A SUITE OF SHARP INTERFACE MODELS FOR SOLID-STATE TRANSFORMATIONS IN ALLOYS

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Abstract.   *A suite of mathematical models for solid-state phase transformations in solid-state alloys is presented. The work deals in particular with dissolution and growth of particles in solid-state alloys. Several models are presented and numerical solution procedures are summarized briefly. Further, some analytic solutions are considered shortly, which are useful to validate the numerical solutions. One model, which incorporates surface energy effects is presented in more detail. From this model it is observed that the surface energy prevents the occurrence of fingering during growth.*

1 INTRODUCTION

1.1 Technological background

In the thermal processing of both ferrous and non-ferrous alloys, homogenization of the existing microstructure by annealing at such a high temperature that unwanted precipitates are fully dissolved, is required to obtain a microstructure suited to undergo heavy plastic deformation as well as providing an optimal starting condition for a subsequent precipitation hardening treatment. Such a homogenization treatment is for example applied prior to hot-rolling of Al killed construction steels, HSLA steels, all engineering steels, as well as in processing aluminium extrusion alloys. Although precipitate dissolution is not the only metallurgical process taking place during homogenization, it is often the most critical of the processes occurring. The minimum temperature at which the annealing should take place can be determined from thermodynamic analysis of the phases present. However, the minimum annealing time at this temperature is not a constant but depends on particle size, particle geometry, particle concentration, overall composition etc. To make the homogenization treatment more efficient, it is highly desirable to have robust physical models for the kinetics of particle dissolution as a function of thermodynamics

and thermokinetics data as well as particle morphology and microstructural dimensions. Using such models the minimum annealing times and optimum heating strategics can be calculated a priori, rather than be determined experimentally, and at great cost.

Apart from their technological relevance, accurate physical models for particle dissolution are, due to the complexity of the processes, also of great scientific and mathematical interest in themselves.

1.2 Existing models for particle dissolution

To describe particle dissolution several older mathematical models have been developed, which incorporate long-range diffusion [1, 2, 3] and non-equilibrium conditions at the interface [4, 5]. In general, the dissolution of particles proceeds via decomposition of the chemical compound, the crossing of the atoms of the interface and long-range diffusion in the matrix. The first two processes are referred to as the interfacial processes. The long-range diffusion models are based on the assumption that the interfacial processes are infinitely fast. Hence, these models provide an upper boundary for the dissolution kinetics.

The first models were based on analytical solutions for the interfacial position as a function of time (see for instance Whelan [1] and Crank [6]). However, in these solutions the volume in which dissolution takes place is infinite. As far as we know, Baty, Tanzilli and Heckel were the first authors in the metallurgical community to applied a Finite Difference Model [2] where the volume is bounded. Tundal and Ryum [3] also applied a Finite Difference Model in which a lognormal particle size distribution is included. They showed that the macroscopic dissolution rates depend strongly on the particle size and possible interactions between subsequent particles. Nolfi's [4] model was, as far as known, the first model in which non-equilibrium conditions at the particle-matrix interface were included. However, the interface migration was not included. The non-equilibrium condition is modelled by a Robin-condition at the interface. Their solution is in terms of a Fourier series. Aaron and Kotler [5] combine Whelan's solution with the incorporation of the Gibbs-Thomson effect to deal with the influence of curvature on the interface motion. Further, they transform the Robin-boundary condition of Nolfi's model into a Dirichlet boundary condition. Recently, Svoboda *et al.* [7] analyzed the kinetics of diffusional transformations where mechanical and chemical forces exerted on interfaces between subsequent phases are incorporated. Their approach is based on thermodynamical concepts that can be found in Hillert [8]. They obtain a thermodynamically based procedure to predict non-equilibrium interface kinetics by using both analytical and numerical techniques.

