

Theory for growth of spherical precipitates with capillarity effects

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Analytical solutions are presented for the growth of spherical precipitates incorporating the effect of interface curvature on local equilibrium at the interface, and the behaviour of the solution is examined. MST/4628

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Introduction

Steels used in the energy industries are strengthened by precipitation. There is usually a combination of many types of particle with a variety of shapes, ranging from needles to plates to spheres. Many of the precipitates approximate to a spherical shape. Although attempts have been made to estimate the kinetics of spherical particle precipitation in power plant steels,^{1,2} there is no analytical solution for the growth of a sphere with capillarity included, since for spheres the radius of curvature also defines the size of the particle.^{3–5} The Gibbs–Thomson capillarity effect is due to the curvature of the interface, which influences the equilibrium compositions at the particle/matrix boundary. A consequence is that small particles will grow less rapidly than large particles even when the far field concentration is identical for all particles. Some quite elegant work by Miyazaki and co-workers^{6,7} has shown experimentally that the capillarity effect is seminal in the development of precipitation reactions in composition gradients.

Thus, although Zener⁸ recognised the importance of capillarity, and even though capillarity features strongly in the theories for the growth of needles and plates,^{9,10} the authors are not aware of any corresponding theory for spherical precipitates; the aim of this work was to develop the necessary theory.

Analysis

For spherical particles, Fick's second law can be written in the spherical coordinate system as†

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

where c is the concentration gradient around the particle, D is the diffusion coefficient, assumed to be independent of concentration, t is time, and r is the radial coordinate. Since $c = c\{t, r\}$,

$$c\{0, r\} = \bar{c} \quad (2)$$

$$c\{t, \rho\} = c^{\beta\gamma} + \frac{2c^{\beta\gamma}\Gamma}{\rho} \quad (3)$$

where \bar{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), and Γ is the capillarity constant given by⁴

$$\Gamma = \left(\frac{\sigma v^\gamma}{kT} \right) \left(\frac{1 - c^{\beta\gamma}}{c^{\beta\gamma} - c^{\beta\beta}} \right) \quad (4)$$

†Braces are used throughout to indicate the argument of a function. Thus, $(\partial/\partial t)\{(1/r^2)(\partial c/\partial r)\}$ means that the partial derivative is evaluated at $(1/r^2)(\partial c/\partial t)$.

where σ is the surface energy per unit area, v^γ is the volume per atom in the precipitate phase γ , k is Boltzmann's constant, T is the temperature, and $c^{\beta\beta}$ is the solute concentration of the precipitate (γ) in equilibrium with β .

The boundary condition of equation (2) indicates that, as the precipitation starts at $t=0$, the concentration everywhere will be equal to the average concentration of the alloy; equation (3), which has been defined in analogy to capillarity corrected concentrations of needle and plate shaped precipitates^{9–11} accounts for the concentration change as the particle approaches to a critical radius ρ_c which can be expressed as

$$\rho_c = \frac{2c^{\beta\gamma}\Gamma}{\bar{c} - c^{\beta\gamma}} \quad (5)$$

As the particle radius approaches the critical radius $\rho = \rho_c$, the concentration in the matrix at the boundary tends towards the average concentration so that growth becomes impossible.⁴ This is shown schematically in Fig. 1, where Fig. 1a represents the flat interface condition, Fig. 1b represents $\rho = 2\rho_c$, and Fig. 1c represents $\rho = \rho_c$.

Following Zener,⁴ it can be shown that ρ varies with time parabolically according to the equation

$$\rho = \alpha(Dt)^{1/2} \quad (6)$$

where α is a dimensionless growth parameter. The concentration $c\{t, r\}$ that satisfies equation (1) and the boundary conditions given by equations (2) and (3) is then

$$c\{t, r\} = \bar{c} + \left[\left(c^{\beta\gamma} + \frac{2c^{\beta\gamma}\Gamma}{\rho} \right) - \bar{c} \right] \frac{\phi\{r/(Dt)^{1/2}\}}{\phi\{\alpha\}} \quad (7)$$

where

$$\phi\{\alpha\} = \frac{1}{\alpha} \exp\left\{-\frac{\alpha^2}{4}\right\} - \frac{\pi^{1/2}}{2} \operatorname{erfc}\left\{\frac{\alpha}{2}\right\} \quad (8)$$

where erfc is the error function.

