Regular article

Cross-diffusion controlled particle dissolution in metallic alloys

F.J. Vermolen[1]**, C. Vuik**[1]**, S. van der Zwaag**[2]

[1] Department of Applied Mathematical Analysis, Delft University of Technology, Mekelweg 4, 2628 CD Delft, The Netherlands
   (e-mail: F.J.Vermolen@math.tudelft.nl)
[2] Laboratory of Aerospace Engineering, Delft University of Technology, Kluiverweg 1, 2629 HS Delft, The Netherlands

Communicated by: G. Wittum

Abstract. A model for particle dissolution is formulated for the case of several simultaneously diffusing and strongly interacting alloying elements. The model is analyzed by using diagonalization of the diffusion matrix. A numerical solution procedure, also based on diagonalization, is proposed. Further, self-similar solutions for the resulting moving boundary problem are derived for the case of both a diagonalizable and non-diagonalizable diffusion matrix. Finally, we use this technique to approximate a two-dimensional problem with Finite Elements.

1 Introduction

In the thermal processing of both ferrous and non-ferrous alloys, homogenization of the as-cast 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. Such a homogenization treatment is applied in hot-rolling of Al killed construction steels, HSLA steels, all engineering steels, as well as aluminum extrusion alloys. Precipitate dissolution is often the most critical of the occurring processes during homogenization. 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 constant but depends on particle size, geometry, overall composition etc.

Due to the scientific and industrial relevance of being able to predict the kinetics of particle dissolution and growth, many models of various complexity have been presented and experimentally validated. The early models were based on analytical solutions for long-distance diffusion in an unbounded medium under the assumption of local equilibrium at the moving interface, see Whelan [25] for instance. The model of Nolfi et al. [15] incorporate the interfacial reaction between the dissolving particle and its surrounding phase. Later modeling particle dissolution has been extended to the introduction of multi-component particles by, among others,

Reiso et al. [18]. All the above mentioned models were based on viewing particle dissolution as a Stefan problem (see for instance [21]). Kale et al. [8] incorporate cross-diffusion in iron-based metallic systems where cross-diffusion coefficients range up in value to about a third of the diagonal coefficients. Some important references from the metallurgical literature where cross-diffusion is treated are the books of Kirkaldy and Young [10] and Glicksman [5]. A paper in which some metallurgical implications of cross-diffusion on particle dissolution are described is written by Vermolen et al. [23].

As far as we know no other paper, besides [23], treated both the movement of the interface and cross diffusion in a vector valued Stefan problem, where several chemical elements diffuse simultaneously. It is our aim to develop analytical expressions and numerical solutions for the solution of the vector-valued Stefan problem in which cross-diffusion is incorporated. Subsequently we apply the analytical expressions to derive boundary conditions for the simultaneous growth of a sphere and dissolution of a cylindrical plate of different compositions. The resulting 2D problem is solved by the use of a Finite Element Method.

2 Basic assumptions in the model

The as-cast microstructure is simplified into a representative cell containing the α-phase and a single particle of phase β of a specific form, size and location of the cell boundary.

The boundary between the β-particle and α-phase is referred to as the interface. In [21] we considered the dissolution of a stoichiometric particle in a ternary and a general multi-component alloy. We denote the chemical species by Sp_i, $i \in \{1, \ldots, n+1\}$, where Sp_{n+1} is the 'original' solvent metallic α-phase in which the particle dissolves. We denote the stoichiometry of the particle by $(Sp_1)_{m_1}(Sp_2)_{m_2}(\ldots)(Sp_n)_{m_n}$. The numbers $m_1, m_2, \ldots$ 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:

$$\left(c_1^{\mathrm{sol}}\right)^{m_1} \left(c_2^{\mathrm{sol}}\right)^{m_2} (\ldots) \left(c_n^{\mathrm{sol}}\right)^{m_n} = K \,. \tag{1}$$

Equation (1) is in line with the assumption of local equilibrium at the interface. The factor K is referred to as the solubility product that is obtained from thermodynamics. It strongly depends on temperature. In the present work, we assume K to be constant.

We assume that the whole metal is divided into periodical cells with symmetrical and differentiable initial concentrations. We introduce a bounded domain over whose boundary there is no flux. For cases of low overall concentrations in the alloy, the α-phase part of the domain may be large and the solution resembles the case where the domain is unbounded. The α-phase part of the domain, in which diffusion takes place, is referred to as $\Omega(t) = (S(t), M) \subset \mathbb{R}^1$, where t denotes time. The β-particle, in which there is no diffusion, is represented by the domain $\Pi(t) = (0, S(t)) \subset \mathbb{R}^1$. We denote the curve that represents the moving interface between the β-particle and α-phase by $S(t) = \overline{\Omega}(t) \cap \overline{\Pi}(t)$. Since cross-diffusion is taken into account, we have for each alloying element, with $x \in \Omega(t)$ and $t > 0$