However, all these mentioned models did not consider the technologically important dissolution of multi-component particles in multi-component alloys. As far as we know Ågren *et al.* [9] was the first to extend the models to multi-component alloys. His formalism was based on a thermodynamic treatment of diffusion in terms of chemical potentials and an interface motion from a material balance. The numerical methods that

were used by Ågren were improved by Crusius *et al.* [10] and the diffusion model was improved in [11], which forms the backbone of the software-package DICTRA suitable for dissolution and growth problems with one spatial dimension. The thermodynamic relation, which defined the boundary conditions at the moving interface, was simplified to a hyperbolic relationship. This has been done for iron-based alloys by Vitek *et al.* [12] and Hubert [13]. Furthermore, Reiso *et al.* [14] investigated the dissolution of Mg_2Si alloys in aluminium alloys by the use of the same principles.

The above mentioned authors viewed particle dissolution as a Stefan problem: a diffusion equation with a sharp moving interface. A recent approach is the phase-field approach, which is derived from a minimization of the energy functional and based on a diffuse interface between the consecutive phases. This approach has, among others, been used by Kobayashi *et al.* [15] and Burman *et al.* [16] to simulate dendritic growth. An extension to multi-component phase-field computation is done by Grafe *et al.* [17], where solidification and solid-state transformation is modelled. For the one-dimensional case they obtain a perfect agreement between the phase-field approach and the software package DICTRA, which is based on a sharp interface between the consecutive phases. Furthermore, some recent comparison studies of phase-field methods with a Stefan problem, solved by a moving mesh method or a level-set method or a mesh-free method, were done by Javierre *et al.* [18] and Kovacevic and Sarler [20] respectively. Some disadvantages of the phase-field approach are that (1) no simple quick estimation of the solution is available, and that (2) physically justifiable parameters in the energy functional are not easy to obtain. Generally those parameters are to be obtained from fitting procedures that link experiment, thermodynamic data-bases and numerical computation. An other disadvantage of the phase-field method is the requirement of a fine grid resolution in the diffuse interface region in order to have agreement with the solution of the 'sharp interface problem'. This poses a severe time-step criterion and hence time consuming computations. This was observed by Burman *et al.* [16] and Javierre *et al.* [18]. Therefore, we limit ourselves here to viewing particle dissolution as a (vector) Stefan problem. We remark that Thornton *et al.* [21] wrote a nice review paper on simulating diffusional phase transformations using several physical model approaches as the updated thermodynamic methods by Ågren, used in the package DICTRA, and the diffuse interface phase-field and (Allen)-Cahn-(Hilliard) approach. Thornton *et al.* [21] also describe several two-dimensional applications of phase coarsening with Ostwald Ripening using the diffuse interface approach. The present paper will focus on the computational aspects of solving Stefan problems with a sharp interface applied to particle dissolution in (multi-component) alloys. For a review on the solution of Stefan problems in multi-component alloys, we refer to [28]. Furthermore, some mathematical issues will be summarized.

Although much work on the mathematical modeling of dissolution of particles had been done, some major limitations remained (until recently):

1. No fast and efficient numerical method for the simultaneous dissolution of a particle and a segregation at the grain boundary was available. Furthermore, no quick

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and well motivated self-similar solution for the dissolution of particles in multi-component has been reported.

2. Some particles may be disk-shaped, hence a two-dimensional model is necessary to compute the dissolution of the particle. With the classical literature of Finite Elements the computation of the interface movement with a sharp angle within the boundary is impossible. Furthermore, the case where two particles dissolve in one cell needs to be discussed.

3. No numerical model, be it 2D or quasi 3D, that treats the interface movement while the interfacial reactions take place exists.

4. Metallurgical experiments on alloys indicate that dissolving particles or phases may break up into smaller particles or phases in some circumstances. No metallurgically sound model in three spatial dimensions, based on the sharp interface approach, exists to deal with these topological changes.

These limitations where lifted in a suite of mathematical models of increasing complexity. This paper presents a coherent total picture of the basic concepts and equations in these models and illustrates their potential.