The rate at which solute is incorporated into the growing precipitate must equal that arriving by diffusion to the interface. Therefore

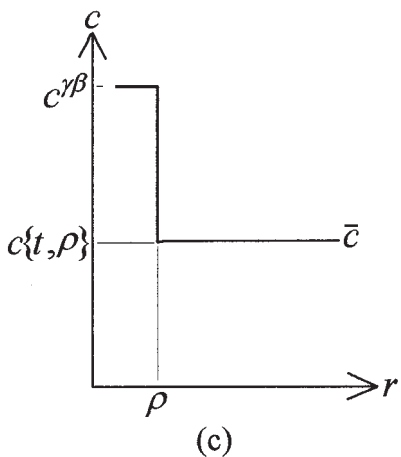
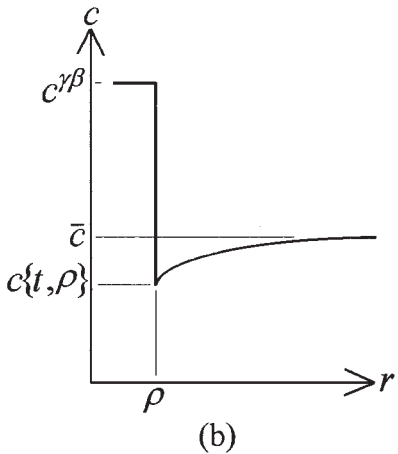
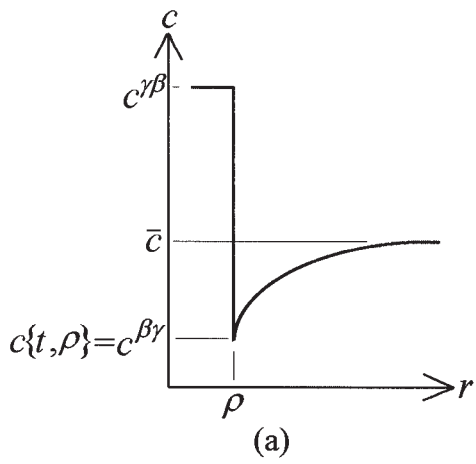
$$g \left[c^{\beta\gamma} - \left(c^{\beta\gamma} + \frac{2c^{\beta\gamma}\Gamma}{\rho} \right) \right] = D \frac{\partial c}{\partial r} \Big|_{r=\rho} \quad (9)$$

where $g = \partial\rho/\partial t$ is the particle growth rate. The concentration gradient given by equation (7) can now be substituted in equation (9), from which an expression for α can be obtained. After some algebra, the following equation is obtained

$$f \left[1 - \Omega \frac{\rho_c}{\rho} \right] = \Omega - \Omega \frac{\rho_c}{\rho} \quad (10)$$

where f is a complex function of α given by

$$f = \frac{1}{2} \alpha^3 \exp\left\{\frac{1}{4} \alpha^2\right\} \phi\{\alpha\}$$



a flat interface; b curved interface, $\rho = 2\rho_c$; c curved interface, $\rho = \rho_c$

1 Schematic representation of concentration gradient illustrating effect of capillarity

and the dimensionless supersaturation is

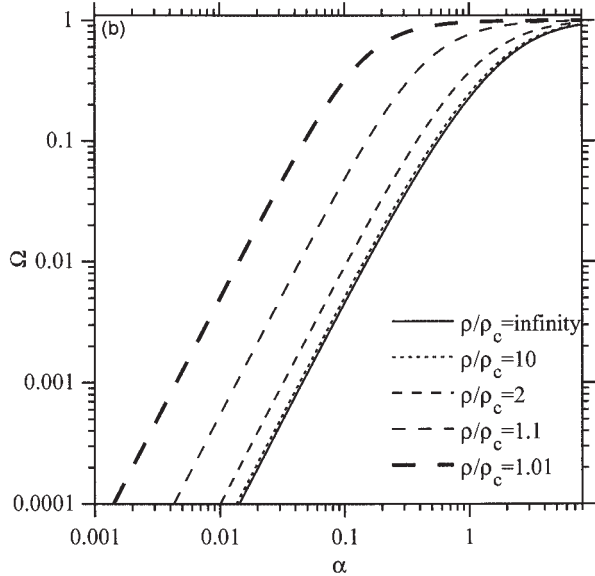
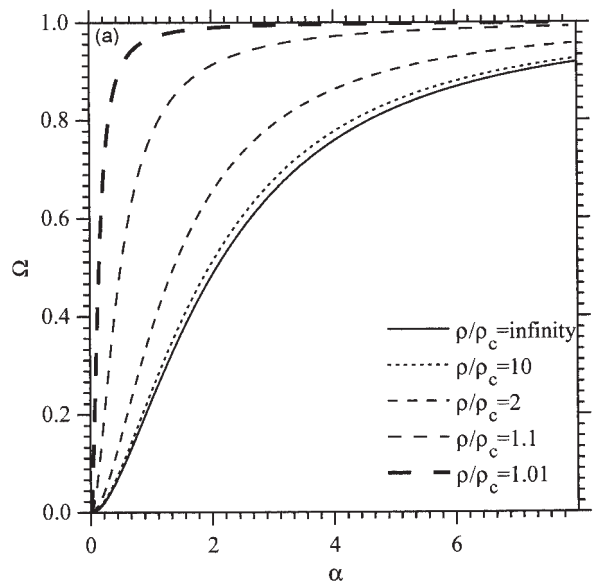
$$\Omega = \frac{\bar{c} - c^{\beta\gamma}}{c^{\gamma\beta} - c^{\beta\gamma}}$$

Provided that the phase diagram is known, equation (10) is now a function of α only, which can be expressed as

$$\Omega = \frac{f}{1 + [(\rho_c/\rho)(f - 1)]} \dots \dots \dots (11)$$

which can be solved numerically as shown in Fig. 2a and b for large and small growth parameters, respectively.

