

A numerical model for the dissolution of spherical particles in binary alloys under mixed mode control

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Abstract

A general numerical model is described for the dissolution kinetics of spherical particles in binary systems for any combination of first order reactions at the particle–matrix interface and long distance diffusion within the matrix. The model is applicable to both finite and infinite media and handles both complete and partial particle dissolution. It is shown that interfacial reactions can have a strong effect on the dissolution kinetics, the solute concentration at the particle–matrix interface and the solute concentration profile in the matrix.

Keywords: Binary alloys; Numerical model; Particle–matrix interface

1. Introduction

Heat treatment of metals is often necessary to optimise their mechanical properties both for further processing and for final use. During the heat treatment the metallurgical state of the material changes. This change can either involve the phases being present or the morphology of the various phases. Whereas the equilibrium phases often can be predicted quite accurately from thermodynamic models, there are no general models for microstructural changes nor general models for the kinetics of these changes. In the latter cases both the initial morphology and the transformation mechanisms have to be specified explicitly. One of these processes, which is both of large industrial and scientific interest and amenable to modelling, is the dissolution of second phase particles in a matrix with a uniform initial composition.

To describe this particle dissolution in rigid media several physical models have been developed, incorporating the effects of long-distance diffusion [1–3] and non-equilibrium conditions at the interface [4,5]. The long-distance diffusion models imply that the processes at the interface between particle and matrix proceed infinitely fast. Therefore, these models provide an upper

boundary for the dissolution rate.

Whelan [1] considered particles dissolving in an infinite medium using the stationary interface approximation. He derived an analytical solution of the diffusion equation in an infinite medium for spherical co-ordinates by the use of the Laplace-transformation in time. The accuracy of the model increases with increasing interparticle distance, i.e. with increasing cell size.

Baty, Tanzilli and Heckel [2] were the first authors to apply a numerical method using a finite difference method to evaluate the interface position as a function of dissolution time. Their model is also applicable to situations in which the interparticle distance is small, i.e. when soft impingement occurs. Their model was based on the assumption of local equilibrium at all stages of the dissolution process. They applied their numerical analysis to dissolving Al_2Cu -particles in aluminium. The poor fit with the experimental data is probably due to the interface reactions, which were not incorporated into their numerical model.

Tundal and Ryum [3] considered the effects of a finite cell size as well. They too applied a numerical method using a finite difference to predict the dissolution kinetics. Their model was based on the assumption of local equilibrium during the entire dissolution process. They introduced a lognormal distribution for both the particle and cell size and showed that macroscopic dissolution rates depend strongly on the shape of the

