Numerical Solution to the Growth of Spherical Precipitates with Capillarity Effects

P.E.J. Rivera-Díaz-del-Castillo and H.K.D.H. Bhadeshia

University of Cambridge

Department of Materials Science and Metallurgy

Pembroke Street, Cambridge CB2 3QZ, U.K.

Abstract

Numerical solutions are presented for the growth of spherical precipitates incorporating the effect of interface curvature on local equilibrium at the interface in two-phase binary systems. This corrects an analytical solution [1].

Introduction

In recent work [1], we provided an analytical solution for the diffusion–controlled growth of a sphere including capillarity. It has been anonymously pointed out to us that this contains an inconsistency.

The concentration field in the matrix surrounding a spherical particle has to meet Fick's second law, which in spherical coordinates is:

$$\frac{\partial c}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial t}\left\{r^2\frac{\partial c}{\partial r}\right\} \tag{1}$$

where c is the concentration around the particle, D is the diffusion coefficient, assumed to be independent of concentration, t stands for time and r is the radial coordinate.

We proposed a solution to equation (1) as follows:

$$c\{t,\rho\} = \overline{c} + \left[\left(c^{\beta\gamma} + \frac{2c^{\beta\gamma}\Gamma}{\rho}\right) - \overline{c}\right]\frac{\phi\{r/\sqrt{Dt}\}}{\phi\{\alpha\}} \tag{2}$$

where

$$\Gamma = \left(\frac{\sigma v^{\gamma}}{kT}\right)\left(\frac{1-c^{\beta\gamma}}{c^{\gamma\beta}-c^{\beta\gamma}}\right) \tag{3}$$

and

$$\phi\{\alpha\} = \frac{1}{\alpha}\exp\left\{-\frac{\alpha^2}{4}\right\} - \frac{\sqrt{\pi}}{2}\mathrm{erfc}\left\{\frac{\alpha}{2}\right\} \tag{4}$$

where $\overline{c}$ is the average concentration of solute in the alloy, ρ is the precipitate radius, $c^{\beta\gamma}$ is the concentration of solute in the matrix (β) in equilibrium with the precipitate (γ), σ is the surface energy per unit area, v^{γ} is the volume per atom in the precipitate phase γ, k is the Boltzmann constant, T is the temperature and $c^{\gamma\beta}$ the solute concentration of the precipitate

(γ) in equilibrium with β, erfc is the complementary error function and $\alpha = \rho/\sqrt{Dt}$ is a growth parameter. Γ is commonly referred as the capillarity constant [2].

Equation (2) is obtained using a similarity transformation [3] but this assumes that $\phi\{\alpha\}$ is constant, which is not. We do not know how to analytically solve this difficulty, but the problem requires a solution given the need to predict the kinetics of precipitation in steels. We therefore present a numerical solution.

Method

Tanzilli and Heckel [4] have presented a numerical solution for sphere growth in the absence of capillarity. Thus, equation (1) can be expressed as

$$\frac{c_n^{j+1} - c_n^j}{\Delta t} = \frac{N-n}{L-\rho} \times \frac{c_{n+1}^j - c_{n-1}^j}{2} \times g^{j+1}$$

$$+D \times \frac{c_{n+1}^j - 2c_n^j + c_{n-1}^j}{(L-\rho)^2/N^2} + \frac{D}{\rho + \frac{(n)(L-\rho)}{N}} \times \frac{c_{n+1}^j - c_{n-1}^j}{(L-\rho)/N} \tag{5}$$

where $n = 0, 1, 2, ..., N$ are the nodes that divide the matrix phase in N elements each of length Δr (Fig. 1), j is a time interval, c_n^j is the concentration in n at the time interval j, Δt is the increment in time, L is the zero mass transfer boundary at the matrix, i.e. where $c_N = c_{N+1}$, and g^{j+1} the interface velocity at the time interval $j+1$. The time increment was set to satisfy the restriction for stable and non-oscillatory solutions to be