Furthermore, an experimental validation of the above mentioned models can be found in [22] and [23]. In the first paper the activation energy for particle dissolution has been analyzed. In the second paper the experimental validation was carried out using DSC-measurements. New work concerns the analysis of particle dissolution where cross-diffusion aspects and a relaxation of thermodynamic equilibrium, are incorporated. Further, the level-set method and moving grid method are analyzed as candidates to model particle growth. In this paper we only consider the moving grid method in more detail in which the application concerns the growth of a particle under the influence of surface energy effects.

1.3 Organization of the paper

The current paper does not aim at being mathematically rigorous but merely aims at being descriptive about the implications of the developed mathematics of these more complex models. First we formulate the mathematical models for particle dissolution in Section 2. Here a one-dimensional multi-component model and two-dimensional model is formulated. Section 2 ends with a brief description of the mathematical implications of the models. Section 3 starts with available self-similar solutions for the one-dimensional (multi-component) models. Next, the numerical methods to solve the one- and two-dimensional models are described. Section 5 deals with applications of the models particle growth influenced by surface energy effects. Finally, some concluding remarks about the work are given and ongoing research is indicated.

2 MODELS

We consider a particle of β phase surrounded by a diffusive phase α of either uniform or nonuniform composition. The boundary between the adjacent phases is referred to as the interface. The metal is divided into representative cells in which a single particle of phase β dissolves in an α phase. Particle dissolution is assumed to proceed via the following consecutive steps: decomposition of the chemical bonds in the dissolving phase, crossing of the interface by the atoms and finally long-distance diffusion in the diffusive phase. In the present paper we assume that the rate of the dissolution process is determined by the last step, *e.g.* at the interface between the adjacent phase we have local equilibrium. Hence the interface concentration are those as predicted by thermodynamics.

In this section, the model for a binary alloy and a multi-component alloy are presented consecutively.

2.1 The model for a binary alloy

We denote the interface, consisting of a point, curve or a surface for respectively a one-, two- or three-dimensional domain of computation by $S = S(t)$. The fixed boundaries of the domain of computation are denoted by Γ. Further, the domain of computation is split into the diffusive part (the α-diffusive phase), denoted by Ω and the β-particle Ω_p. The distribution of the alloying element is determined by diffusion in the diffusive phase Ω, which gives

$$\frac{\partial c}{\partial t} = D\Delta c = D \text{ div grad } c, \text{ for } \mathbf{x} \in \Omega(t) \text{ and } t > 0. \tag{1}$$

Here D represents the diffusion coefficient and $\mathbf{x}$ denotes the spatial position within the domain of computation. In the present study we treat D as a constant. Within the particle the concentration is equal to a given constant, hence

$$c = c^{part}, \text{ for } \mathbf{x} \in \Omega_p(t) \text{ and } t \geq 0. \tag{2}$$

On the interface, $S(t)$, we have local equilibrium, i.e. the concentration is as predicted by the thermodynamic phase diagram, i.e.

$$c = c^{sol}, \text{ for } \mathbf{x} \in S(t) \text{ and } t > 0. \tag{3}$$

Further, at a boundary not being the moving interface, Γ, we have no flux of atoms, i.e.

$$D\frac{\partial c}{\partial n} = 0, \text{ for } \mathbf{x} \in \Gamma(t) \text{ and } t > 0. \tag{4}$$

In the above equation $\dfrac{\partial c}{\partial n}$ denotes the outward normal derivative of c on the fixed boundary Γ. From a local mass balance, the equation of motion of the interface can be derived, this equation is commonly referred to as the Stefan condition, and is given by:

$$(c^{part} - c^{sol})v_n = D\frac{\partial c}{\partial n}, \text{ for } \mathbf{x} \in S(t) \text{ and } t > 0. \tag{5}$$