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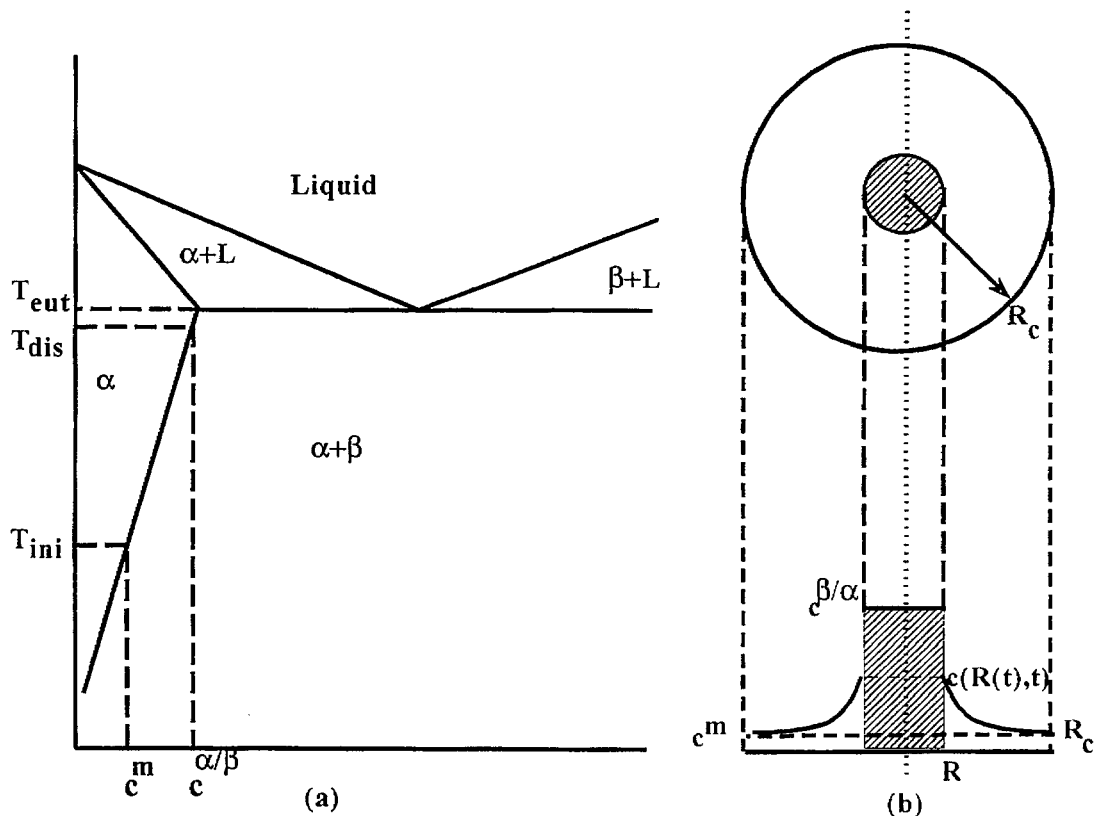


Fig. 1. A schematic binary phase diagram for system A–B (a) and a spherical particle in a spherical cell (b).

particle size distribution curve and possible interactions between the neighbouring cells.

Nolfi's model [4] did not include the interface migration, but as far as is known it is the first model which incorporated non-equilibrium conditions at the interface. In the Nolfi model non-equilibrium conditions at the interface were incorporated by the introduction of a Robin-condition, which relates the concentration gradient at the interface with the concentration at the interface. This semi-analytical solution consists of an infinite series solution for the concentration profile. Their method, however, is only accurate in the early stages of the dissolution process.

Aaron and Kotler [5] incorporated the non-equilibrium conditions at the interface too. However their approach is only applicable for those situations in which the interparticle distance is sufficiently large, i.e. the diffusion fields do not impinge. They transformed the Robin problem of Nolfi into a Dirichlet problem, in which the interface concentration is fixed at all stages of the dissolution process. Combining Whelan's [1] analytical approach for the interface velocity as a function of the annealing time with a relation between the interface concentration and the interface position, they evaluated the interface position using a zeropoint iteration method. Aaron and Kotler also incorporated the effects of the particle curvature into their model using the

Gibbs–Thomson equation [5]. In their model both the interface position and the interface concentration were taken momentarily stationary during the evaluation of the interface position as a function of time.

The present model attempts to combine in a mathematically rigid manner the effects of both the finite cell size in which the particle can dissolve and the finite rate of interfacial processes on the dissolution kinetics of spherical particles. As the effect of the particle curvature on the total dissolution time was shown to be small [5], except for very small starting particles, this effect is ignored in our model. Furthermore, as this work concentrates on the effects of processes occurring at or near the particle–matrix interface, interactions between neighbouring cells are excluded.

2. The model

The model treats a binary system with limited solubility of B-atoms in the α phase (see Fig. 1(a)). For compositions corresponding to the two phase region at the starting temperature T_{ini} , the material with average composition c^0 is assumed to consist of equally sized spherical β -phase particles of uniform and constant composition $c^{\beta/\alpha}$ and radius R_0 , in a uniform matrix consisting of an α phase of composition c^m . Upon

raising the temperature to the homogenisation temperature T_{dis} the solubility of B in α increases provided T_{dis} is lower than the eutectic temperature T_{eut} and the particle starts to dissolve. The solubility at the homogenisation temperature is denoted as $c^{\alpha/\beta}$. Assuming a uniform spatial distribution of particles the average interparticle distance L can be used to calculate the radius of the equivalent spherical cell in which the particle dissolves:

$$R_c = \left(\frac{3}{4\pi}\right)^{1/3} L \quad (1)$$

Assuming that the total number of B-atoms in each equivalent cell is constant, net transfer of B-atoms between the cells can be excluded. This implies:

$$\frac{\partial c(R_c, t)}{\partial r} = 0 \quad (2)$$

In this model particle dissolution is assumed to proceed by the following sequential mechanisms: (i) decomposition of the β -phase compound; (ii) crossing of alloying elements through the interface between the β -phase particle and the α -matrix; and (iii) diffusion of the alloying element inside the solvent matrix (see Fig. 2). Each of these mechanisms consumes time. The slowest mechanism controls the rate of the entire process. The combination of the first two mechanisms is referred to as the interface reactions or interface controlled mechanisms. If during the whole dissolution process the first two mechanisms proceed sufficiently fast with respect to the long-distance diffusion, then the concentration of the solute at the interface will be maximal and equal to the solid solubility. Therefore, long-distance diffusion controlled dissolution implies local equilibrium at the interface. However, during the initial stages of the dissolution process the concentration at the interface between α - and β -phase is not

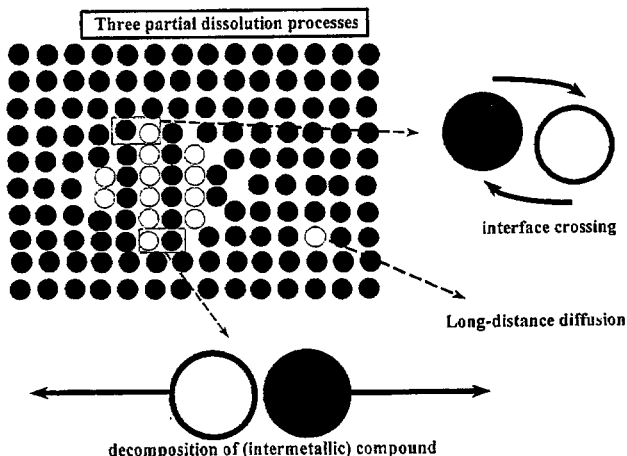


Fig. 2. A schematic overview of the steps that determine particle dissolution.

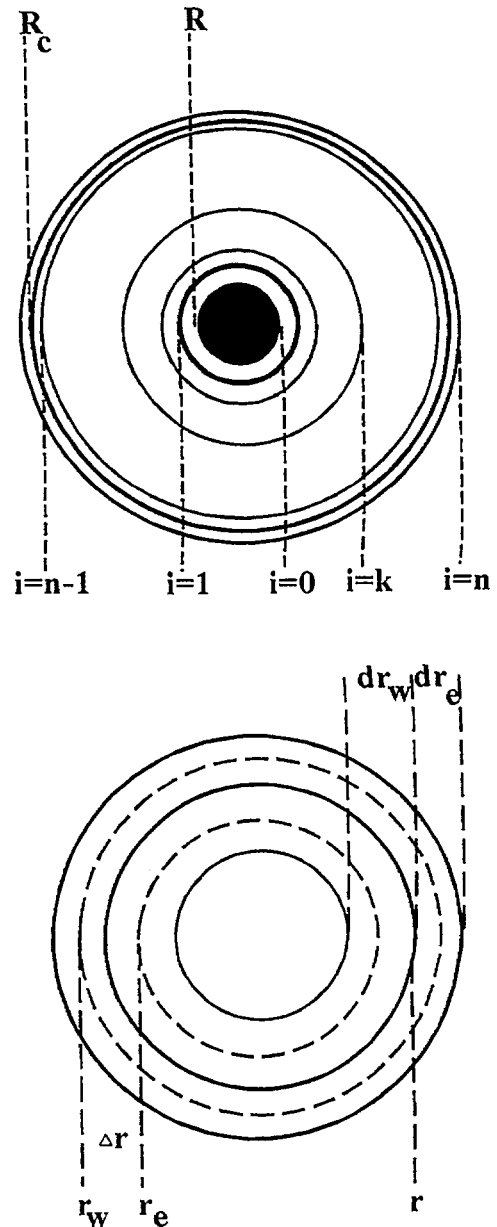


Fig. 3. The grid which has been used to solve the spherical diffusion equation with appropriate boundary conditions and moving interface.

likely to change like a step function when the material is up-quenched. The more complex the compound of which the particle consists and the higher the diffusion coefficient of B in α is, the more likely the interface reactions are to contribute to the total dissolution rate.

