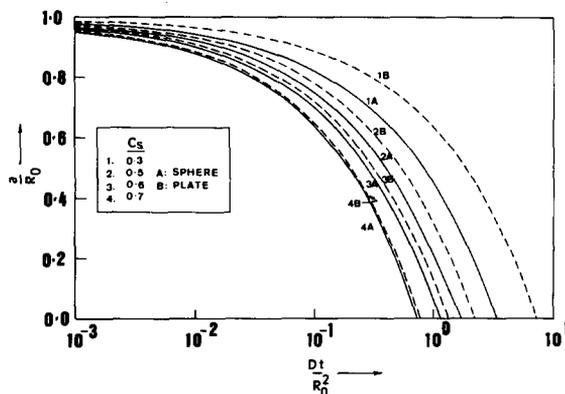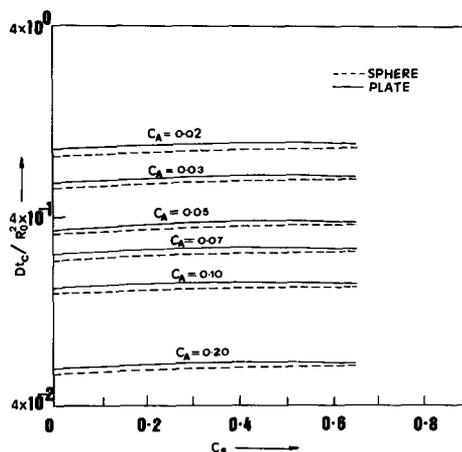
Fig. 2. Dimensionless theoretical plots of particle radius vs. dissolution time of spheres showing comparison between the present analysis and spherical finite (TH) model.

Fig. 4. Theoretical plots of dimensionless critical time for plates and spheres as a function of interface concentration C_s and initial volume fraction C_A of the second phase.
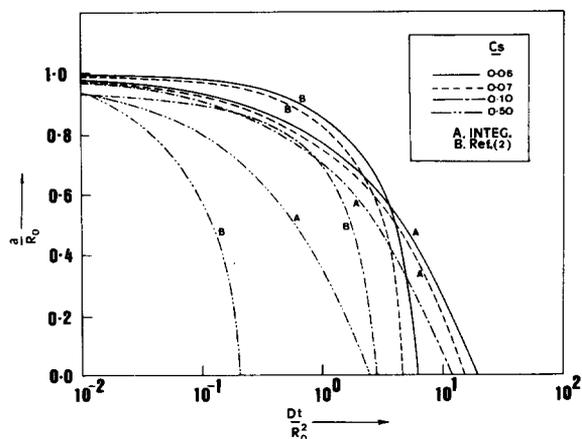
Fig. 5. Dimensionless theoretical plots of particle radius vs. time for infinite-extent $(t < t_c)$ dissolution based on the present integral analysis and Whelan's stationary interface model.

exact and numerical solutions and can also be applied to situations involving a composition-dependent diffusivity [22]. For the sphere problem, a more judicious choice of concentration function, or the application of HBIM to discretized diffusion field by using linear piecewise continuous profiles in the manner of refs. 9 and 10 will improve the accuracy of results. However, the inherent complexities of the infinite- and finite-geometry diffusion problems involving non-planar moving interfaces aré perhaps most adequately and safely dealt with by using numerical finite-difference procedures.

4. Conclusions

A diffusional analog of the heat balance integral method was used to derive the kinetics of finite extent, moving boundary diffusion-controlled dissolution of spheres. The theoretical results of the analysis showed fair agreement with a rigorous finite difference model of the problem at considerably reduced computation times. The choice of a suitable mathematical function to represent the concentration distribution in the matrix is acknowledged as a major difficulty in improving the accuracy of the solution presented here. However, spatial subdivision of the concentration field into linear (or quadratic) profiles in the manner of finite-element methods is expected to improve the accuracy of the analytical approach presented here.

stack of equisized plates. This figure also shows that, for both these geometries, the normalized critical time Dt_c/R_0^2 is almost independent of C_s but manifests a strong dependence on C_A.

