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SOME MATHEMATICAL ASPECTS OF PARTICLE DISSOLUTION AND CROSS-DIFFUSION

IN MULTI-COMPONENT ALLOYS

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Some mathematical aspects of particle dissolution and cross-diffusion in multi-component alloys

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Abstract

A general model for the dissolution of stoichiometric particles, taking into account the influences of cross-diffusion, in multi-component alloys is proposed and analyzed using a diagonalisation argument. We give a self-similar solution for the resulting Stefan-problem and state when the solutions are mass-conserving. We also give criteria for well-posed models on cross-diffusion. Furthermore, we show that particle dissolution in multi-component alloys can under certain circumstances be approximated by a model for particle dissolution in binary alloys.

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

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dissolved, is required to obtain a microstructure suited to undergo heavy plastic deformation as an optimal starting condition for a subsequent precipitation hardening treatment. Such a homogenization treatment, to name just a few examples, is applied in hot-rolling of Al killed construction steels, HSLA steels, all engineering steels, as well as aluminium extrusion alloys. Although precipitate dissolution is not the only metallurgical process taking place, it is often the most critical of the occurring processes. The minimum temperature at which the annealing should take place can be determined from thermodynamic analysis of the phases present. The minimum annealing time at this temperature, however, is not a constant but depends on particle size, particle geometry, particle concentration, overall composition etc.

Due to the scientific and industrial relevance of being able to predict the kinetics of particle dissolution, many models of various complexity [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17] have been presented and experimentally validated. In recent years the simpler models covering binary and ternary alloys have been extended to cover multi-component particles [18, 19, 20]. These advanced models cover a range of physical assumptions concerning the dissolution conditions and the initial microstructure. Furthermore, mathematical implications (such as a possible bifurcation of the solution, monotonicity of the solution and well-posedness) are addressed and mathematically sound extensions to the case of n compound particles, with proven theorems concerning existence of mass-conserving solutions and solution bounds, have been derived.

The current paper aims at being descriptive about the implications of the mathematics of these more complex particle dissolution models. First we formulate the model for particle dissolution in multi-component alloys in which cross-diffusion of the alloying elements is taken into account. Using diagonalisation, we show that the case of cross-diffusion can be formulated similarly to the case where no cross-diffusion takes place, only the thermodynamic relation for the interfacial (equilibrium) concentrations changes. We analyze its well-posedness and existence of solutions. Subsequently, we give asymptotic solutions for the dissolution of a planar particle. Furthermore, we show that under certain circumstances the multi-component problem (a 'vector-valued' Stefan problem) can be approximated by a binary problem ('scalar' Stefan problem). Finally some conclusions are formulated.

2   Basic assumptions in the model

The as-cast microstructure is simplified into a representative cell containing the 'matrix' of phase α and a single particle of phase β of a specific form, size and location of the cell boundary. The particle volume We consider a particle of a multi-component β phase surrounded by a 'matrix' of phase α. The particle volume fraction in this representative cell is equal to that in the real metal. Also the composition of the matrix is taken such that it reflects the situation in the real metal. Both a uniform and a spatially varying composition can be assumed in the model. The boundary between the β-particle and α-matrix is referred to as the interface. Particle dissolution is assumed to proceed by a number of the subsequent steps [9, 11]: decomposition of the particle, atoms from the particle crossing the interface and diffusion of these atoms in(to) the α-phase. Here we take the effects of cross-diffusion into account. We assume in this work that the first two mechanisms proceed sufficiently fast with respect to diffusion. Hence, the interfacial concentrations are those as predicted by thermodynamics (local equilibrium).

In [20] 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 an n-dimensional Gibbs hyperspace has to be made. The Gibbs surfaces become hypersurfaces. We expect that similar consequences follow 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:

$$(c_1^{\text{sol}})^{m_1}(c_2^{\text{sol}})^{m_2}(...)(c_n^{\text{sol}})^{m_n} = K = K(T). \tag{1}$$

The factor K is referred to as the solubility product. It depends on temperature T according to an Arrhenius relationship.