To incorporate the effects of the interface reactions as well, the number of B-atoms that flow out of the particle into the A-rich phase, $dN(t)/dt$ is assumed to be finite and to depend on $c(R(t), t) - c^{\alpha/\beta}$ where $R(t)$ is the particle radius at time t . Generally, each of the potential functions describing $dN(t)/dt$, can be written as an infinite series:

$$\frac{dN(t)}{dt} = 4\pi R^2(t) \sum_{n=0}^{\infty} K_n(t)(c(R(t), t) - c^{\alpha/\beta})^n \quad (3)$$

It is of little use to apply this whole infinite series since the coefficients of this series are unknown and therefore it would complicate the mathematical approach of the problem needlessly. To obtain a useful boundary condition at the interface, a first order reaction at the interface has been assumed. This assumption, which has also been made by Nolfi et al. [4], leads to:

$$\frac{dN(t)}{dt} = 4\pi R^2(t) K_1(t)(c(R(t), t) - c^{\alpha/\beta}) \quad (4)$$

The parameter $K_1(t)$ can be regarded as an atomic transfer coefficient of the interface. Equalling the flux of atoms out of the particle to the flux of atoms into the A-rich matrix, the following boundary condition at the interface is obtained:

$$K(c(R(t), t) - c^{\alpha/\beta}) = D \left(\frac{\partial c(r, t)}{\partial r} \right)_{r=R(t)} \quad (5)$$

With $K \equiv (M_\alpha/\rho_\alpha)K_1$, M_α and ρ_α respectively are the averaged molar mass in kilograms and density of phase α in kg m^{-3} . D is the diffusion coefficient of B in A in $\text{m}^2 \text{s}^{-1}$. The parameter K in m s^{-1} is a measure of the rate of the interface reactions relative to the rate of long-distance diffusion in the alloy. So with increasing values of K , the interface reactions proceed more rapidly relative to long-distance diffusion and long-distance diffusion controls the rate of dissolution to a larger extent. For the case that local equilibrium at the interface exists ($c(R(t), t) = c^{\alpha/\beta}$), the parameter K has to be infinite to have a non-zero mass flow.

During dissolution B-atoms migrate away from the interface. No diffusion inside the particle is assumed. Application of Fick's Second Law for a spherical geometry with axial symmetry yields:

$$\frac{\partial c(r, t)}{\partial t} = D \left[\frac{\partial^2 c(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial c(r, t)}{\partial r} \right], \quad \forall R < r < R_c, \quad \forall t \geq 0 \quad (6)$$

The diffusion coefficient is taken to be independent of composition. The initial boundary value problem, stated by Eqs. (2), (5) and (6) has a solution, if and only if $c(r, t)$ has at least continuous derivatives up to the second derivative with respect to r , at the interval $R < r < R_c$ and up to the first derivative with respect to t for all $t > 0$. Moreover, it can be proven that the solution of Eq. (6) is unique [6]. As the number of B-atoms in the cell is constant, it can be derived that:

$$\frac{dR(t)}{dt} = \frac{D}{\left(\frac{\rho_\beta}{M_\beta} c^{\beta/\alpha} - \frac{\rho_\alpha}{M_\alpha} c(R(t), t) \right) M_\alpha} \left(\frac{\partial c(r, t)}{\partial r} \right)_{r=R(t)}, \quad \forall t \geq 0 \quad (7)$$

in which ρ_α and ρ_β are the averaged densities of phases α and β and M_α and M_β are the averaged molar masses of phases α and β .