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{n} \frac{\partial}{\partial x}\left(D_{ij}\frac{\partial c_j}{\partial x}\right), \text{ for } i \in \{1, \ldots, n\} \,. \tag{2}$$

The above equations follow from thermodynamic considerations, their derivation can for instance be found in [10]. Here D_{ij} and c_i respectively denote the coefficients of the diffusion matrix and the concentration of the species i in the α-rich phase. This relaxes the assumption that the alloying elements diffuse independently and the coupling between the equations can be strong. When cross-diffusion is neglected, the diffusion matrix is diagonal. The coefficients D_{ij}, $i \neq j$ are referred to as the cross-terms. An alternative formulation of cross-diffusion is treated by Farkas [4] where only the diagonal entries of the above diffusion matrix D are used, however these diagonals are taken to depend linearly on the concentration of all the other species and hence a strong coupling arises in an other way. We assume that the diffusion matrix does not depend on the concentration, time and space, i.e. the matrix is treated as constant in the present work. Further, it is assumed that the diffusion matrix D is non-singular. This assumption is motivated in [10].

Let c_i^0 denote the initial concentration of each element in the α-phase, then we take as initial conditions

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

Since there is no flux over the outer boundary, we have

$$\sum_{j=1}^{n} D_{ij}\frac{\partial c_j}{\partial x}(M, t) = 0 \,, \text{ for } i \in \{1, \ldots, n\} \,.$$

Since D is non-singular this implies

$$\frac{\partial c_j}{\partial x}(M, t) = 0 \,, \text{ for } j \in \{1, \ldots, n\} \,. \tag{3}$$

The concentration of element i in the particle is denoted by the constant c_i^{part}. This assumption follows from the constraint

that the stoichiometry of the particle is maintained during dissolution in line with Reiso et al. [18]. The balance of atoms of alloying element i leads to the following equation (Stefan condition):

$$\left(c_i^{\mathrm{part}} - c_i^{\mathrm{sol}}\right)\frac{dS(t)}{dt} = \sum_{j=1}^{n} D_{ij}\frac{\partial c_j}{\partial x}(S(t), t) \,. \tag{4}$$

Equation (4) implies

$$\sum_{k=1}^{n} \frac{D_{ik}}{c_i^{\mathrm{part}} - c_i^{\mathrm{sol}}}\frac{\partial c_k}{\partial x}(S(t), t) = \sum_{k=1}^{n} \frac{D_{jk}}{c_j^{\mathrm{part}} - c_j^{\mathrm{sol}}}\frac{\partial c_k}{\partial x}(S(t), t) \,. \tag{5}$$

Above formulated problem is a Stefan-problem, i.e. a diffusion process 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 $S(t)$. The coupling exists in both the diffusion equations, Stefan condition and the values of the concentrations at the interfaces between the particle and α-rich phase. This strong coupling complicates the qualitative analysis of the equations. For a mathematical overview of Stefan problems we refer to the textbooks of Crank [3], Chadam and Rasmussen [1], Visintin [24] and Kassab [9].

3 Analysis

In this section we consider some general mathematical properties of the vector-valued Stefan problem in which we deal with the extra coupling from cross-diffusion. We will partly or entirely decouple the diffusion equations depending on whether the diffusion matrix, D, is diagonalizable. First we state the vector-valued Stefan problem with the diffusion matrix. Here we deal with a factorization of the diffusion matrix where we use Jordan decomposition or diagonalization. Subsequently we give some remarks concerning the case when D is not diagonalizable.

3.1 Diagonalization of the diffusion matrix

In this section we consider a vector-notation of the equations. We define the vectors

$$\underline{c} := (c_1, c_2, \ldots c_n)^T \,,$$

$$\underline{c}^p := \left(c_1^{\mathrm{part}}, c_2^{\mathrm{part}}, \ldots, c_n^{\mathrm{part}}\right)^T \,,$$

$$\underline{c}^s := \left(c_1^{\mathrm{sol}}, c_2^{\mathrm{sol}}, \ldots, c_n^{\mathrm{sol}}\right)^T$$

then the diffusion equations become in vector notation

$$\frac{\partial \underline{c}}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial \underline{c}}{\partial x}\right) \,. \tag{6}$$

The boundary and initial conditions follow similarly in vector notation. The equation of motion of the interface becomes in vector notation:

$$\left(\underline{c}^p - \underline{c}^s\right)\frac{dS}{dt} = D\frac{\partial \underline{c}}{\partial x}(S(t), t) \,. \tag{7}$$

