A numerical analysis for the dissolution of second phase particles in ternary alloys
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Abstract

To predict the kinetics of the dissolution of binary second-phase particles in ternary alloys one needs detailed models to compute the displacement of the parent-product interface. To compute this displacement the diffusion equation for both alloying elements has to be solved. The boundary conditions at the parent-product interface are linked via an approximately hyperbolic relationship obtained from thermodynamic phase diagrams. The fluxes of the elements out of the particle are linked to maintain the stoichiometry of the particle during the entire dissolution process. The present work concerns an analysis of the influence of the physical parameters in the dissolution kinetics. The numerical method is applicable to the dissolution of a sphere, cylinder, flat plate and a spherical segregation layer around a spherical grain.

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 alloy 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.
Mathematically particle dissolution in aluminium alloys is considered as a diffusion problem with a moving boundary: i.e. a Stefan problem. To obtain a one-dimensional Stefan problem the alloy is divided into cells in which a particle dissolves. At the cell edge no mass transport is assumed, resulting in a Neumann boundary condition. Particle dissolution is assumed to proceed sequentially by the decomposition of the (intermetallic) compound, the crossing of the interface and long-range diffusion by the solute atoms. For those cases in which diffusion is very sluggish relative to the proceeding steps, a Dirichlet boundary condition results due to a rapid accumulation of the alloying atoms at the interface. In this case, diffusion determines the rate of particle dissolution.

To describe particle dissolution in solid media several models for binary alloys have been developed, incorporating the effects of long-distance diffusion. A finite element model has been developed to describe the dissolution of second phases with an angular geometry in binary alloys. These articles did not cover the technologically important dissolution of stoichiometric multicomponent particles in ternary alloys. The dissolution of such spherical and planar stoichiometric particles has been studied by Ågren and Vitek. Reiso has investigated the dissolution of Mg2Si spherical particles in a very dilute aluminium alloy. The effects of soft impingement were neglected in this work.

In this paper first the mathematical problem to be solved is posed, then the solution algorithm is described. The coupled Stefan problems are solved using a one-dimensional finite difference method. Finally, some examples of the application of the algorithm are shown.

2 A mathematical model for dissolution in a ternary alloy

Consider a binary second phase particle, consisting of two chemical elements, surrounded by a homogeneous matrix in a ternary alloy at a given temperature. The initial concentration in the matrix of alloying element p is \( c_p^0 \) and the concentration of alloying element p in the particle is denoted as \( c_p^b \). When the temperature is increased dissolution sets in.

Outside the dissolving phase diffusion the concentration of alloying element p at distance r from the cell centre at time t, \( c_p(r,t) \), satisfies the one-dimensional diffusion equation (\( a=0 \) for planar geometry, \( a=1 \) for cylindrical geometry, \( a=2 \) for spherical geometry):

\[
\frac{\partial c_p(r,t)}{\partial t} = D_p \frac{\partial}{\partial r} \left[ r^a \frac{\partial c_p(r,t)}{\partial r} \right] \quad \forall (r,t) \in \left\{ S(t), R_e \right\} \times (0, \infty)
\]  

(1)

where \( D_p \) denotes the diffusion coefficient of the alloying element through the matrix. \( S(t) \) and \( R_e \) respectively correspond to the interface and the outer boundary. No flux of both alloying elements is assumed through \( R_e \).
\[ \frac{\partial c_p(R_t, t)}{\partial r} = 0 \quad \forall t \in (0, \infty) \]  

(2)

If only diffusion in the matrix determines the rate of dissolution, it follows from thermodynamic considerations\(^{12}\) that, corresponding to a particle stoichiometry \(B_nC_m\), the concentrations of both alloying elements at the moving boundary, \(c_p^i\) \((p \in \{1, 2\})\), are coupled by:

\[ \left( c_1^i(t) \right)^n \left( c_2^i(t) \right)^n = K(T) \quad \forall t \in (0, \infty) \]  

(3)

The interface between the second phase and surrounding matrix, \(S(t)\), moves due to the balance of atoms of alloying element \(p\) at the interface. This yields for the case that the second phase remains stoichiometric the following two relations for the interfacial movement and interfacial gradients:

\[ \frac{dS(t)}{dt} = \frac{D_1}{c_1^p - c_1^i} \frac{\partial c_1(r \downarrow S(t), t)}{\partial r} = \frac{D_2}{c_2^p - c_2^i} \frac{\partial c_2(r \downarrow S(t), t)}{\partial r}, \forall t \in (0, \infty) \]  

(4)

The above set of equations, eqs. (1–4), is a Stefan problem which consists of two diffusion problems with a coupled Dirichlet and Neumann condition at the moving boundary. We thus have to find two concentration profiles \(c_p\) such that eqs. (1–4) are met at all times. More about the background of this model can be found in \(^{13}\).