From Eq. (7) it follows that the value of $\partial c(R, t)/\partial r$ determines the value of $dR(t)/dt$. Apparently, the amount of B-atoms present in the immediate vicinity of the dissolving particle governs the rate of the interface velocity $dR(t)/dt$. The initial boundary value problem combined with Eq. (7) falls into the class of Stefan problems with a free boundary [7].

3. The numerical treatment

The mathematical problem is to solve an initial boundary value problem in which the position of one of the boundaries moves as a function of time. Formally this means that when evaluating the particle radius at each time step during the iteration process, a new initial boundary value problem has to be solved, in which the initial condition is given by the concentration profile at the last iteration. The stationary interface approach uses the initial concentration profile as the last iteration during the whole iteration process, whereas the numerical approach indeed uses the concentration profile as a subsequent initial condition for the evaluation of the concentration at the next time step. To relax the stationary interface approximation a finite difference method has been used. A finite difference method is secure since the concentration profile in the α phase is continuous at least up to the second derivative to position and the first derivative of time. The grid that has been used has been shown in Fig. 3. The grid is

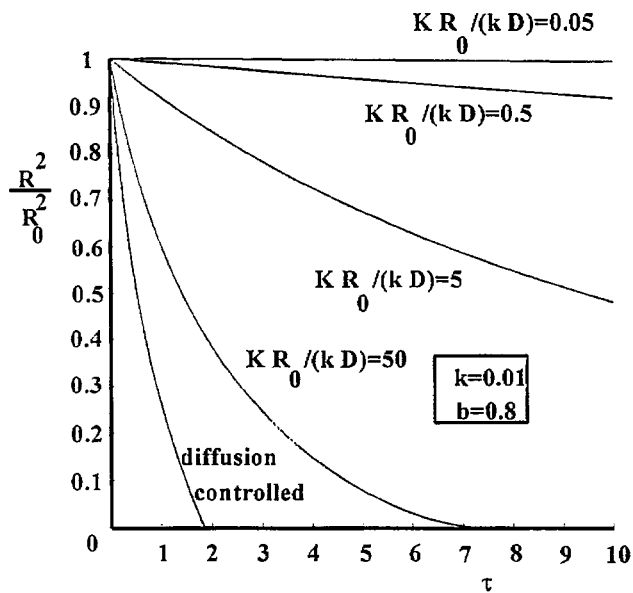


Fig. 4. Values of $(R/R_0)^2$ as a function of the normalised time τ with $k = 0.01$ and $b = 0.8$ for several values of the reaction rate parameter $KR_0/(kD)$.