Approximately spherical particles precipitate at small values of supersaturation in many alloys, such as secondary



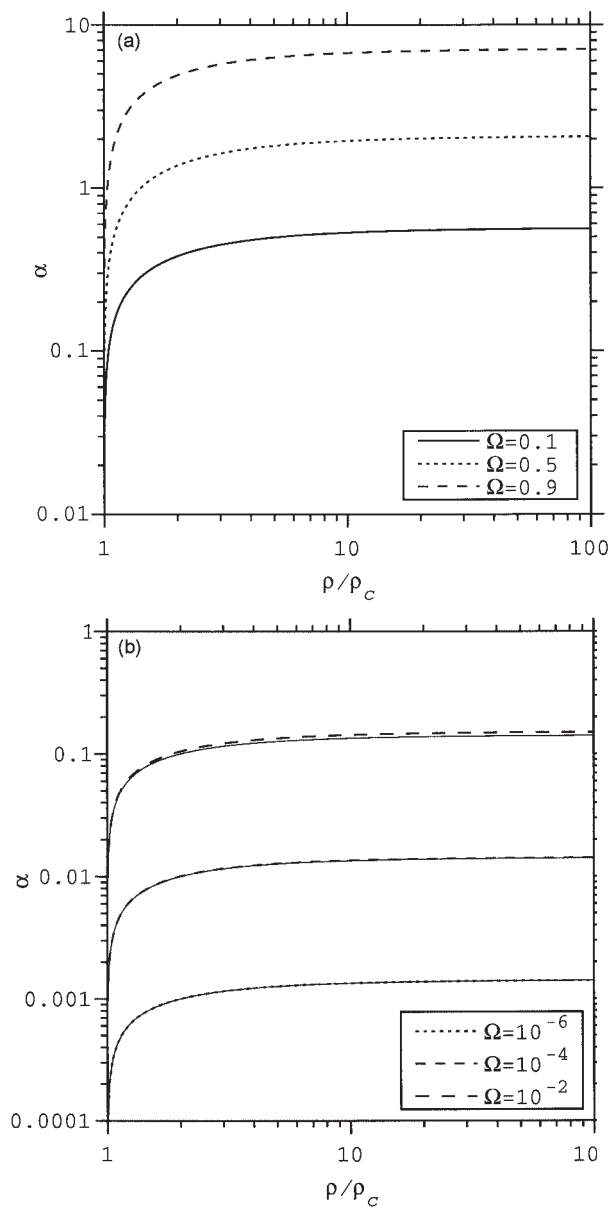
2 Effect of supersaturation Ω and normalised radius ρ/ρ_c on growth parameter α : in b emphasis is on small values of Ω

hardened steels.^{1,2} It is desirable therefore to obtain a simple asymptotic relationship for equation (11) with $\Omega \ll 1$. Figure 2b shows that $\alpha \rightarrow 0$ as $\Omega \rightarrow 0$. Using the Taylor series expansion of $\exp\{(1/2)\alpha^2\}$ around zero, and expanding $\text{erfc}\{(1/2)\alpha^2\}$ as $\alpha \rightarrow 0$,¹² it can be seen that $f\{\alpha\} \approx (1/2)\alpha^2$. Thus

$$\alpha = \left(\frac{2\Omega[1 - (\rho_c/\rho)]}{1 - \Omega(\rho_c/\rho)} \right)^{1/2} \quad \text{for } \Omega \ll 1 \dots \dots \dots (12)$$

In order to assess the effect of particle radius on growth rate, the value of α against the tip radius for given values of Ω is plotted in Fig. 3a and b at large and small supersaturations respectively. The solid lines adjacent to each dotted line in Fig. 3b represent the values calculated using equation (12) for the respective supersaturation.

The capillarity correction on the parabolic growth parameter α is shown in Fig. 2. It can be seen that for small values of ρ/ρ_c , there are differences of up to an order of magnitude when compared with a model without the correction. When $\rho \gg \rho_c$, equation (11) reduces to Zener's equation as expressed by Coates.^{13,14}



3 Variation of growth parameter α with normalised particle radius ρ/ρ_c for *a* large and *b* small values of supersaturation Ω

Summary

Equations taking into account the capillarity effect have been derived for the growth of spherical precipitates. The results obtained using this model are significantly different from the corresponding theory without capillarity at low values of supersaturation. A simple asymptotical expression for the growth rate parameter has been obtained for small values of supersaturation ($\Omega \leq 0.01$).

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