To analyze (6) it is convenient to look at a decomposition of the diffusion matrix D. Therefore, we use the Decomposition Theorem in linear algebra, which states that for each $D \in \mathbb{R}^{n \times n}$ there exists a non-singular $P \in \mathbb{R}^{n \times n}$ such that $\Lambda = P^{-1}DP$, where Λ represents a Jordan block-matrix (see for instance Golub and van Loan [6]). For cases where D has n independent eigenvectors, i.e. D is diagonalizable, Λ is a diagonal matrix with the eigenvalues of D on the main diagonal. Further, the columns of the matrix P consist of the eigenvectors of D. When D is defect, then P consists of the generalized eigenvectors of D, which are obtained from solution of

$$(D - \lambda I)\underline{w}_{i+1} = \underline{w}_i, \quad \text{with } \underline{w}_1 = \underline{v},$$

where I is the identity matrix and $\underline{v}$ and $\underline{w}_i$ are an eigenvector and generalized eigenvectors of D respectively, belonging to the eigenvalue λ whose geometric multiplicity is less than the algebraic multiplicity. For the coming we assume that the eigenvalues are real. Using the transformed concentrations

$$\underline{u} := P^{-1}\underline{c}, \qquad \underline{u}^s := P^{-1}\underline{c}^s,$$
$$\underline{u}^p := P^{-1}\underline{c}^p, \quad \underline{u}^0 := P^{-1}\underline{c}^0,$$

and (6) and (7) gives

$$\frac{\partial \underline{u}}{\partial t} = \frac{\partial}{\partial x}\left(\Lambda \frac{\partial \underline{c}}{\partial x}\right), \tag{8}$$

$$\left(\underline{u}^p - \underline{u}^s\right)\frac{dS}{dt} = \Lambda \frac{\partial \underline{u}}{\partial x}(S(t), t). \tag{9}$$

For a diagonalizable matrix D system (8) is fully uncoupled. The homogeneous Neumann conditions at the non-moving boundary are similar for the transformed concentrations due to the linear nature of the transformation. Further, we have for $t = 0$ and $j \in \{1, \ldots, n\}$

$$u_j = \begin{cases} u_j^0, & \text{for } x \in \Omega(0), \\ u_j^{\text{part}}, & \text{for } x \in \Pi(0). \end{cases}$$

From the decomposition of the diffusion matrix, with $\underline{c} = P\underline{u} \Rightarrow c_i = \sum_{j=1}^n p_{ij}u_j$, the coupling between the interfacial concentrations via the hyperbolic relation (1) changes into

$$\left(\sum_{j=1}^n p_{1j}u_j^s\right)^{m_1}\left(\sum_{j=1}^n p_{2j}u_j^s\right)^{m_2}(\ldots)\left(\sum_{j=1}^n p_{nj}u_j^s\right)^{m_n} = K. \tag{10}$$

We note that the decoupled transformed concentrations satisfy a maximum principle [17]. However, when D is not diagonalizable then the maximum principle does not hold necessarily for all transformed concentrations. For the transformed system we introduce the concept of a mass-conserving solution for each alloying element:

Definition 1. *Let u^0 be constant on $[0, M]$, then a solution of the Stefan problem is called conserving if the solution satisfies*

$$\int_0^M \left(u(x, t) - u^0\right)dx = \left(u^{\text{part}} - u^0\right)S(0), \quad \forall t > 0.$$

With this definition of mass-conserving solutions we established the following proposition in [21]:

Proposition 1. *Let all concentrations, which are used in* (9)*, be non-negative and D be diagonalizable, then solutions are non-conserving whenever*

$$u^{\text{sol}} \leq u^{\text{part}} \leq u^0 \text{ or } u^0 \leq u^{\text{part}} \leq u^{\text{sol}}.$$

Proposition 1 is used to select solutions that satisfy mass conservation and hence are allowable.

Kirkaldy et al. [10] use a thermodynamic argument to show that the diffusion matrix D has positive and real-valued eigenvalues for metallic systems. Therefore, we will restrict ourselves to the treatment of matrices D with real and positive eigenvalues. If D is symmetric and diagonally dominant, then it follows from Gerschgorin's Theorem that the matrix is positive definite and hence its eigenvalues are positive.

4 Numerical method

Various numerical methods are known to solve Stefan problems: front-tracking, front-fixing and fixed domain methods. Since the concentration at the interface varies with time in a bounded domain, we restrict ourselves to a front-tracking method. Recently a number of promising methods are proposed for multi-dimensional problems: phase field methods and level set methods, such as in [2, 11, 16, 19]. However, imposing local equilibrium condition at the interface in such models is not as straightforward as in front-tracking methods that are used here. A coupling between thermodynamics and a phase field model is presented by Grafe et al. [7].

Our main interest is to give an accurate discretization of the boundary conditions for this Stefan problem with one spatial co-ordinate. Therefore we use the classical moving grid method of Murray and Landis [13] to discretize the diffusion equations. In this paper we briefly describe the method, for more details for the case of a diagonalizable matrix, we refer to [21].

Transformation of the concentrations
We assume that the matrix D does not depend on time. First the eigenvalues and eigenvectors of the diffusion matrix are computed for the transformation of the concentration. Thereafter, the particle and initial concentrations are also transformed. The diffusion equation is discretized by using a Finite Difference Method where the time integration is implicit to guarantee numerical stability. A great advantage of the diagonalization argument is that a fully implicit method for diffusion, which is unconditionally stable, can be used easily to integrate the concentration profile in time since the equations are decoupled. This also holds when the diffusion matrix is not diagonalizable.