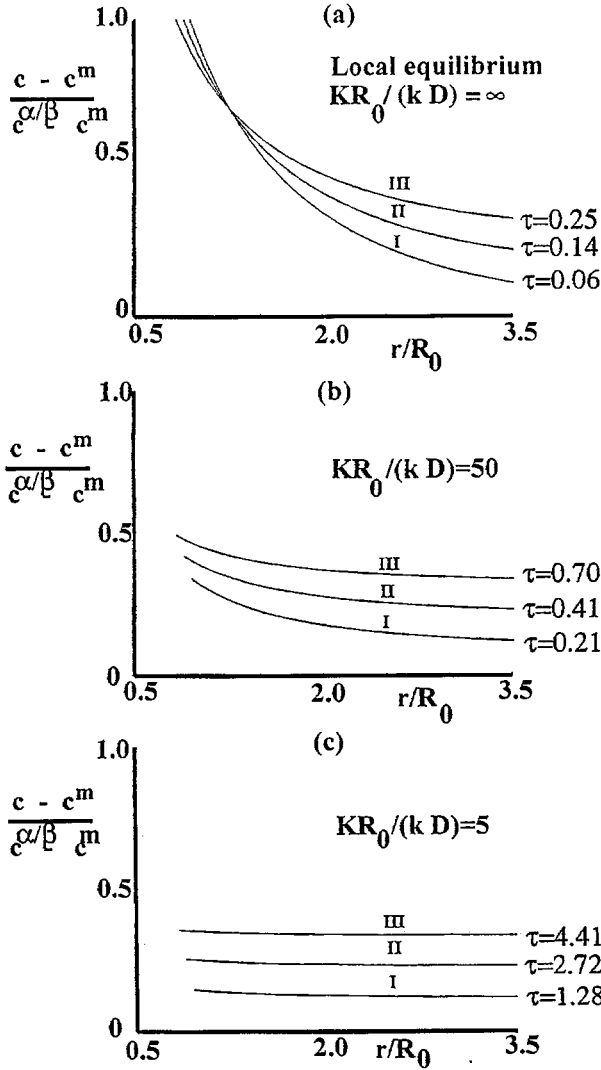


Fig. 5. Subsequent concentration profiles for $KR_0/(kD) = \infty$ (a), $KR_0/(kD) = 50$ (b) and $KR_0/(kD) = 5.0$ (c) for $k = 0.01$ and $b = 0.8$. Curves I, II and III respectively are for $(R^2/R_0^2) = 0.9$, $(R^2/R_0^2) = 0.8$ and $(R^2/R_0^2) = 0.7$. The parameter τ indicates the normalised dissolution time required to reach that particular R/R_0 ratio. $R/R_0 = 1$ at $\tau = 0$.

adjusted after each iteration such that the zeroth grid-surface coincides with the position of the interface (see Fig. 3). This has been done for the following reasons: (i) the interface can be used as a gridpoint, which can be used in the boundary condition at the interface (see Eq. (4)); and (ii) the grid is enlarged after each iteration. One could argue that the error becomes larger due to the larger gridspacing. This is not true, since errors smooth out with iteration time, in other words the errors become smaller after some iterations. To reduce the inaccuracy the integral mass balance is used to determine the interface position at each iteration. This integral mass balance is given by:

$$\frac{4\pi}{3} R(t)^3 \frac{\rho_\beta}{M_\beta} c^{\beta/\alpha} + \frac{\rho_\alpha}{M_\alpha} 4\pi \int_{R(t)}^R r^2 c(r, t) dr = \frac{4\pi}{3} R_c^3 \frac{\rho_\alpha}{M_\alpha} c^0 \quad (8)$$

Discretisation of Eq. (6) for the α phase, taking the movement of the grid-surfaces into account, yields:

$$a_p(i)c_i^{j+1} - a_w(i)c_{i-1}^{j+1} - a_e(i)c_{i+1}^{j+1} = a_p^0 c_i^j \quad (9)$$

i and j represent the indices of position and time respectively. Here an implicit difference scheme has been used to guarantee numerical stability. The coefficients $a_p(i)$, $a_w(i)$, $a_e(i)$ and a_p^0 are defined as follows:

$$a_p^0 = \frac{1}{D\Delta t}$$

$$a_w(i) = \frac{r_w^2}{r^2 \Delta r} \frac{dr_w}{dr} - \left(\frac{N-i}{N-1} \right) \frac{dR^j}{dt} \frac{1}{2D\Delta r}$$

$$a_e(i) = \frac{r_E^2}{r^2 \Delta r} \frac{dr_E}{dr} + \left(\frac{N-i}{N-1} \right) \frac{dR^j}{dt} \frac{1}{2D\Delta r}$$

$$a_p(i) = a_p^0 + a_w(i) + a_e(i), \quad \forall i \in \{1, 2, 3, \dots, N-1\} \quad (10)$$

The parameters r , r_w , r_E , Δr , dr_w and dr_E are defined in Fig. (4). At the particle/matrix interface the boundary condition can be discretised as follows:

$$K(c(R^j) - c^{\alpha/\beta}) = D \frac{c_1^j - c(R^j)}{\Delta r^j} \quad (11)$$

The discretisation at the cell boundary is given by:

$$\frac{c_n^j - c_{n-1}^j}{\Delta r^j} = 0 \quad (12)$$

As errors smooth out as the calculations proceed, the time step is enlarged during each iteration. The concentration profile and the interface position are determined