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 (the cell size). 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 described with (semi) explicit expressions. The spatial co-ordinate is denoted by r, $0 \leq S(t) \leq r \leq M$. This domain is referred to as $\Omega(t) := \{r \in \mathbb{R} : S(t) \leq r \leq M\}$. The α-matrix where diffusion takes place is given by $\Omega(t)$ and 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)

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

Above equations follow from thermodynamic considerations, their derivation can for instance be found in [21, 3]. 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. The diffusion matrix D is notated as follows:

$$D = \begin{pmatrix} D_{11} & \dots & D_{1n} \\ \dots & \dots & \dots \\ D_{n1} & \dots & D_{nn} \end{pmatrix}.$$

This relaxes the assumption that the alloying elements diffuse independently. When cross-diffusion is neglected, the diffusion matrix is diagonal. 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)

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

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

it, i.e.

$$\frac{\partial c_i}{\partial r} = 0, \text{ for } i \in \{1, ..., n\}. \tag{3}$$

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 [16]. The dissolution rate (interfacial velocity) is obtained from a mass-balance of the atoms of alloying element i. The mass-balance per unit area leads to

$$(S(t + \Delta t) - S(t))c_i^{\text{sol}} = (S(t + \Delta t) - S(t))c_i^{\text{part}} - \sum_{j=1}^{n} D_{ij} \frac{\partial c_j}{\partial r} \Delta t.$$

Division by Δt gives

$$\frac{(S(t + \Delta t) - S(t))}{\Delta t}(c_i^{\text{part}} - c_i^{\text{sol}}) = \sum_{j=1}^{n} D_{ij} \frac{\partial c_j}{\partial r}.$$

Subsequently we take the limit $\Delta t \to 0$ and we obtain the following equation for the interfacial velocity

$$(c_i^{\text{part}} - c_i^{\text{sol}})\frac{dS}{dt} = \sum_{j=1}^{n} D_{ij} \frac{\partial c_j}{\partial r}(S(t), t).$$

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

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

$$\tag{4}$$

The right-hand 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 coupling exists in both the diffusion equations, equation of motion 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 [22], Chadam and Rasmussen [23] and Visintin [24].

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. Therefore, we first give some analytical results for the binary case, in which we consider diffusion of one alloying element only. Next we consider the 'degenerate' vector-valued Stefan problem where one of the diffusivities is zero, where loss of uniqueness of the solution results. Subsequently 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 diagonalisation. We end up with some remarks concerning the case when D is not diagonalizable.

3.1 The binary case

First we consider the case that one of the diffusion coefficients is equal to zero. The treatment is binary, i.e. we consider only one diffusing alloying element. The concentration in this section is denoted by u. Let the domain that includes the α-particle and β-phase be given by $x \in [0, M]$, then consider the following problem for $t > 0$

$$
\begin{cases}
\dfrac{\partial u}{\partial t} = D\dfrac{\partial^2 u}{\partial x^2}, & x \in (S(t), M), \\[2ex]
(u^{\text{part}} - u^{\text{sol}})\dfrac{dS}{dt} = D\dfrac{\partial u}{\partial x}(S(t), t), \\[2ex]
u(S(t), t) = u^{\text{sol}}, \\[2ex]
\dfrac{\partial u}{\partial n}(M, t) = 0, \\[2ex]
u = u^{\text{part}}, & x \in [0, S(t)).
\end{cases}
\tag{5}
$$

Here we assume that u^{sol} is a given constant. We now introduce the definition of a mass-conserving solution:

Definition 1 *A solution of the Stefan problem is called conserving if the solution satisfies*

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

With this definition of mass-conserving solutions we established the following proposition in [18]:

Proposition 1 *Let all concentrations, which are used in problem* (5)*, be non-negative, then the following combinations give non-conserving solutions in the sense of Definition 1:*

- $u^{sol} < u^{part} < u^0$,

- $u^0 < u^{part} < u^{sol}$.