Discretization of the interior region
We use an implicit finite difference method to solve the diffusion equations in the inner region. An explicitly treated convection term due to grid-movement is included. Since the magnitude of the gradient is maximal near the moving interface we use a geometrically distributed grid such that

the discretization near the interface is fine and coarse farther away from the moving interface. Furthermore, we use a virtual grid-point near the moving boundary. The distance between the virtual node and the interface is chosen equal to the distance between the interface and the first grid-node. The resulting set of linear equations is solved using a tridiagonal matrix solver.

Discrete boundary conditions at the interface
We define the discrete approximation of the concentration as $u_{i,k}^j$, where j, i and k respectively denote the time-step, the index of the chemical (alloying) element and gridnode. The virtual gridnode behind the moving interface and the gridnode at the moving interface respectively have indices $k = -1$ and $k = 0$. At the moving interface, we obtain from discretization of the Stefan condition for $j \in \{1, \dots, n-1\}$

$$\frac{\lambda_i}{u_i^{\text{part}} - u_i^{\text{s}}} \frac{u_{i,1}^{j+1} - u_{i,-1}^{j+1}}{2\Delta r} = \frac{\lambda_{i+1}}{u_{i+1}^{\text{part}} - u_{i+1}^{\text{s}}} \frac{u_{i+1,1}^{j+1} - u_{i+1,-1}^{j+1}}{2\Delta r}.$$

Note that the concentration profile of each element is determined by the value of the interfacial concentration. Above equation can be re-arranged into a zero-point equation for all chemical elements. All interfacial concentrations satisfy the hyperbolic relation (1). Combination of all this, gives for $i \in \{1, \dots, n-1\}$ and $i = n$

$$f_i\left(u_{i,0}^{j+1}, u_{i+1,0}^j\right) := \lambda_i \left(u_{i,1}^{j+1} - u_{i,-1}^{j+1}\right)\left(u_{i+1}^{\text{part}} - u_{i+1}^{\text{s}}\right) +$$

$$- \lambda_{i+1}\left(u_{i+1,1}^{j+1} - u_{i+1,-1}^{j+1}\right)\left(u_i^{\text{part}} - u_i^{\text{s}}\right) = 0$$

$$f_n\left(u_1^{\text{s}}, \dots, u_n^{\text{s}}\right) := \left(\sum_{j=1}^n p_{1j}u_j^{\text{s}}\right)^{m_1} (\dots)$$

$$\times \left(\sum_{j=1}^n p_{nj}u_j^{\text{s}}\right)^{m_n} - K = 0.$$

To approximate a root for the 'vector-function' f we use Newton's method combined with discrete approximations for the non-zero entries in the first $n-1$ rows of the Jacobian matrix. The iteration is terminated when sufficient accuracy is reached. This is explained in more detail in [21].

Adaptation of the moving boundary
The interface position is computed by the use of the Stefan condition. In [20] the forward (explicit) Euler and Trapezium time integration methods are described and compared. It was found that the (implicit) Trapezium method was superior in accuracy. Furthermore, the iteration step to determine the interfacial concentrations is included in each Trapezium step to determine the interfacial position. Hence, the work per time iteration remains the same for both time integration methods. Therefore, the Trapezium rule is used to determine the interfacial position as a function of time. We terminate the iteration when sufficient accuracy is reached, i.e. let ε be the inaccuracy, then we stop the iteration when the inequality

$$\sum_{i=1}^n \left|u_i^{\text{s}}(p+1) - u_i^{\text{s}}(p)\right| + \frac{\left|S^{j+1}(p+1) - S^{j+1}(p)\right|}{S^{j+1} - M} < \varepsilon$$

holds. Here S^j denotes the discrete approximation of the interfacial position at time-step j. The integer p represents the iteration number during the determination of the interfacial concentrations and position. We finally remark that a numerical solution for diffusion in ternary alloys including cross-diffusion for fixed boundaries can be found in Naumann and Savoca [14].

5 Similarity solutions

We consider analytical solutions satisfying (2) for the concentrations. To facilitate the analysis we consider the transformed solution $\underline{u}$. The components of the vectors $\underline{u}$, $\underline{u}^p$, $\underline{u}^s$ and $\underline{u}^0$ are denoted by the index i in subscript. Proposition 1 is used to reject solutions that are not physical. To facilitate the analysis we consider the Stefan problem on an unbounded domain in one co-ordinate where $x > S(t)$, $t > 0$:

$$(P_1) \begin{cases} \dfrac{\partial \underline{u}}{\partial t} = \Lambda \dfrac{\partial^2 \underline{u}}{\partial x^2} \\[2mm] \left(\underline{u}^p - \underline{u}^s\right)\dfrac{dS}{dt} = \Lambda \dfrac{\partial \underline{u}}{\partial x}(S(t), t) \\[2mm] \underline{u}(x,0) = \underline{u}^0, \qquad\qquad S(0) = S_0, \\[2mm] \underline{u}(S(t), t) = \underline{u}^s. \end{cases}$$

First we deal with the diagonalizable case where we consider an exact solution and an asymptotic approximation. Subsequently we deal with the non-diagonalizable case where we also consider an exact solution and an asymptotic approximation. A self-similar solution, where the boundaries do not move, can be found in the book of Glicksman [5], chapters 23 and 24.