The influence of interface movement on the infinite-extent theoretical dissolution kinetics of spheres calculated from the present HBIM method is shown in Fig. 5, where dimensionless plots based on Whelan's [11] stationary interface model are compared with the present HBIM results. It is noted that interface migration effects cause progressively larger deviations between the two models with increasing values of the super-saturation parameter that is defined as $2(C_s - C_m)/(C_p - C_s)$, or as $2C_s/(1 - C_s)$, on the normalized composition scale used here.

The accuracy of the HBIM is sensitive to the choice of assumed composition profile [18], and higher order polynomial approximations may in fact inhibit the accuracy of the results [19]. Moreover, polynomial functions are perhaps inadequate for non-planar shapes [20] although physically more realistic profiles (e.g. logarithmic for cylinders [21]) render the ensuing algebraic manipulations mathematically intractable in view of the non-linear form of the moving-boundary condition, eqn. (6). The averaging procedure used in the HBIM (eqns. (8) and (25)) precludes an accurate representation of actual concentration distribution, although a fair estimate can be made of the transformation kinetics of spheres at greatly reduced computation times, as shown in Fig. 1. The method is remarkably accurate for planar dissolution problem when compared with

References

1 D. Carnright and S. H. Davis, Metall. Trans. A, 20 (1989) 225.
2 R. A. Tanzilli and R. W. Heckel, Trans. Metall. Soc. AIME, 242 (1968) 2313.
3 S. K. Pabi, Phys. Status Solidi A, 51 (1979) 281.
4 T. R. Goodman, in J. P. Hartnett and T. F. Irvine (eds.), Advances in Heat Transfer, Vol. I, Academic Press, New York, 1964.
5 M. Imber and P. N. S. Huang, Int. J. Heat Mass Transfer, 16 (1973) 1951.
6 G. Poots, Int. J. Heat Mass Transfer, 5 (1962) 339, 525.
7 D. S. Riley and P. W. Duck, Int. J. Heat Mass Transfer, 20 (1977) 294.
8 P. W. Duck and D. S. Riley, Int. J. Heat Mass Transfer, 20 (1977) 297.
9 G. E. Bell, Int. J. Heat Mass Transfer, 21 (1978) 1357.
10 G. E. Bell, Int. J. Heat Mass Transfer, 22 (1979) 1681.
11 M. J. Whelan, Met. Sci. J., 3 (1969) 95.
12 H. B. Aaron, D. Fainstein and G. R. Kotler, J. Appl. Phys., 41 (1970) 4404.
13 B. Ya. Luybov and V. V. Shebelev, Phys. Met. Metallogr. (Engl. Transl.), 35 (2) (1973) 95.

14 F. V. Nolfi, P. G. Shewmon and J. S. Foster, *Trans. AIME,* *245* (1969) 1427.
15 S. K. Pabi, *Acta Metall., 27* (1979) 1693.
16 R. C. West (ed.), *CRC Handbook of Chemistry and Physics,* CRC Press, West Palm Beach, FL, 1978.
17 D. L. Baty, R. A. Tanzilli and R. W. Heckel, *Metall. Trans., 1* (1970) 1651.
18 L. Fox, in J. R. Ockendon and W. R. Hodgkins (eds.), *Moving Boundary Problems in Heat Flow and Diffusion,* Clarendon, Oxford, 1975, p. 210.
19 D. Langford, *Int. J. Heat Mass Transfer, 16* (1973) 2424.
20 E. M. Sparrow, *J. Appl. Mech., 82* (1960) 598.
21 T. J. Lardner and F. V. Pohl, *J. Appl. Mech., 28* (1961) 310.
22 R. Asthana and P. K. Rohatgi, *Scr. Metall., 24* (2) (1990) 427.