Further, we call a solution allowable if it satisfies the following definition:

Definition 2 *A solution of the Stefan problem is allowable if and only if it is both mass conserving in the sense of Definition 1 and asymptotically stable with respect to perturbations.*

Problems that have only non-allowable solutions are called ill-posed. Some results on mass conserving solutions are proven in [18] and [25]. It is well-known that whenever the diffusion coefficient D is negative, then the solution is not stable with respect to perturbations. This implies that the case $D < 0$ is ill-posed in the sense of Definition 2.

Let us consider the case $D = 0$, which may happen after a diagonalisation when the diffusion matrix is singular. For $D = 0$, the one-dimensional version of problem (5) changes into

$$
\begin{cases}
\dfrac{\partial u}{\partial t} = 0, & x \in (S(t), M) \\[2mm]
u(S(t), t) = u^{\text{sol}}, \\[2mm]
\dfrac{\partial u}{\partial x}(M, t) = 0, \\[2mm]
u = u^{\text{part}}, & x \in [0, S(t)).
\end{cases}
\tag{6}
$$

We assume that the function that describes the interface position S is smooth in a time-interval $[0, T]$, i.e.

$$(C) : S \in C^1(0, T) \cap C^0[0, T].$$

Now we show that $D = 0$ never allows growth of the β-particle. First, we need the following Lemma for the proof of this assertion:

Lemma 1 *Let S satisfy smoothness (C),*

1. *suppose $S(\hat{t}) > S(0)$, then there exists a minimal $t = \tilde{t}$, such that $S(\tilde{t}) = S(\hat{t})$ and $S(t) < S(\tilde{t})$ for all $t \in (0, \tilde{t})$,*

2. *suppose $S(\hat{t}) < S(0)$, then there exists a minimal $t = \tilde{t}$, such that $S(\tilde{t}) = S(\hat{t})$ and $S(t) > S(\tilde{t})$ for all $t \in (0, \tilde{t})$.*

Proof: Let $V \subset (0, \hat{t}]$ be the set that contains the times that $S(t) \geq S(\hat{t})$, i.e.

$$V := \{t \in (0, \hat{t}] : S(t) \geq S(\hat{t})\}.$$

The existence of a minimal $t = \tilde{t}$, amounts to the establishing of the existence of a minimum for V. Since all t are positive, $t = 0$ is a lower bound of V. Further $\hat{t} \in V$ and thus $V \neq \emptyset$. First we show that V is closed and since it has a lower bound, it follows from the completeness axiom (see for instance [26, 27]) that V has a minimum. To show that V is closed, we show that its complement within $(0, \hat{t}]$, $V^c := (0, \hat{t}] \setminus V$, is open. Suppose that $\bar{t} \in V^c$, then $S(\bar{t}) < S(\hat{t})$. Since S is continuous (see (C)), it follows that there exists $\delta > 0$ such that $S(t) < S(\hat{t}), \forall |t - \bar{t}| < \delta$. Since this holds for each $\bar{t} \in V^c$, the set V^c is open and hence V is a closed set. This implies the existence of a minimum of V and hence $\tilde{t}$ exists as a minimal t such that $S(t) < S(\tilde{t}) = S(\hat{t})$ for all $t \in (0, \tilde{t}]$ and the first part of Lemma 1 is proven. The proof of the second part of Lemma 1 is analogous. $\square$

Theorem 1 *Let $S(t)$ satisfy smoothness (C) and let the equations in (6) be satisfied, then*

1. *$S(\hat{t}) \leq S(0)$ for any $\hat{t} \in [0, T]$ if $u^{part} \neq u^0$,*

2. *S is undetermined if $u^{part} = u^0$.*

Proof: By contradiction, suppose $S(\hat{t}) > S(0)$ and suppose that S satisfies smoothness (C), then, according to Lemma 1, there exists a $\tilde{t} \in (0, \hat{t})$ such that $S(\tilde{t}) = S(\hat{t})$ and $S(t) < S(\tilde{t})$ for all $t \in (0, \tilde{t})$. Since $u = u^{part}$ whenever $x \in [0, S(t))$, Definition 1 implies

$$u^{part}S(0) + (M - S(0))u^0 = S(\tilde{t})u^{part} + (M - S(\tilde{t}))u^0,$$

implying
$$(u^{part} - u^0)(S(0) - S(\tilde{t})) = 0.$$

This implies either $u^0 = u^{part}$ or $S(\tilde{t}) = S(0)$. First we assume that $u^{part} \neq u^0$, then $S(\tilde{t}) = S(0)$, which contradicts the assertion $S(\tilde{t}) > S(0)$ and the first part of the theorem is proven. Furthermore, if $u^{part} = u^0$ holds, then $S(\hat{t})$ is undetermined. This proves the second part of the theorem. □