Here v_n denotes the normal component of the interface velocity outward from Ω. The problem is completed with the initial concentration c^0 and the initial position of the interface $S(0)$. The problem, consisting of equations (1), (2), (3), (4) and (5) is referred to as a Stefan problem for particle dissolution or particle growth. For the case of growth of particles, the Gibbs-Thomson effect is important in the early stages of growth after nucleation. The earliest-stage phenomenon of nucleation differs totally from the present Stefan problem. Models for nucleation are commonly based on Monte-Carlo simulations or on evolution of the statistical particle size distribution (see for instance the work of Myhr and Grong [30], where a hyperbolic partial differential equation is solved for the probability density of the particle size). Therefore, we do not consider nucleation in the present study. Future studies will be devoted to the Gibbs-Thomson effect. For now, we refer to Mullins and Sekerka who show that spherical particles can only preserve their spherical shape during growth if the Gibbs-Thomson effect is included (i.e. the *Mullins-Sekerka instability* [31], [32]). We will only show some preliminary finite element results in the present paper, which confirm this behavior numerically.

2.2 The model for a multi component alloy

We consider a particle of a multi-component β phase surrounded by a 'matrix' of phase α, of either uniform or non-uniform composition. The boundary between the β-particle and α-matrix is referred to as the interface. The metal is divided into representative cells in which a single particle of phase β dissolves in an α-matrix. Particle dissolution is assumed to proceed by a number of subsequent steps [4, 33]: decomposition of the chemical bonds in the particle, crossing of the interface by atoms from the particle and long-distance diffusion in the α-phase. In the models of thermodynamic equilibrium, we assume in this section that the first two mechanisms proceed sufficiently fast with respect to long-distance diffusion and do not affect the dissolution kinetics. Hence, the interfacial concentrations are those as predicted by thermodynamics (local equilibrium). Later this assumption is dropped. In [34] we considered the dissolution of a stoichiometric particle in a ternary alloy. The hyperbolic relationship between the interfacial concentrations for ternary alloys is derived using a three-dimensional Gibbs space. For the case that the particle consists of n chemical elements apart from the atoms that form the bulk of the β-phase, a generalization to a n-dimensional Gibbs hyperspace has to be made. The Gibbs surfaces become hypersurfaces. We expect that similar consequences apply and that hence the hyperbolic relation between the interfacial concentrations remains valid for the general stoichiometric particle in a multi-component alloy. We denote the chemical species by Sp_i, $i \in \{1, ..., n+1\}$. We denote the stoichiometry of the particle by $(Sp_1)_{m_1}(Sp_2)_{m_2}(Sp_3)_{m_3}(...)(Sp_n)_{m_n}$. The numbers $m_1, m_2, ...$ are stoichiometric constants. We denote the interfacial concentration of species i by c_i^{sol} and we use the following hyperbolic relationship for the interfacial concentrations:

$$f(c_1^{sol}, c_2^{sol}, \ldots, c_n^{sol}) = (c_1^{sol})^{m_1}(c_2^{sol})^{m_2}(...)(c_n^{sol})^{m_n} - K_{sol} = 0, \qquad K_{sol} = K_{sol}(T). \quad (6)$$

The factor K_{sol} is referred to as the solubility product. It depends on temperature T according to an Arrhenius relationship. In principle, the model can handle any form of temperature dependence for the solubility product.