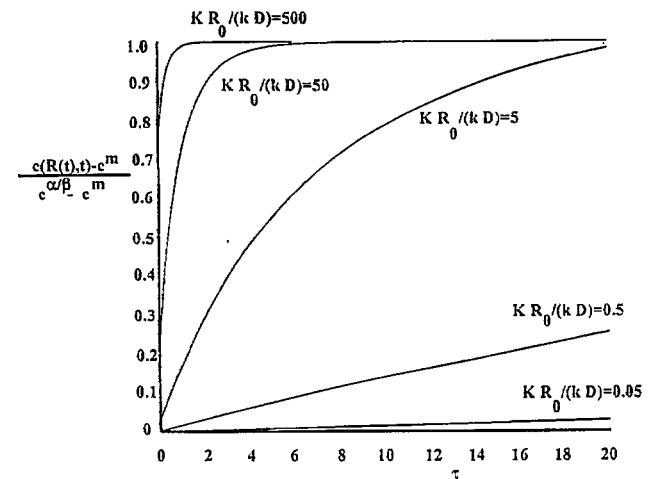


Fig. 6. The interface concentration as a function of the normalised time for $b = 2$ and $k = 0.25$ for different values of the reaction rate parameter K .

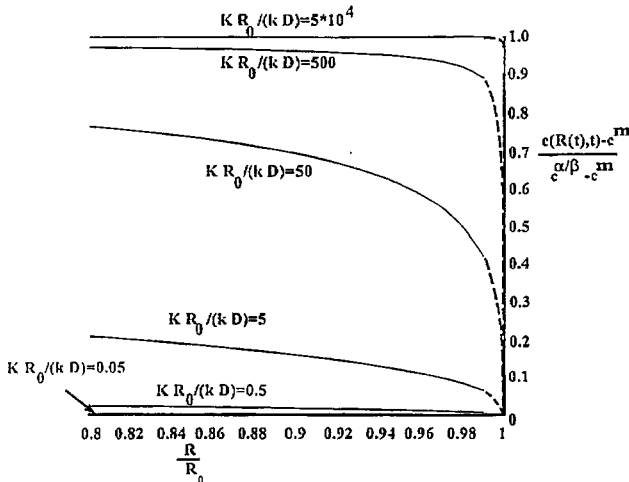


Fig. 7. The normalised interface concentration as a function of the normalised particle radius.

during each iteration. After the determination of the interface position the grid spacing is determined such that the first grid point is fixed on the interface during the whole calculation. This procedure is repeated until the particle has dissolved either completely ($c^0 < c^{\alpha/\beta}$) or partially ($c^0 > c^{\alpha/\beta}$).

4. Results and discussion

To observe the influence of the interface reactions on the total dissolution behaviour, the dissolution rate of a spherical particle has been calculated for a number of K values using otherwise identical starting conditions. To describe the starting conditions in general manner, the following dimensionless parameters have been introduced:

$$k = \frac{c^{\alpha/\beta} - c^m}{c^{\beta/\alpha} - c^{\alpha/\beta}} \text{ and } b = \frac{c^0 - c^m}{c^{\alpha/\beta} - c^m} \quad (13)$$

The parameters k and b represent a normalised concentrational difference in the vicinity of the interface and the degree of supersaturation respectively. Together these parameters fully define the normalised system. The parameter b is used to distinguish the cases in which a particle can dissolve either completely ($b < 1$) or partially ($b > 1$). The normalised particle area $R^2(t)/R_0^2$ is plotted in Fig. 4 as a function of the normalised time $\tau = 2kDt/R_0^2$ for different values of K for the starting conditions $k = 0.01$ and $b = 0.8$. From Eqs. (5) and (7) and using the chain rule for differentiation, it can be shown that the quantity $d(R/R_0)/d\tau$ is proportional to the dimensionless parameter $KR_0/(kD)$. Therefore, this normalisation factor has been used in the figures describing the influence of the reaction rate parameter K . These various curves correspond to differ-

ent rate-controlling dissolution processes. As can be seen from Fig. 4 the lower the value of K , in other words the more rate-controlling the interface reactions are, the slower dissolution proceeds. This reduction in dissolution kinetics is due to the extra time which is needed for the B-atoms to leave the particle (decomposition of chemical bonds and interface crossing). The interface reactions cause a lower absolute value of the concentration gradient in the vicinity of the interface. Note that the slopes of the normalised dissolution curves in Fig. 4 at the start of the dissolution process depend on K . For particles consisting of chemical compounds (for instance particles consisting of Al_2Cu in aluminium alloys) interface reactions are more likely to be rate-controlling than for the simple systems in which the precipitates consist of one element only.