5.1 The exact solution for the diagonalizable case

As a trial solution of (P_1) we assume that the interfacial concentrations $\underline{u}^s$ are constant. Furthermore, we assume that the diffusion matrix, D, is diagonalizable. Suppose that the vector $\underline{u}^s$ is known then using a similar procedure as in [21], one obtains the solution for each component:

$$u_i = u_i^0 + \left(u_i^0 - u_i^s\right)\frac{\operatorname{erfc}\left(\frac{x-S_0}{2\sqrt{\lambda_i t}}\right)}{\operatorname{erfc}\left(\frac{k}{2\sqrt{\lambda_i}}\right)}, \quad \text{for } i \in \{1, \dots, n\}.$$

The assumption that $S(t) = S_0 + k\sqrt{t}$ gives the following expression for k

$$\frac{u_i^0 - u_i^s}{u_i^p - u_i^s}\sqrt{\frac{\lambda_i}{\pi}}\frac{e^{-\frac{k^2}{4\lambda_i}}}{\operatorname{erfc}\left(\frac{k}{2\sqrt{\lambda_i}}\right)} = \frac{k}{2}, \quad \text{for } i \in \{1, \dots, n\}.$$

Above equation has to be solved for the parameter k. However, the transformed interfacial concentrations $\underline{u}^s$ are not known either and hence one is faced with the following problem

$$(P_2) \begin{cases} \dfrac{k}{2} \dfrac{\operatorname{erfc}\left(\frac{k}{2\sqrt{\lambda_i}}\right)}{e^{-\frac{k^2}{4\lambda_i}}} = \dfrac{u_i^0 - u_i^s}{u_i^p - u_i^s} \sqrt{\dfrac{\lambda_i}{\pi}}, \quad \text{for } i \in \{1, \dots, n\}, \\[2em] \left(\sum_{j=1}^n p_{1j} u_j^s\right)^{m_1} \left(\sum_{j=1}^n p_{2j} u_j^s\right)^{m_2} (\dots) \left(\sum_{j=1}^n p_{nj} u_j^s\right)^{m_n} = K. \end{cases}$$

Here the unknowns are the transformed interfacial concentrations $\underline{u}^s$ and rate-parameter k. In above problem there is no time-dependence, hence the ansatz of time-independent transformed interfacial concentrations (and hence the physical interfacial concentrations) is not contradicted. Due to the non-linear nature of the equations, the solution may be not unique. We apply a numerical zero-point method to obtain a solution of (P_2).

Example
We illustrate the importance of the cross-diffusion term. The following input parameters are used where we vary the value of the cross term D_{12}:

$$\underline{c}^0 = (0, 0)^T, \qquad \underline{c}^{\text{part}} = (50, 50)^T,$$

$$D = \begin{pmatrix} 1 & D_{12} \\ D_{12} & 2 \end{pmatrix}, \qquad K = 1.$$

The above diffusion matrix is symmetric. From Fig. 1 it is clear that the influence of the cross terms is significant. Since Kale et al. [8] indicate that the cross diffusion term can have the same order of magnitude as the diagonal terms in the diffusion matrix we choose the values of D_{12} in the range $[-1, 0]$.

From (P_2) there is no explicit relation for k. In [22] we show that an approximate explicit solution for k can be derived provided that $||\underline{u}^s - \underline{u}_0|| \ll ||\underline{u}_p - \underline{u}_s||$.

5.2 The exact solution for the non-diagonalizable case

In this section we consider a ternary example, so $n = 2$. Examples with more components can be treated similarly. When
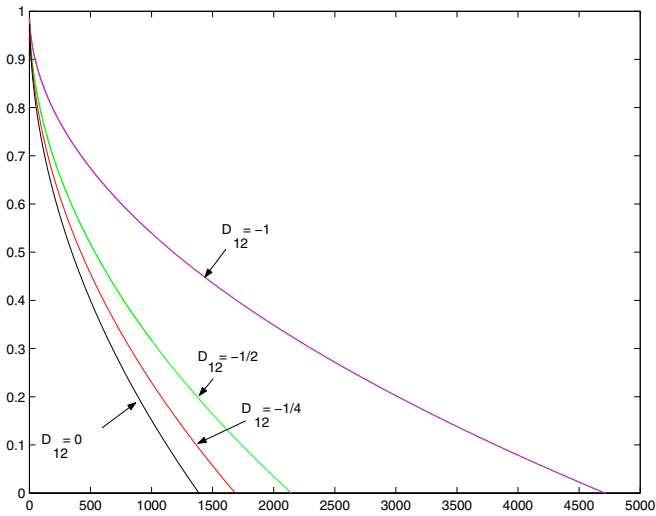