We denote the position of the moving interface between the β-particle and α-phase by $S(t)$. Consider a one-dimensional domain, i.e. there is one spatial variable, which extends from 0 up to M. Since particles dissolve simultaneously in the metal, the concentration profiles between consecutive particles may interact and hence soft-impingement occurs. This motivates the introduction of finitely sized cells over whose boundary there is no flux. For cases of low overall concentrations in the alloy, the cell size M may be large and the solution resembles the case where M is infinite. The latter case can be treated easily with (semi) explicit expressions. The spatial co-ordinate is denoted by r, $0 \leq S(t) \leq r \leq M$. The α-matrix where diffusion takes place is given by $\Omega(t) := \{r \in \mathbb{R} : 0 \leq S(t) \leq r \leq M\}$. The β-particle is represented by the domain $0 \leq r < S(t)$. Hence for each alloying element, we have for $r \in \Omega(t)$ and $t > 0$ (where t denotes time)

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{n} D_{ij} \Delta c_j, \ \text{for } i \in \{1, ..., n\}. \tag{7}$$

Here D_{ij} and c_i respectively denote the (cross-)diffusion coefficients and the concentration of the species i in the α-rich phase. If $D_{ij} < 0$ for some $i \neq j$, then, the transport of element i is delayed by the presence of element j. For $D_{ij} > 0$, the opposite holds. Experiments with Differential Scanning Calorimetry by Chen *et al.* [23] for Al-Si-Mg alloys indicate that disregarding cross-diffusion terms gives a good approximation. However, for some other alloys the full diffusion matrix should be taken into account. A physical motivation of the above partial differential equation is given by Kirkaldy and Young [35]. The geometry is planar, cylindrical and spherical for respectively $a = 0, 1$ and 2. Let c_i^0 denote the initial concentration of each element in the α phase, i.e. we take as initial conditions (IC) for $r \in \Omega(0)$

$$(IC) \begin{cases} c_i(.,0) = c_i^0(.) \text{ for } i \in \{1, ..., n\} \\ \\ S(0) = S_0. \end{cases}$$

At a boundary not being an interface, i.e. at Γ or when $S(t) = 0$, we assume no flux through it, i.e.

$$\frac{\partial c_i}{\partial n} = 0, \ \text{for } i \in \{1, ..., n\}. \tag{8}$$

Furthermore at the moving interface $S(t)$ we have the 'Dirichlet boundary condition' c_i^{sol} for each alloying element. The concentration of element i in the particle is denoted by c_i^{part}, this concentration is fixed at all stages. This assumption follows from the constraint that the stoichiometry of the particle is maintained during dissolution in line with Reiso *et al.* [14]. The dissolution rate (interfacial velocity) is obtained from a mass-balance.

Summarized, we obtain at the interface for $t > 0$ and $i, j \in \{1, ..., n\}$:

$$\left.\begin{aligned} c_i &= c_i^{sol} \text{ for } \mathbf{x} \in \mathbf{S(t)}, \\ v_n &= \sum_{j=1}^{n} \frac{D_{ij}}{c_i^{part} - c_i^{sol}} \frac{\partial c_j}{\partial n} \text{ for } \mathbf{x} \in S(t) \end{aligned}\right\} \Rightarrow \sum_{k=1}^{n} \frac{D_{ik}}{c_i^{part} - c_i^{sol}} \frac{\partial c_k}{\partial n} = \sum_{k=1}^{n} \frac{D_{jk}}{c_j^{part} - c_j^{sol}} \frac{\partial c_k}{\partial n} \text{ for } \mathbf{x} \in S(t).$$

(9)

The right part of above equations follows from local mass-conservation of the components. Above formulated problem falls within the class of Stefan-problems, i.e. diffusion with a moving boundary. Since we consider simultaneous diffusion of several chemical elements, it is referred to as a 'vector-valued Stefan problem'. The unknowns in above equations are the concentrations c_i, interfacial concentrations c_i^{sol} and the interfacial position $S(t)$. All concentrations are non-negative. The model was analyzed in [26, 27, 25].

The influence of cross-diffusion is investigated in terms of a parameter study in [25] and in terms of self-similar solutions as exact solutions for the unbounded domain in [26]. An analysis of several numerical analysis in terms of stability criteria is presented in [27]. For a mathematical overview of Stefan problems we refer to the textbooks of Crank [6], Chadam and Rasmussen [36] and Visintin [37].