To characterise the influence of the interface reactions on the shape of the concentration profile, the concentration profiles have been calculated for three different values of K , namely $K = \infty$ and $KR_0/(kD) = 50$ and 5.0 , using the same starting conditions ($k = 0.01$, $b = 0.8$). In Fig. 5 the calculated normalised concentration profiles are plotted versus the normalised position r/R_0 for three fixed normalised dissolution times. To highlight the differences in the evolution of the concentration profiles for different values of the reaction rate parameter, K , only the most relevant part ($0.5 < r/R_0 < 3.5$) of the concentration profiles is plotted (as $(R_0/R_c)^3 = bk/(k+1)$, the situation in Fig. 5 corresponds to $R_c/R_0 = 5.02$). When local equilibrium at the interface is maintained at all stages of the dissolution process (i.e. $K = \infty$), the profiles at subsequent times have to intersect. This is because $\partial c(R_c, t)/\partial r = 0$ and $\partial^2 c(R_c, t)/\partial r^2 > 0$, the concentration at the cell edge increases with time (see Eq. (6)) while at the interface $c(R(t), t) \equiv c^{\alpha/\beta}$, and the interface is moving in the negative direction during the whole dissolution process (see Fig. 5(a)). This means that $c(R(t-dt), t) < c(R(t-dt), t-dt) = c^{\alpha/\beta}$ and $c(R_c, t) > c(R_c, t-dt)$. Using the Intermediate Value Theorem of Weierstrass [8] for this continuous function, it is clear that there must be at least one intersection. Due to the monotonous decrease of the concentration as a function of the distance from the particle/matrix interface, it is clear that the intersection point for two subsequent concentration profiles is unique (see Fig. 5(a)). For interface controlled particle dissolution the interface concentration increases with time while the position of the interface moves towards the negative direction. This means that for interface controlled dissolution $c(R(t-dt), t) < c(R(t-dt), t-dt)$ does not have to hold a priori. However, at the cell boundary the same boundary conditions ($\partial c(R_c, t)/\partial r = 0$ and $\partial^2 c(R_c, t)/\partial r^2 > 0$) still apply. This implies that for subsequent times the concentration profiles do not intersect in all cases (see Fig. 5(b) and (c)).

To quantify the influence of the interface reactions on the value of the interface concentration, the interface concentration has been plotted as a function of the normalised time. At the start of the dissolution process the interface concentration increases towards the equilibrium concentration $c^{a/\beta}$ (see Fig. 6) for finite K values. Here, only the situation that the particle dissolves partially has been considered (starting conditions $k = 0.25$ and $b = 2.0$), since the interface concentration then has to increase up to the equilibrium concentration. This has been done for various values of the parameter K . It is clear that the time it takes for the interface concentration to reach the equilibrium concentration strongly increases with decreasing K . In this case dissolution is delayed considerably by the interface reactions.

Finally, the normalised interface concentration has been plotted in Fig. 7 as a function of the normalised particle radius for different values of $KR_0/(kD)$ but for the same starting conditions $k = 0.25$ and $b = 2.0$. While the particle dissolution proceeds the interface concentration increases towards the solid solubility and the particle radius decreases towards the final and minimal particle diameter.

5. Conclusions

It has been shown that interface reactions can significantly affect the dissolution kinetics for spherical parti-

cles in a uniform matrix of finite dimensions. These interface reactions also control the interface concentration and the concentration profiles. These parameters can be predicted quantitatively by the numerical model for dissolution under mixed mode control presented here.

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