### 3 Numerical solution of the Stefan problem

Various numerical methods for solving Stefan problems are known. Crank \(^{13}\) distinguishes roughly three types of methods: front-tracking, front fixing and fixed-domain methods. In this work a front tracking method is applied.

The algorithm is summarised as follows: The interfacial concentration of one alloying element, say \(c_1^i\), is chosen as starting value in a smart way. The interfacial concentration of the other alloying element, \(c_2^i\), is obtained from eq. (3). Using these two Dirichlet boundary conditions at the moving boundary, the diffusion equations for both alloying elements, eq. (1), are solved. If the calculated concentration profiles do not satisfy eq. (5), then a different starting value for \(c_1^i\) is determined to repeat the iteration.

First the procedure for choosing the interfacial concentration at the first time step will be outlined. Subsequently the used finite difference method to determine the concentration profile is presented. Finally the iteration procedure to obtain a couple of Dirichlet conditions at each time step is described.
3.1 The interfacial concentrations at the initial time step

For a fast convergence of the iteration scheme, the choice of the interfacial concentrations at the initial stage of dissolution is based on the analysis of Reiso\textsuperscript{11} for the dissolution of a Mg$_3$Si phase in an aluminium matrix. This analysis is applicable to spherical and planar second phases dissolving in an infinite aluminium matrix.

For a spherical phase dissolving in an infinite matrix, it can be derived for each alloying element:\textsuperscript{1}

$$\frac{dS(t)}{dt} = \frac{c_{x,1}^{t} - c_{p,1}^{\text{n}}}{c_{p,1}^{b} - c_{p,1}^{t}} \left( \frac{D}{S(t)} + \sqrt{\frac{D}{\pi}} \right)$$

(5)

Combining eqs. (4,5), yields at the early stages, i.e. for $t \ll 0$, the following equation to be solved to determine the interfacial concentrations at the initial stage of the dissolution process:

$$\frac{c_{1}^{t} - c_{1}^{\text{n}}}{c_{1}^{b} - c_{1}^{t}} = \frac{D_{1}}{D_{1}} \sqrt{K(T)(c_{1}^{t})^{n} - c_{2}^{n}}$$

$$m, n \neq 0$$

(6)

The interfacial concentration of the second element, $c_{2}^{t}$, is then obtained from eq. (3).

3.2 The numerical solution of the one-dimensional diffusion equation

A finite difference discretisation is easily applicable since the concentration profile in the matrix is continuous at least up to the second derivative to position and the first derivative of time. The mesh, describing the matrix, is adjusted after each iteration such that the zeroth mesh surface coincides with the interfacial position, roughly following the procedure of Murray-Landis\textsuperscript{14}. This has been done for the following reasons: 1. The interface can be used as a mesh surface, which can be used in the boundary condition at the interface. 2. The mesh expands as dissolution proceeds. As the error smooths out with iteration time and the absolute value of the concentration gradients decreases with iteration time it is then, for reasons of computation time, beneficial to have a coarser mesh.

The numerical procedure is based on a mass balance in each mesh surface. This is to avoid the occurrence of singularities for curved surfaces as the particle size tends to zero or at the grain centre when describing the dissolution of a spherical segregation layer. For reasons of accuracy a virtual gridpoint has been used behind the interfacial position and behind the cell edge or the grain centre. The introduction of the virtual gridpoints guarantees an overall accuracy of $O(dx^2)$, also at the boundaries. To avoid instability as much as possible, an
implicit discretisation scheme has been chosen. The term resulting from the
convective derivative has been taken explicitly for accuracy. The system of
linear equations can be arranged into a matrix equation, which can be solved
using a three diagonal pivoting algorithm. A more elaborate description of the
discretisation equations is given in13.