3 ANALYTIC SOLUTIONS

The early models on particle dissolution and growth based on long-distance diffusion consisted of analytic solutions in an unbounded medium under the assumption of local equilibrium at the interface, see Ham [38, 39], Zener [40], Whelan [1] and Aaron and Kotler [5] to mention a few. These analytic models have been developed for idealized geometries such as planar, cylindrical and spherical geometries and are mostly based on the so-called Boltzmann transformation where the concentration c is written as $c(x, t) = \overline{c}(\eta)$ where $\eta = x/\sqrt{t}$. Recently the self-similar solutions have been extended to multi-component alloys by Atkinson *et al.* [41] and Vermolen *et al.* [26]. In the latter paper an effective diffusion coefficient was determined which is useful for a quick estimate of the dissolution or growth speed. Recently, the Zener solutions for the various geometries have been extended to multi-component alloys [42]. We remark that these solutions hold for the case of local equilibrium at the moving interface, that is, the concentrations at the interface are those as given by the phase diagrams.

The model of Nolfi *et al.* [4] incorporates the interfacial reaction between the dissolving particle and its surrounding phase by the use of a Fourier series solution for the concentration profile. The interface motion was not included in this solution. Vermolen *et al.* [43] constructed a semi-analytic solution based on Fourier Series in which the interface motion was incorporated. Further solutions with Laplace transforms have been reported by Aaron & Kotler [5] and Whelan [1]. These solutions were extended to multi-component

alloys by Reiso *et al.* [14]. The analytic solutions are very valuable for the evaluation of the accuracy of the numerical procedures.

4   NUMERICAL SOLUTION PROCEDURES

In the literature one can find various numerical methods to solve Stefan problems. These methods can be distinguished in the following categories: front-tracking, front-fixing and fixed-domain methods. In a front-fixing method a transformation to body fitted curvilinear coordinates is used (a special case is the Isotherm Migration Method (IMM) [6]). A drawback is that such a transformation can only be used for a relatively simple geometry. Fixed-domain methods are the enthalpy method (EM), and the variational inequality method (VI). In these methods a new unknown is introduced, which is the integral of the primitive variable. The free boundary is implicitly defined by this unknown. Since in our approach the equations hold for the concentration and there are no energies involved in the model, the enthalpy method and phase-field method are not used. We refer to [44] and [45] among others where the phase-field method is used to compute the solution of the moving boundary problem. An other recent method where the free boundary is implicitly defined is the level-set method as described by Chen *et al.* [46] for Stefan problems. Here the interface is identified by the zero level-set of a marker function. The advantages of this method is that topological changes, such as breaking up, of the dissolving or growing phases are dealt with easily. On the other hand, since both the interfacial velocity and interfacial concentrations are here determined by the concentration gradient, a grid grid-refinement near the free boundary can be attractive. This implies that the grid moves anyway and hence the benefits for the level-set method due to a fixed grid no longer apply. Though, the level-set method remains the best candidate due to the ability of dealing with changing topologies and because remeshing steps are not needed. The IMM and VI methods are only applicable when the interface is an equi-concentration line. However, in our application where either multi-component particles or interfacial reactions are taken into account, the interface is not an equi-concentration line. Hence, (IMM) and (VI) methods are no suitable candidates. Therefore we use a front-tracking method which has the added benefit that a first order reaction at the interface can be incorporated in the model. The moving grid method solves one partial differential equation only. The mesh is moved using an arbitrary Lagrangian Eulerian method. Here, the method is relatively cheap compared to the level-set method, where also a first order hyperbolic partial differential equation for the level set function has to be solved with a continuous extension of the interface velocity at each time-step. However, it is sometimes necessary to change the topology of the elements, then, the moving grid method requires a remeshing step, which involves an expensive two dimensional interpolation step. This is a very expensive step in the moving grid method. Further, topological changes of growing and dissolving (for instance the dissappearrance) phases are hard to implement into moving mesh methods. For these cases the level-set method becomes more attractive. We refer to [27, 47, 19] for more details on our level set method and moving grid method.