Fig. 1. The interfacial position as a function of time for the exact self similar solution for several values of the cross diffusion terms

the matrix $D \in \mathbb{R}^{2 \times 2}$ is not diagonalizable then we obtain $\Lambda = \begin{pmatrix} \lambda & 1 \\ 0 & \lambda \end{pmatrix}$ as the decomposed form of the diffusion matrix. The set of transformed diffusion equations become

$$\begin{cases} \dfrac{\partial u_1}{\partial t} = \lambda \dfrac{\partial^2 u_1}{\partial x^2} + \dfrac{\partial^2 u_2}{\partial x^2}, \\[1em] \dfrac{\partial u_2}{\partial t} = \lambda \dfrac{\partial^2 u_2}{\partial x^2}. \end{cases} \tag{11}$$

From the above system it can be seen that the equation for u_2 is uncoupled. Its solution is computed using the self-similarity transformation and subsequently substituted into the equation for u_1. We consider self-similarity solutions $u_1, u_2(x, t) = \overline{u}_1, \overline{u}_2(\eta)$, where $\eta := \dfrac{x - S_0}{\sqrt{t}}$, and we apply a similar procedure as in Sect. 5.1. to obtain a system of ordinary differential equations for $\overline{u}_1$ and $\overline{u}_2$. These equations are solved to obtain the following expressions for the $\overline{u}_1$ and $\overline{u}_2$.

$$\overline{u}_1 = \dfrac{C_1}{2\lambda^2}\left(-\eta\lambda\, e^{-\frac{\eta^2}{4\lambda}} + \lambda\sqrt{\pi\lambda}\operatorname{erf}\left(\dfrac{\eta}{2\sqrt{\lambda}}\right)\right)$$

$$+ C_2\sqrt{\pi\lambda}\operatorname{erf}\left(\dfrac{\eta}{2\sqrt{\lambda}}\right) + C_3$$

$$\overline{u}_2 = C_1\sqrt{\pi\lambda}\operatorname{erf}\left(\dfrac{\eta}{2\sqrt{\lambda}}\right) + C_4$$

Again we use the trial solution $S(t) = S_0 + k\sqrt{t}$. A combination with the boundary conditions delivers expressions for the integration constants C_1, C_2, C_3 and C_4. Substitution of these constants into the expressions of u_1 and u_2 gives the transformed concentrations. Further, the rate factor of the interface movement, k, is obtained from combination of the Stefan condition and the expression for u_2. Then we get the following set of equations to be solved for k, u_1^s and u_2^s:

$$\dfrac{k}{2}\dfrac{\operatorname{erfc}\left(\frac{k}{2\sqrt{\lambda}}\right)}{e^{-\frac{k^2}{4\lambda}}} = \dfrac{u_2^0 - u_2^s}{u_2^p - u_2^s}\sqrt{\dfrac{\lambda}{\pi}},$$

$$\dfrac{k}{2}\dfrac{\operatorname{erfc}\left(\frac{k}{2\sqrt{\lambda}}\right)}{e^{-\frac{k^2}{4\lambda}}} = \dfrac{u_1^0 - u_1^s}{u_1^p - u_1^s}\sqrt{\dfrac{\lambda}{\pi}}$$

$$+ \dfrac{u_2^0 - u_2^s}{2\left(u_1^p - u_1^s\right)\sqrt{\lambda\pi}}\left(1 + 2\dfrac{k^2}{4\lambda} - \dfrac{k}{2\sqrt{\lambda}}\dfrac{2\lambda}{\sqrt{\pi}}\dfrac{e^{-\frac{k^2}{4\lambda}}}{\operatorname{erfc}\left(\frac{k}{2\sqrt{\lambda}}\right)}\right)$$

$$\left(p_{11}u_1^s + p_{12}u_2^s\right)^{m_1}\left(p_{21}u_1^s + p_{22}u_2^s\right)^{m_2} = K. \tag{12}$$

Note that $\underline{p}_1$ and $\underline{p}_2$ respectively represent the eigenvector and generalized eigenvector that correspond to the eigenvalue λ of the defective matrix D. The above system of equations can be solved using a zero-point method. We remark here that we derived for this non-diagonalizable case an approximate solution under the condition $|u_2^s - u_2^0| \ll |u_2^p - u_2^s|$ in [22].