3.3 The determination of the interfacial concentrations of both elements

The solid solubilities of both alloying elements are linked by isothermal
intersections of ternary phase diagrams, their relationship can considered as
approximately hyperbolic, i.e. by Eq. 3. This must hold at the same time as Eq.
5. As the concentration profiles of both alloying elements depend on the
interfacial concentrations, the concentration gradients of the elements also
depend on the interfacial concentration. Hence, we are faced with the following
non-linear problem:

\[
f(c_i') = \frac{D_i}{D_i} \frac{c_i^{'} - c_i'(c_i')} \left[ \nabla c_i \cdot n \right]_{s(t)} - 1 = 0
\]

(7)

From the combination of the initial boundary value problems and the
relationship between both interfacial conditions for both elements it is clear that
both \( \nabla c_1 \) and \( \nabla c_2 \) depend on the interfacial concentration \( c_i' \). So the problem
has been reduced to obtaining a root for the above function \( f \). Figure 1 displays
\( f \) as a function of \( c_i' \) for the first iteration. This case corresponds to \( c_i' = 33\% \),
\( D_1/D_i = 5 \), \( D_i = 2.15 \times 10^{-13} \text{ m}^2/\text{s} \), \( S(t=0) = 10^{-6} \text{ m} \), \( K(T) = 0.35 \), \( c_i'' = 0.06 \), \( c_i'' = 0.025 \) and a particle stoichiometry of \( B_2C_2 \). Nor any
discontinuities, nor any singularities are to be expected for this function. Setting
\( c_i' \) very large, minimises \( c_i' \), maximises \( \nabla c_1 \cdot n \) and sets \( \nabla c_2 \cdot n \) very negative, then
\( f > 0 \), for the case of setting \( c_i' \) such that \( \nabla c_1 \cdot n \) is sufficiently small, it follows \( f < 0 \). For this continuous real function follows that at least one root exists. To
solve the above equation, a “discrete Newton Raphson” iteration scheme is
proposed and described in the remainder of this section.
For the subsequent iteration time steps the interfacial concentrations from the last iteration are used. These initial guesses that are put into the iteration process, guarantee a fast iteration process. As the function $f$ can only be evaluated at discrete values of $c_i^t$, the function is evaluated at $c_i^t - \varepsilon$, $c_i^t$ and $c_i^t + \varepsilon$, for $\varepsilon > 0$, obtaining the following iteration scheme, with an accuracy for the differentiation of $f$ with respect to $c_i^t$ of $O(\varepsilon^2)$:

\begin{equation}
\begin{aligned}
c_i^t(n+1) &= c_i^t(n) - \frac{2\varepsilon f(c_i^t(n))}{f(c_i^t(n)+\varepsilon)-f(c_i^t(n)-\varepsilon)} \\
\end{aligned}
\end{equation}

In which the concentration profiles of both elements have to be evaluated at each iteration step, $n$, until $|c_i^t(n+1) - c_i^t(n)| < \varepsilon$, corresponding to $|f(c_i^t(n+1)) - f(c_i^t(n))| < \delta(\varepsilon) = \frac{f(c_i^t(n)+\varepsilon) - f(c_i^t(n)-\varepsilon)}{2}$.

$\varepsilon$ is a measure for the accuracy for $c_i^t$, the accuracy of the interfacial concentrations and $\delta(\varepsilon)$ is a measure for the deviation of $f$ from zero, which depends on $\varepsilon$. From a numerical point of view it is important to note that $\varepsilon$ has to be sufficiently small but beyond the accuracy of the numerical scheme to evaluate the concentration. In most cases the above iteration scheme converged within 4 iteration steps.
Once the root of eq. 7 has been determined, the position of the moving boundary at the next time step is determined by:

\[
S(t + dt) = S(t) + \frac{1}{2} dt \sum_{p=1}^{\tilde{p}} \left( \frac{D_p}{c_p} \frac{c_{p,i} - c_{p,i-1}}{2\Delta r} \right)
\]  

(9)

This iteration is repeated until the particle dissolved.