Theorem 2 *Let S satisfy smoothness (C) and the equations in (6) be satisfied, then*

1. *$S(\hat{t}) = S(0)$ whenever $u^{sol} \neq u^{part} \neq u^0$;*

2. *$S(\hat{t})$ is undetermined, but $S(\hat{t}) \leq S(0)$, if $u^{sol} = u^{part} \neq u^0$.*

Proof: From Theorem 1 follows that $S(\hat{t}) \leq S(0)$ whenever $u^{part} \neq u^0$. Suppose that $S(\hat{t}) < S(0)$, then from Lemma 1 follows that there exists $\tilde{t}$ such that $S(\tilde{t}) = S(\hat{t})$ and $S(t) > S(\tilde{t})$ for all $t \in (0, \hat{t})$. From Definition 1 follows

$$u^{part}S(0) + (M - S(0))u^0 = S(\tilde{t})u^{part} + \int_{S(\tilde{t})}^{S(0)} u(x, t)dx + (M - S(0))u^0, \qquad (7)$$

Since $\dfrac{\partial u}{\partial t} = 0$ for $x > S(\tilde{t})$, the integral in the above equation can be written by

$$\int_{S(\tilde{t})}^{S(0)} u(x, t)dx = (S(0) - S(\tilde{t}))u^{sol},$$

and the equation of mass-conservation, equation (7), changes into

$$(*) \qquad (u^{part} - u^{sol})(S(0) - S(\tilde{t})) = 0.$$

Hence $u^{sol} = u^{part}$ or $S(\tilde{t}) = S(0)$. Suppose that $u^{sol} \neq u^{part}$, then $S(\tilde{t}) = S(0)$ and the first part of the theorem is proven. Further, if $u^{sol} = u^{part}$, then (*) holds for all $S(\tilde{t}) = S(\hat{t})$ and hence this quantity is undetermined, which proves the second part of the theorem. Note from Theorem 1 that then $S(\hat{t}) \leq S(0)$. □

The above theorem implies that $S(t)$ is non-moving if $u^{part} \neq u^{sol}$, otherwise, whenever $u^{part} = u^{part}$, the function S is undetermined and hence uniqueness is violated. Similarly, whenever $u^{part} = u^0$, the solution is undetermined. We state this result in the following corollary:

Corollary 1 *The solution of problem (6) is not uniquely defined when $u^{sol} = u^{part}$ or $u^{part} = u^0$.*

3.2 The 'degenerate' vector-valued Stefan problem

We now consider the vector-valued Stefan problem as constituted by equations (1),(2),(3) and (4). We start by analyzing the case that one of the diffusivities is equal to zero, say $D_1 = 0$. When one of the diffusivities is zero, we refer to the problem as being 'degenerate'. First we remark that $S(t) > S(0)$ gives a contradiction with regard to Theorem 1. Hence we know that $S(t) \leq S(0)$. We will now prove the following theorem:

Theorem 3 *Let $S(t)$ satisfy smoothness condition (C), then the problem as constituted by equations (1), (2), (3) and (4), supplemented with initial conditions $u_j^0 \neq 0$ for $j \in \{2, \ldots, n\}$, has a solution, $S(t) = S(0)$, when one of the diffusivities is zero, say $D_1 = 0$.*