Example
In the illustration in Fig. 2 both the exact (see (12)), approximate solution ([22]) and numerical solution are displayed. It
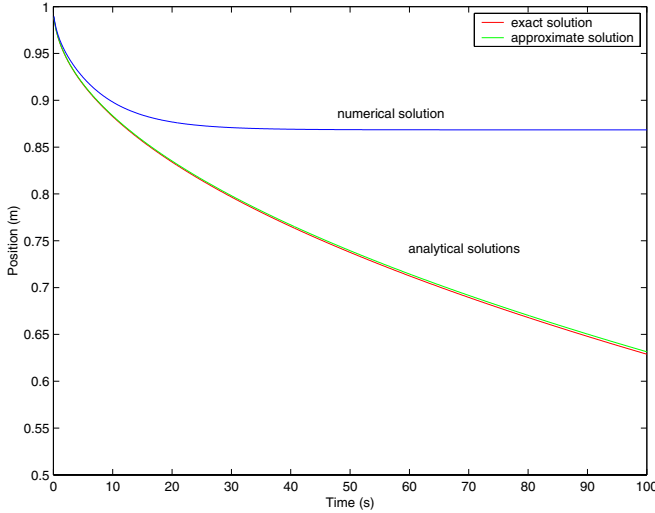
Fig. 2. The interface position as a function of time for the case that the diffusion matrix is not diagonalizable. The analytical and numerical solution are shown

can be seen that the difference between both analytical approaches is very small for the following data-set that is used for the calculations:

$$\underline{c}^0 = (0, 0)^T, \quad \underline{c}^{\mathrm{part}} = (50, 50)^T,$$

$$D = \begin{pmatrix} 2 & 1 \\ 0 & 2 \end{pmatrix}, \qquad K = 1.$$

The eigenvalue of the above matrix is equal to 2 and the matrix is not diagonalizable. In Fig. 2 a comparison is shown with the numerical solution (see Sect. 4). The interface concentration starts with $\underline{c}^s = (0.8673, 1.1560)^T$. It can be seen that the agreement is perfect in the initial stages. However, the solutions start to deviate at later stages where soft impingement starts to play an important role. Finally, we remark that the above treatment can be extended to the more general case of n simultaneously diffusing alloying elements.

6 Application to a Finite Element Model

In applications a one-dimensional approach is not always suitable (see [12] for instance where three-dimensional effects have to be taken into account). We limit ourselves to rotational symmetry such that the model only contains two spatial co-ordinates. The geometry is sketched in Fig. 3. The chemical composition of the two phases are different. The cylindrical particle only dissolves at the rim, whereas the spherical particle grows. Note that we have two moving boundaries in this example. We consider a ternary alloy with artificial input data:

$$D = \begin{pmatrix} 1 & -0.1 \\ -0.1 & 2 \end{pmatrix}, \quad \underline{c}^0 = (5, 5)^T,$$

$$\underline{c}^{\mathrm{part}} = (50, 50)^T, \quad K_S = 1, \quad K_C = 50. \tag{13}$$

Here K_S and K_C respectively denote the solubility product of the spherical particle and cylindrical plate. As initial ge-
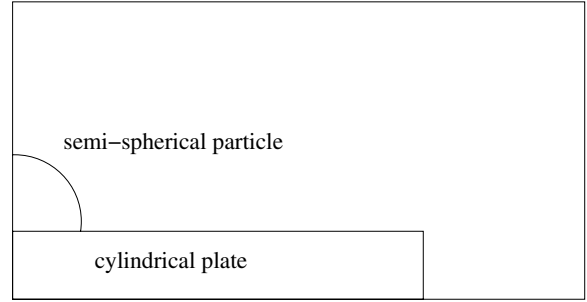

Fig. 3. Sketch of the initial geometry of the growing semi-spherical particle and the dissolving cylindrical plate. Note that we have rotational symmetry
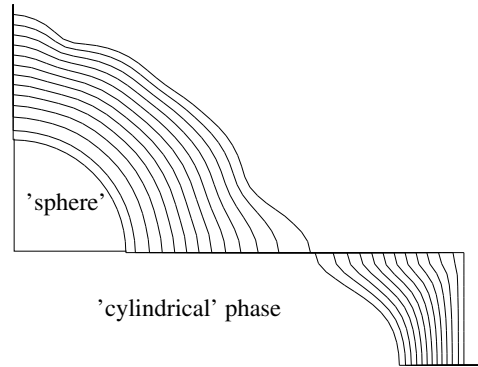

Fig. 4. Simultaneous growth of a 'spherical' particle and decay of a 'cylindrical' phase at consecutive times. Input data are as given in (13). Further, only the area in the vicinity of the moving interfaces is shown

ometrical data we used a sphere with radius 1 and a cylindrical plate with radius 4. The initial cylinder height is 1 and the whole domain measures 5×5. Further the sizes are in micrometer and the diffusion coefficients are in terms of $\mu m^2/s$. Since the Finite Element Code that we use here is not applicable to this vector-valued Stefan problem yet, we solve the diffusion equation for one element only. Furthermore, we assume that interface concentrations are constant in time and position. To obtain the interface concentrations, we solve the equations in problem (P_2) after the use of the diagonalization argument. The transformed interface and particle concentration and eigenvalue of one element is used in the two-dimensional Finite Element code SEPRAN to compute the evolution of the interfaces. The result is shown in Fig. 4. As time proceeds the real interface concentrations are a function of time. Furthermore, it can be seen that in Fig. 4 that the growing spherical phase exhibits a fingering behavior, i.e. the interface is unstable. As the off-diagonal terms of the diffusion matrix become more negative, the movement of the two interfaces is delayed.