4 Numerical experiments

To illustrate the applicability of the model, some calculations have been carried out for the case of stoichiometric spherical second phase MgSi and MgX in a ternary aluminium alloy. The diffusion coefficients \( D_H \) and \( D_{Mg} \), taken from Fujikawa\(^6\) and Yamane\(^7\) for a temperature of 793K, were 2.15 \( \times \) 10\(^{-13}\) m\(^2\)/s and 3.24 \( \times \) 10\(^{-13}\) m\(^2\)/s respectively. Furthermore, the initial particle radius, the cell radius, initial matrix concentrations have respectively been taken 1 \( \times \) 10\(^{-6}\) m, 8 \( \times \) 10\(^{-6}\) m, 0\%, 0\%. For \( K(T) \) the value of 0.35 has been used. As the calculation concerns a MgX particle \( c_{Mg} = 66.7\% \).

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Figure 2: Two numerical experiments: a comparison between the dissolution of a precipitate in a binary and ternary alloy. x represents either the normalised interfacial velocity or the normalised interfacial position (a). A sketch of the interfacial concentrations as a function of time (b). Curves are explained in the text.
Curve I and II in Figure 2a correspond to the interfacial velocity and position for the case of dissolution of a spherical Mg₂Si-phase in aluminium respectively. It can be seen that the interfacial velocity decreases at the first stages of the dissolution process due to the decrease of the absolute values of the concentration profiles. At the final stages of dissolution, the interfacial area has become so small that the interfacial velocity has to be large to fulfil the Stefan condition (see eq. 4). Curves III and IV represent the interfacial velocity and position for the case that $D_x=5 \cdot D_{Si}$. For the case that $D_x=10 \cdot D_{Si}$ the results are given by curves V and VI. It can be seen from Figure 2a that the addition of a second alloying element can influence the dissolution process strongly.

Figure 2b represents the interfacial concentration of both alloying elements as a function of time. Curves I and II correspond to the interfacial concentrations of Mg and Si respectively. For the case that $D_x=5 \cdot D_{Si}$ the interfacial concentrations of Mg and X are presented by curves III and IV. Curves V and VI correspond to the interfacial concentrations of Mg and X for the case that $D_x=10 \cdot D_{Si}$. The difference in the behaviour of the starting values of the interfacial concentrations results by $D_{Si} < D_{Mg} < 5 \cdot D_{Si}$. A more detailed numerical analysis in which the stoichiometry, cell size and diffusion coefficient has been varied can be found in 15.

The next numerical experiment considers the influence of the geometry of the dissolving Mg₂Si phase in a ternary aluminium alloy, see Figure 3.

Figure 3: The free boundary position as a function of time corresponding to different geometries of a Mg₂Si-second phase in Aluminium. Curves are explained in the text.
Curves I, II and III correspond to the dissolution of a spherical, cylindrical and planar second phase respectively. Curve IV corresponds to the dissolution of a layer of segregation at the boundary of a hypothetical spherical grain. All curves have been calculated for T=793K and initial matrix concentrations of Si and Mg respectively 0.06 and 0.025%. For the initial particle radius (curve I and II), the initial half thickness of infinite plate (curve III) and the initial thickness of the segregation layer (curve IV) a value of 1 μm has been taken. The values of the cell sizes are given in table 1.

<table>
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<th>Table 1: The cell sizes for the different geometries.</th>
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<tr>
<td>Curve I</td>
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The dissolution of a spherical segregation layer may serve as a first order approximation for the dissolution of segregations at the grain boundary. In the case of a spherical or a cylindrical second phase the area of the moving boundary decreases as dissolution proceeds, therefore dissolution may be enhanced if the concentration gradients are large enough. However, for the case of a dissolving spherical segregation layer, the area of the moving boundary increases as dissolution proceeds, causing a delay of the dissolution process.

5 Conclusions

A mathematical model has been developed suitable for the dissolution of a stoichiometric phase in a ternary alloy. A discrete variant of the Newton-Raphson zero-point iteration method determines the right concentrations at the Dirichlet boundary very accurately and quickly. It is shown that the value of the diffusion coefficient of the second alloying element can influence the overall dissolution kinetics severely. It is also shown that the dissolution time of a binary second phase depends strongly on its geometry due to the evolution differences in the interfacial area to particle volume ratio during dissolution.

References

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