Proof: Suppose that $S(t) = S(0)$ for $t \in [0, T]$, then $S(t)$ is known, and from (4) follows when $u_1^{\text{sol}} \neq u_1^{\text{part}}$

$$0 = S'(t) = \frac{D_1}{u_1^{\text{part}} - u_1^{\text{sol}}} \frac{\partial u_1}{\partial x}(S(t), t) = \frac{D_j}{u_j^{\text{part}} - u_j^{\text{sol}}} \frac{\partial u_j}{\partial x}(S(t), t) \text{ for } j \in \{2, \ldots, n\}.$$

Since generally $D_j \neq 0$ for $j \in \{2, \ldots, n\}$, this implies

$$\frac{\partial u_j}{\partial x}(S(t), t) = 0, \text{ for } j \in \{2, \ldots, n\}, t \in [0, T].$$

Since $\dfrac{\partial u_j}{\partial x} = 0$ for both $x = S(t) = S(0)$ and $x = M$, and $u_j(x, 0) = u_j^0$ for $x \in [0, M]$, it follows from the maximum principle of the diffusion equation (see Protter and Weinberger [28])

$$u_j(x, t) = u_j^0, \text{ for } j \in \{2, \ldots, n\},$$

and

$$u_j^{\text{sol}}(x, t) = u_j^0, \text{ for } j \in \{2, \ldots, n\}.$$

The concentration u_1^{sol} is determined from relation (1) using the above values for u_j^{sol}, $j \in \{2, \ldots, n\}$. Further from relation (1) it is clear that when $u_j^0 = 0$ for any $j \in \{2, \ldots, n\}$ $S(t) = S(0)$ is not a solution (u_1^{sol} is not bounded then). $\qquad \square$

Suppose now, under hypothesis of Theorem 2, $S(t) \leq S(0)$ for $0 < t \leq T$, suppose further that there exists a $t = \hat{t}$ such that $S(\hat{t}) < S(0)$, then from Lemma 1 there exists a $\tilde{t} \in (0, \hat{t})$ such that $S(\tilde{t}) = S(\hat{t})$ and $S(t) > S(\tilde{t})$ for all $t \in (0, \tilde{t})$. Definition 1 then gives for mass-conserving solutions

$$S(0)u_1^{\text{part}} + (M - S(0))u_1^0 = S(\tilde{t})u_1^{\text{part}} + \int_{S(\tilde{t})}^{S(0)} u_1(x, t)dx + (M - S(0))u_1^0.$$

Since $u_1(S(t), t) = u_1^{\text{sol}}$ and $\dfrac{\partial u_1}{\partial x} = 0$, the above equation changes into

$$(S(0) - S(\tilde{t}))u_1^{\text{part}} = \int_{S(\tilde{t})}^{S(0)} u_1^{\text{sol}}(x, t)dx.$$

Suppose $u_1^{\text{sol}} = u_1^{\text{part}}$, then the above equation is satisfied. Knowing the value of $u_1^{\text{sol}} = u_1^{\text{part}}$, then the other interfacial concentrations $\{u_2^{\text{sol}}, \ldots, u_n^{\text{sol}}\}$ are determined from the problem defined by (1), (2), (3) and (4). If the values of $\{u_2^{\text{sol}}, \ldots, u_n^{\text{sol}}\}$ are such that $\dfrac{dS}{dt} \leq 0$ (see [18]), then from Theorem 1, there exists a solution $S(t) < S(0)$ and hence at least two solutions are possible. Hence, uniqueness is violated for this case. Furthermore, there possibly also exist non-monotonous solutions. We summaries this in the following remark:

Remark 1 *Under hypothesis of Theorem 3, the solution may not be unique.*

We further remark that the condition of 'non-growing' solutions, i.e. $\dfrac{dS}{dt} \leq 0$ implies that the solutions are allowable in the sense of Definition 1 (see also Proposition 1). We just established in this subsection that when one of the diffusivities is zero and when the initial concentrations are non-zero then a non-moving boundary is a possible solution. Further, under some circumstances the solution may not be unique. Therefore, this is not likely to be a very interesting case from a metallurgical point of view.