7 Conclusions

A model based on a vector-valued Stefan problem has been developed to predict the dissolution kinetics of stoichiometric particles in multi-component alloys. Cross-diffusion is taken into account, which gives a strong coupling between the diffusion equations of the several alloying elements. A diagonalization of the diffusion matrix leads to a vector-valued Stefan problem with a weaker coupling. If the off-diagonal entries of the diffusion matrix are negative, then the delay of particle

dissolution due to these terms increases as the magnitude of the off-diagonal entries increase.

Future work will be the implementation of vector-valued Stefan problems into the Finite Element Method for two and three spatial co-ordinates.

References

1. Chadam, J., Rasmussen, H.: Free boundary problems involving solids. Scientific & Technical Harlow: Longman 1993
2. Chen, S., Merriman, B., Osher, S., Smereka, P.: A simple level-set method for solving Stefan problems. J. Comp. Phys. 135, 8–29 (1997)
3. Crank, J.: Free and moving boundary problems. Oxford: Clarendon Press 1984
4. Farkas, M.: Two ways of modelling cross-diffusion. Nonlin. Anal., theory, methods and applications 30, 1225–1233 (1997)
5. Glicksman, M.E.: Diffusion in solids. New York: John Wiley and Sons 2000
6. Golub, G.H., van Loan, C.F.: Matrix Computations. Baltimore: The Johns Hopkins University Press 1996
7. Grafe, U., Bottger, B., Tiaden, J., Fries, S.G.: Coupling of multi-component thermodynamic databases to a phase-field model: application to solidification and solid state transformations of superalloys. Scrip. Mater. 42(12), 1179–1186 (2000)
8. Kale, G.B., Bhanumurthy, K., Khera, S.K., Asundi, M.K.: Ternary diffusion in FCC phase of Fe-Ni-Cr alloy system at 1223 K. Mater. Trans., JIM 32(11), 1034–1041 (1991)
9. Kassab, A.J.: Stefan and moving front problems. Oxford: Elsevier Applied Science 1995
10. Kirkaldy, J.S., Young, D.J.: Diffusion in the condensed state. London: The Institute of Metals 1987
11. Kobayashi, R.: Modeling and numerical simulations of dendritic crystal growth. Phys. D 63, 410–423 (1993)
12. Kuijpers, N.C.W., Vermolen, F.J., Vuik, C., van der Zwaag, S.: A model of the β-AlFeSo to α-Al(FeMn)Si transformation in Al-Mg-Si alloys. in preparation (2003)
13. Murray, W.D., Landis, F.: Numerical and machine solutions of transient heat conduction problems involving freezing and melting. Transactions ASME (C), Journal of heat transfer 245, 106–112 (1959)
14. Naumann, E.B., Savoca, J.: An engineering approach to an unsolved problem in multi-component diffusion. AICHE Journal 47(5), 1016–1021 (2001)
15. Nolfi, F.V. jr., Shewmon, P.G., Foster, J.S.: The dissolution and growth kinetics of spherical particles. Trans. Metall. Soc. of AIME 245, 1427–1433 (1969)
16. Osher, S., Sethian, J.A.: Fronts propagating with curvature-dependent speed: Algorithms based on Hamilton-Jacobi formulations. J. Comp. Phys. 79, 12–49 (1988)
17. Protter, M.H., Weinberger, H.F.: Maximum principles in differential equations. Englewood Cliffs: Prentice-Hall 1967
18. Reiso, O., Ryum, N., Strid, J.: Melting and dissolution of secondary phase particles in AlMgSi-alloys. Metall. Trans. A 24A, 2629–2641 (1993)
19. van Til, W., Vuik, C., van der Zwaag, S.: An inventory of numerical methods to model solid-solid phase transformations in aluminium alloys. NIMR-report number P.004.001, Delft, (2000)
20. Vermolen, F.J., Vuik, C.: A numerical method to compute the dissolution of second phases in ternary alloys. J. Comput. Appl. Math. 93, 123–143 (1998)
21. Vermolen, F.J., Vuik, C.: A mathematical model for the dissolution of particles in multi-component alloys. J. Comput. Appl. Math. 126, 233–254 (2001)
22. Vermolen, F.J., Vuik, C., van der Zwaag, S.: Some mathematical aspects of particle dissolution and cross-diffusion in multi-component alloys. Delft University of Technology, Department of Applied Mathematical Analysis 01–13, (2001) Delft, The Netherlands
23. Vermolen, F.J., Vuik, C., van der Zwaag, S.: Particle dissolution and cross-diffusion in multi-component alloys. Mater. Sc. and Engng. A, 347(1–2), 265–279 (2003)
24. Visintin, A.: Models of phase transitions, Progress in nonlinear differential equations and their application. Boston: Birkhäuser 1996, p. 38
25. Whelan, M.J.: On the kinetics of particle dissolution. Met. Sc. 3, 95–97 (1969)