$$\Delta t \leq 0.25 \frac{\Delta r^2}{D} \tag{6}$$

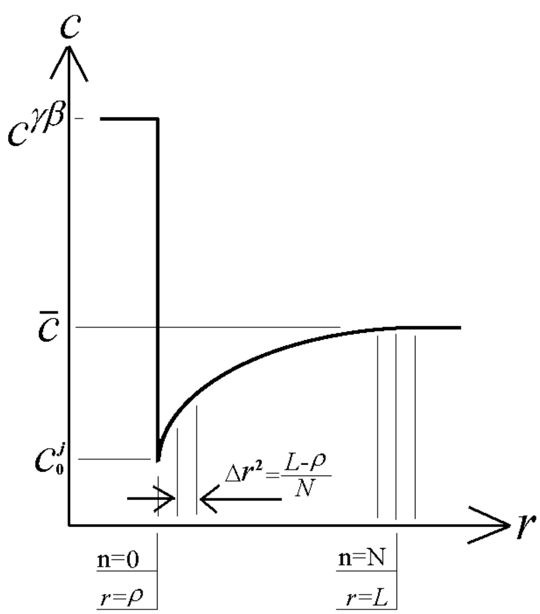

Fig. 1 *Definition of finite-difference terminology.*

When capillarity effects are considered, the mass transfer equation (5) is similarly expressed as

$$\frac{\rho^{j+1} - \rho^j}{\Delta t} = \frac{D}{c^{\gamma\beta} - c_0^j} \times \frac{-c_2^j + 4c_1^j - 3c_0^j}{2(L-\rho)/N} \tag{7}$$

where ρ^j is the particle radius at time interval j and

$$c_0^j = \overline{c} - (\overline{c} - c^{\beta\gamma})\left(1 - \frac{\rho_c}{\rho^j}\right) \tag{8}$$

where

$$\rho_c = \frac{2c^{\beta\gamma}\Gamma}{\overline{c} - c^{\beta\gamma}} \tag{9}$$

is the critical radius, c_0^j the solute concentration at the matrix interface (Fig. 1), which is equivalent to the boundary conditions [1] met by setting the initial concentrations of all the nodes equal to $\overline{c}$ at $t = 0$ except c_0, which is calculated assuming an initial particle radius of $\rho/\rho_c = 1.01$. Equations (5,7,8) were thus simultaneously solved and their results are shown in Fig. 2, where the variation of the growth parameter α is plotted as a function of ρ/ρ_c for a variety of compositions (Fig. 2a); α was scaled with a starting radius of $\rho^0 = 1.01$ and Ω with values of $c^{\gamma\beta} = 1$ and $c^{\beta\gamma} = 0$. The variation of the interface velocity g with ρ/ρ_c is shown in Fig. 2b. The convergence of equations (5,7,8) was achieved when as Δt was decreased to a convenient value, a negligible change in g^j was produced, and the value of N was such that $c_N \simeq \overline{c}$.

In Fig. 2a α approaches asymptotically the value predicted by Zener's theory; this is expected as for large ρ/ρ_c the capillarity effect becomes less important. Consistent with this, the velocity (Fig. 2b) approaches a value given by $g = D\alpha^2/(2\rho)$ at large radii, while it approaches zero for small values as the driving force for growth vanishes due to capillarity.

The accuracy of the predictions given by the analytical solution [1] is illustrated in Fig. 2b where g is plotted with dotted lines against ρ/ρ_c for the indicated values of Ω. The approximate values given by the analytical method adequately predict the velocity trends; in the range of solutions observed, the maximum error was of the order of 11%; thus the analytical solution may be used for calculations where large precision is not required.

Summary

A numerical solution for the growth of particles when capillarity effects are prominent is presented. The behaviour of the solution is similar to that of an earlier (incorrect) analytical solution [1], and its precision may be acceptable for many kinetic predictions.