3.3 The vector-valued Stefan problem: decomposition of the diffusion matrix

Subsequently, we change into a vector notation of the equations. We define the vectors $\underline{c} := (c_1, c_2, \ldots \ c_n)^T$, $\underline{c}^p := (c_1^{\text{part}}, c_2^{\text{part}}, \ldots \ , c_n^{\text{part}})^T$, $\underline{c}^s := (c_1^{\text{sol}} \ c_2^{\text{sol}} \ \ldots \ , c_n^{\text{sol}})^T$, then the diffusion equations become in vector notation

$$\frac{\partial}{\partial t}\underline{c} = \frac{1}{r^a}\frac{\partial}{\partial r}\left\{r^a D\frac{\partial}{\partial r}\right\}\underline{c}. \tag{8}$$

In the above equation the diffusion matrix, D, is assumed to be independent of the concentrations, time and position. The boundary and initial conditions follow similarly in vector notation. The equation of motion of the interface becomes in vector notation:

$$(\underline{c}^p - \underline{c}^s)\frac{dS}{dt} = \frac{\partial}{\partial r}D\underline{c}(S(t), t).$$

To analyze equation (8) it is convenient to look at a decomposition of the diffusion matrix D. Therefore we use the Decomposition Theorem in linear algebra, which says 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. We refer to Birkhoff and MacLane [29] for the proof of the theorem. For cases where D has n independent eigenvectors, i.e. D is diagonalizable, Λ is diagonal with the eigenvalues of D on the main diagonal. Further, the columns of the matrix P consists of the eigenvectors of D. In the more general case of a Jordan decomposition we have that the matrix P consists of the generalized eigenvectors of D, which are obtained from solution of

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

where $I \in \mathbb{R}^{n \times n}$ 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.

Substitution of the decomposition of D into Eq.(8) gives

$$\frac{\partial}{\partial t}\underline{c} = \frac{1}{r^a}\frac{\partial}{\partial r}\left\{r^a\frac{\partial}{\partial r}\right\}P\Lambda P^{-1}\underline{c} \Leftrightarrow \frac{\partial}{\partial t}P^{-1}\underline{c} = \frac{1}{r^a}\frac{\partial}{\partial r}\left\{r^a\frac{\partial}{\partial r}\right\}\Lambda P^{-1}\underline{c}$$

$$(\underline{c}^p - \underline{c}^s)\frac{dS}{dt} = \frac{\partial}{\partial r}P\Lambda P^{-1}\underline{c}(S(t),t) \Leftrightarrow P^{-1}(\underline{c}^p - \underline{c}^s)\frac{dS}{dt} = \frac{\partial}{\partial r}\Lambda P^{-1}\underline{c}(S(t),t).$$

We define the transformed concentrations as

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

then the diffusion equation and equation of motion change into

$$\frac{\partial}{\partial t}\underline{u} = \frac{1}{r^a}\frac{\partial}{\partial r}\left\{r^a\frac{\partial}{\partial r}\right\}\Lambda\underline{u}$$

$$\tag{9}$$

$$(\underline{u}^p - \underline{u}^s)\frac{dS}{dt} = \frac{\partial}{\partial r}\Lambda\underline{u}(S(t),t).$$

Above equations involve Jordan matrices with the eigenvalues of the diffusion matrix. For non-defective matrices, with n linearly independent eigenvectors, the matrix in the above expressions is diagonal and the system is fully uncoupled. Hence the strong coupling in the partial differential equations has been reduced herewith. 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 $t = 0$

$$u_j = \begin{cases} u_j^0, & \text{for } x \in \Omega(0), \\ u_j^{\text{part}}, & \text{for } x \in [0, M] \setminus \Omega(0). \end{cases} \quad j \in \{1, \ldots, n\}$$

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

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

Although this condition becomes more complicated, the analysis is facilitated using the diagonalisation of the diffusion matrix.

In the Jordan-matrix we have one uncoupled concentration for each eigenvalue of D. This implies that whenever one eigenvalue is negative, an uncoupled diffusion equation with a negative diffusivity results for the decomposed system. In other words, we face the following equation

$$\frac{\partial u_i}{\partial t} = -\mu\frac{1}{r^a}\frac{\partial}{\partial r}\left\{r^a\frac{\partial u_i}{\partial r}\right\}, \quad \text{with } \mu := -\lambda < 0, \text{ for } x \in \Omega(t), t > 0.$$

It is well-known that the above equation is unstable with respect to perturbations and hence

the problem is ill-posed. This motivates the requirement that the eigenvalues of the diffusion matrix have to be non-negative.