Further, for review papers we refer to Thornton *et al.* [21] and Vermolen *et al.* [28]. The first paper focusses more on an incorporation of the relevant thermodynamics and diffuse interface models. The second paper deals with numerical aspects of the solution of the sharp interface model. A recent book on the level set method and its applications is due to Osher and Fedkiw [29].

5 APPLICATION OF MOVING GRID TO CURVATURE DEPENDENCE

In the present application we consider a binary alloy in which a particle dissolves or grows. The calculations that we present here are for two spatial dimensions. Due to crystal defects, such as dislocations, the free energy of the phases present is raised. This causes the so-called Gibbs-Thomson effect, which makes the interface concentration sensible to the local curvature. This effect was not taken into account in the previous section. Let c_0^{sol} be the equilibrium interface concentration that follows from the phase diagram, then, the interface concentration at a location at the interface with curvature κ, is given by

$$c^{\text{sol}} = c_0^{\text{sol}} \exp\left(\frac{2\gamma V_m \kappa}{RT}\right), \text{ for } \mathbf{x} \in \mathbf{S(t)}. \tag{10}$$

This is an important effect if the curvature of the particle is small. Here γ, V_m and R respectively denote the surface energy, molar volume and ideal gas constant. The above equation requires the determination of the curvature κ on each location at the moving interface $S(t)$. The present approach solves second Fick's Law for the concentration with a moving grid method to model the movement of the boundary. Using a finite element method to solve the equations with a moving grid, that is, for the concentration we solve the following problem:

$$
\begin{cases}
\text{Find } c(\mathbf{x}, t) \in H^1(\Omega(t)), \text{ subject to } c(\mathbf{x}, t) = c^{\text{sol}}(\mathbf{x}, t) \text{ for } \mathbf{x} \in S(t), \\
\\
\text{such that } \int_{\Omega(t)} \left\{\frac{\partial c}{\partial t} - \mathbf{v}_{\text{mesh}} \cdot \nabla c\right\} v(\mathbf{x}) d\Omega = -\int_{\Omega(t)} \nabla c \cdot \nabla v d\Omega, \\
\\
\text{for all } v \in H^1(\Omega(t)), \text{ subject to } v = 0 \text{ for } \mathbf{x} \in S(t).
\end{cases}
\tag{11}
$$

In the above equation $\mathbf{v}_{\text{mesh}} = \frac{\mathbf{x}(t+\Delta t) - \mathbf{x}(t)}{\Delta t}$ is the mesh velocity. Linear triangular elements are used for the discretization. The displacement of the moving boundary is computed in a mass conserving manner, see [47]. To determine the interface curvature, we use the observation that three points uniquely define the circle containing these points, unless these points are on a straight line. The radius of this circle is the local radius of curvature, of which its reciprocal in turn defines its local curvature. This local curvature is used for the determination of the local interface concentration, see equation (10). The curvature is allowed to be negative whenever the interface is concave-upward with respect to the particle. For other cases the curvature is positive. A sketch is presented in Figure 1. A

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consequence of the Gibbs-Thomson effect is that the fingers with smaller (or negative) curvature have a larger growth rate than fingers with a higher curvature. Hence, the Gibbs-Thomson effect prevents positive fingers from moving rapidly into the matrix and to accelerate the movement into the matrix of the negative fingers.
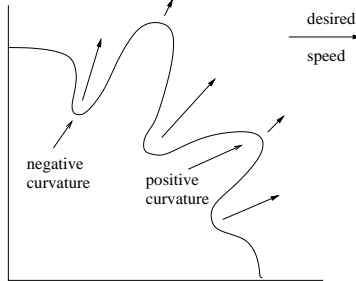

Figure 1: Positive and negative curvature and desired speed.