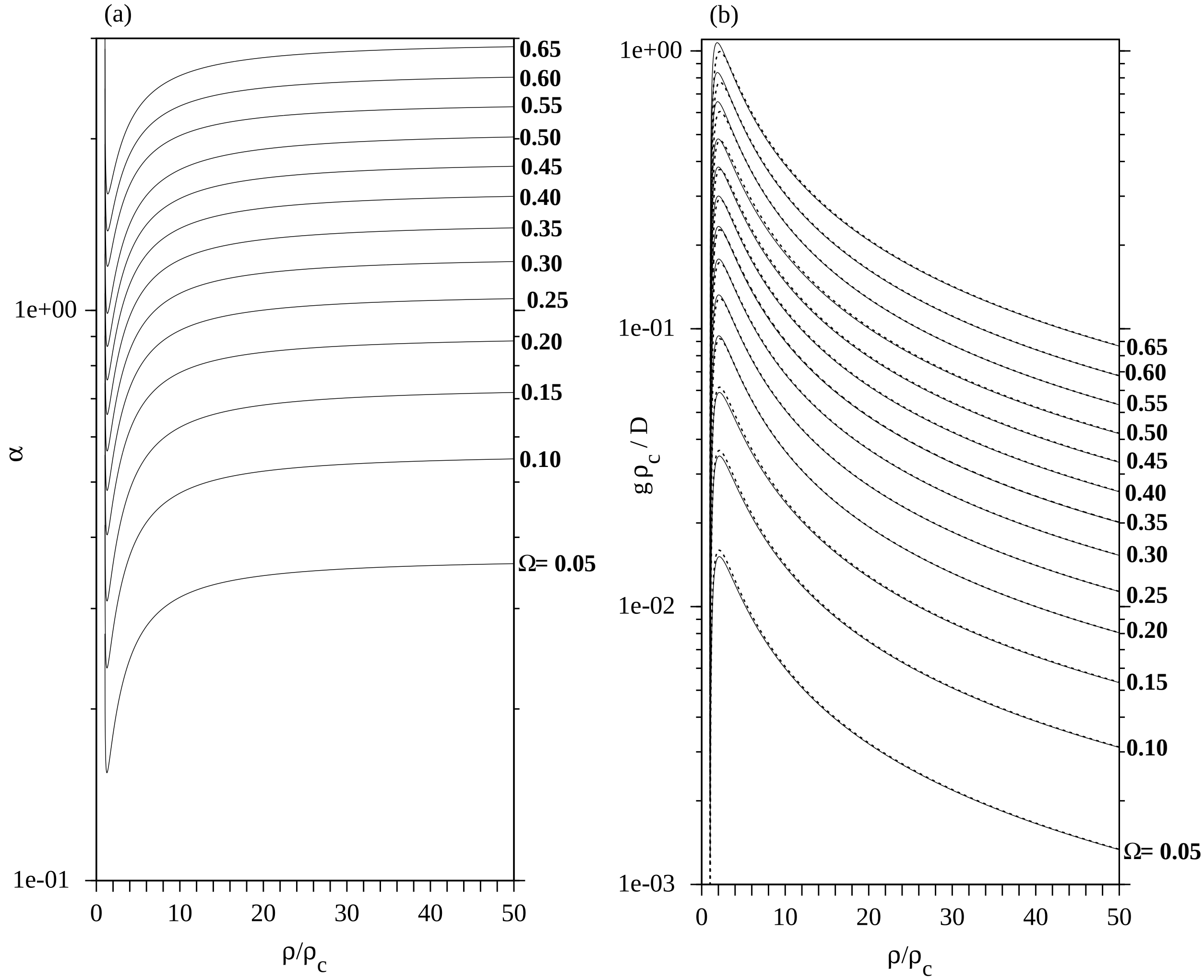

Fig. 2 *Finite difference solution for* (a) α *and* (b) g. *The dotted lines represent calculations using the analytical solution.*

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