The second derivative is needed for the local curvature. Further, the sign of the vector product of the line segments connecting the adjacent points is used to determine the sign of the curvature. This is all subsitituted into equation (10). The numerical determination of the second derivative is a notorious problem in computing the local curvature due to rounding errors.
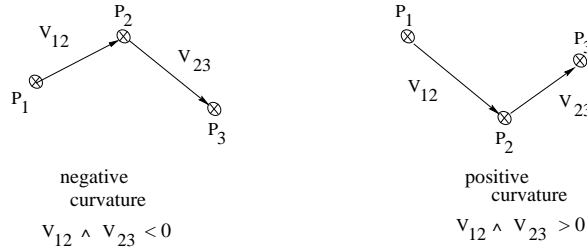

Figure 2: Positive and negative curvature.

A problem that occured here was the fact that a small error in the curvature, gives a relatively large influence on the interface concentration due to its exponential dependence (see equation (10)). This gives unrealistic results. Since this is a numerical artefact, we removed it by introducing a 'cut-off' procedure, by adjusting the interface concentration to the average of the interface concentration and the initial concentration. The choice is somewhat arbitrary, but the results become more realistic. The 'cut-off' procedure gives that

$$\text{If } c^{\text{sol}} > c^0 \text{ then } c^{\text{sol}} \to \frac{c^{\text{sol}} + c^0}{2}.$$

A next idea was to smooth the curvature by using an approximating spline. This implies that for the determination of the local curvature, the interface points are somewhat shifted so that the interface becomes smoother. The second derivative was approximated subsequently. Our preliminary numerical experiments look promising. Additional research on this idea is needed.

Finally, we apply the idea of determining the local radius of curvature by using a circle intersecting three adjacent points as discussed in combination with the 'cut-off' procedure. The cut-off procedure is combined with the decrease of the time-step when the mesh is refined. Here we got convergence for decreasing time-step and mesh-width.

As an application we consider the growth of a circular particle with $D = 0.1$ $\mu m/s$, $c^0 = 0.5$, $c^{\text{part}} = 1$, $c_0^{\text{sol}} = 0.0001$ and initial radius of 0.3 μm. These data imply that the particle will grow. As Mullins & Sekerka [31] point out, the growth will occur under fingering if the surface energy γ is lower than a threshold value (see Figure 3). To illustrate the influence of the surface energy γ we plot the results for the case that $\frac{2\gamma V_m}{RT} = 2.406$, which is a value for which no fingering occurs during growth, in Figure 4. It can be seen that no fingering occurs, which is in line with the expectations from the theory of Mullins & Sekerka.
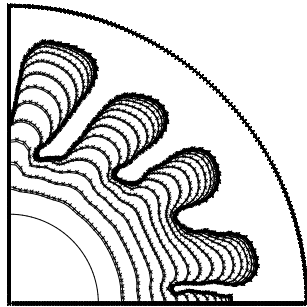

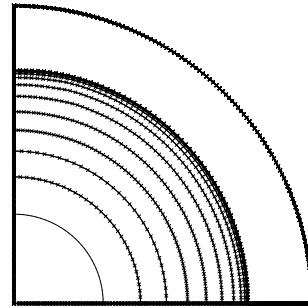
Figure 3: Growth modeled with $\gamma = 0$.

Figure 4: Growth modeled with $\frac{2\gamma V_m}{RT} = 2.406$.

From this we see that the statement due to Mullins & Sekerka that the Gibbs-Thomson effect prevents the occurrence of fingering of a growing particle is also supported numerically. For more details concerning this study on the issue of fingering, we refer to Pinson [48].

6 CONCLUSIONS

A suite of mathematical models for the diffusional phase transformations has been presented. Some applications with a two-dimensional model incorporating the Gibbs-Thomson effect are shown for a binary alloy. The Gibbs-Thomson effect can be used to prevent fingering of a growing particle.

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