For the case that one of the eigenvalues is zero, then we have an uncoupled equation without diffusion, i.e.

$$\frac{\partial u_i}{\partial t} = 0, \text{ for } x \in \Omega(t), t > 0.$$

Theorem 4 *Let S satisfy smoothness (C), then the problem as constituted by equations (9) and (10), supplemented with initial conditions $c_j^0 \neq 0$ for $j \in \{2, \ldots, n\}$ and homogeneous Neumann boundary conditions at $x = M$, has a solution $S(t) = S(0)$ when one of the diffusivities is zero, say $D_1 = 0$.*

Proof: The proof of the theorem is analogous to the proof of the Theorem 3, where the hyperbolic relation between the set $\{u_1^{\text{sol}}, \ldots, u_n^{\text{sol}}\}$ differs and where we must have $c_j^0 \neq 0$ for $j \in \{2, \ldots, n\}$ to avoid a contradiction with the existence of a solution $S(t) = S(0)$. Note that u_1^0 is allowed to be zero provided that $c_j^0 \neq 0$ for $j \in \{2, \ldots, n\}$. □

As a consequence of the above result, we will restrict ourselves to the treatment of a matrices, D, which have real and positive eigenvalues. If D is symmetric and diagonally dominant, then it follows from Gerschgorin's Theorem that the matrix positive definite and hence its eigenvalues are positive.

Furthermore, from the Spectral Theorem in standard linear algebra follows that if $D \in \mathbb{R}^{n \times n}$ is symmetric then D is diagonalizable, the eigenvalues are real and $P^{-1} = P^T$. For this case above relation changes into

$$D = P\Lambda P^T.$$

3.4 The non-diagonazible case

We explain this for the ternary case, i.e. $D \in \mathbb{R}^{2 \times 2}$, first with non-moving boundaries. In Section 4 we will treat the case where the boundary moves. The Jordan decomposition then gives

$$\Lambda = \begin{pmatrix} \lambda & 1 \\ 0 & \lambda \end{pmatrix},$$

where we only consider $\lambda > 0$. Hence the system of 2 equation is reduced to for $x \in (0, 1), t > 0$:

$$\begin{cases} \dfrac{\partial u}{\partial t} = \lambda \dfrac{\partial^2 u}{\partial x^2} \\[2mm] \dfrac{\partial v}{\partial t} = \lambda \dfrac{\partial^2 v}{\partial x^2} + \dfrac{\partial^2 u}{\partial x^2}. \end{cases} \tag{11}$$

We will fix the boundaries and consider smooth solutions of the above equations in the sense of

$$(S): \qquad u, v \in C^{2,1}((0,1) \times \mathbb{R}^+) \cap C^{1,0}([0,1] \times \mathbb{R}_0^+).$$

Furthermore, let us consider the following boundary- and initial conditions

$$(IBC) \begin{cases} u(0,t) = u^s, & v(0,t) = v^s, \\[2mm] u(x,0) = u^0, & v(x,0) = v^0, \\[2mm] \dfrac{\partial u}{\partial x}(1,t) = 0, & \dfrac{\partial v}{\partial x}(1,t) = 0. \end{cases}$$

The solution of the upper equation in (11) satisfies a maximum principle, i.e. u has no extreme for $x \in (0,1)$ and $t > 0$. A proof of this fact is given by Protter and Weinberger [28]. Since u satisfies a maximum principle and a homogeneous Neumann boundary condition at $x = 1$, it follows that u is concave-upward or concave-downward whenever $u^s > u^0$ or $u^s < u^0$ respectively, i.e.

$$\frac{\partial^2 u}{\partial x^2} > 0, \quad \text{whenever } u^s > u^0,$$

$$\frac{\partial^2 u}{\partial x^2} < 0, \quad \text{whenever } u^s < u^0.$$

For the function v we will show that an interior minimum cannot exist for any $x \in (0,1)$, $t > 0$ whenever $u^s > u^0$ and similarly no interior maximum cannot exist whenever $u^s < u^0$:

Proposition 2 *Let the functions u and v satisfy equations (11) and smoothness condition (S) with initial and boundary conditions (IBC), then*

1. *no internal minimum exists for v whenever u is concave-upward,*

2. *no internal maximum exists for v whenever u is concave-downward.*

Proof: Since u and v are smooth, it follows that an internal extreme, say for $(x,t) = (\hat{x}, \hat{t}) \in (0,1) \times \mathbb{R}^+$ is necessarily a stationary point, i.e. for v this gives $\dfrac{\partial v}{\partial t} = 0 = \dfrac{\partial v}{\partial x}$ for $(x,t) = (\hat{x}, \hat{t})$. Furthermore, for an extreme at $(\hat{x}, \hat{t})$ to be an internal (local) minimum we must have $\dfrac{\partial^2 v}{\partial x^2}(\hat{x}, \hat{t}) \geq 0$ and similarly for an internal (local) maximum we have $\dfrac{\partial^2 v}{\partial x^2}(\hat{x}, \hat{t}) \leq 0$. For any stationary point $(\hat{x}, \hat{t})$ for v we obtain from (11)

$$\lambda \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 v}{\partial x^2} = 0 \Leftrightarrow \lambda \frac{\partial^2 u}{\partial x^2} = -\frac{\partial^2 v}{\partial x^2} \text{ for } (x,t) = (\hat{x}, \hat{t}).$$

Suppose that $\dfrac{\partial^2 u}{\partial x^2}(\hat{x}, \hat{t}) > 0$, then $\dfrac{\partial^2 v}{\partial x^2}(\hat{x}, \hat{t}) < 0$ and hence an internal minimum cannot exist for $(\hat{x}, \hat{t})$. Since $\dfrac{\partial^2 u}{\partial x^2} > 0$ for $u^s > u^0$, an interior minimum cannot exist for v when $u^s > u^0$ and the first part of Proposition 2 is proven, the proof of the second part of Proposition 2 is analogous. □

We will derive, for the case of a 'half-infinite' domain, a criterion for u^s and u^0 for the existence of an internal extreme. For this semi-unbounded domain $x > 0$ and $t > 0$ we consider self-similar solutions in the form of $u, v(x,t) = \overline{u}, \overline{v}(\eta)$, $\eta := \dfrac{x}{\sqrt{t}}$. For simplicity we

will take $u^0 = 0 = v^0$. Substitution into (11) implies

$$\begin{cases} -\dfrac{\eta}{2}\overline{u}' = \lambda\overline{u}'' \\[3mm] -\dfrac{\eta}{2}\overline{v}' = \lambda\overline{u}'' + \overline{v}'' \end{cases} \tag{12}$$

Here we use as boundary conditions

$$(BC)\begin{cases} \overline{u}(0) = u^s, \quad \overline{v}(0) = v^s, \\[3mm] \lim_{\eta\to\infty} u(\eta) = 0 = \lim_{\eta\to\infty} v(\eta). \end{cases}$$

For simplicity we set $f = f(\eta) = \overline{u}'$ and $g = g(\eta) = \overline{v}'$, then we obtain the following solution for f:

$$f = C_1 e^{-\frac{\eta^2}{4\lambda}},$$

and for the function g we obtain the following linear differential equation:

$$g' + \frac{\eta}{2\lambda}g = \frac{\eta}{2\lambda^2}f$$

The above differential equation is solved using an integrating factor to obtain

$$g = \left(C_1\frac{\eta^2}{4\lambda^2} + C_2\right)e^{-\frac{\eta^2}{4\lambda}}.$$

Integration of the functions f and g gives:

$$\overline{v} = C_1\frac{1}{4\lambda^2}\int_0^\eta s^2 e^{-\frac{s^2}{4\lambda}}ds + C_2\int_0^\eta e^{-\frac{s^2}{4\lambda}}ds + D_1$$

$$\overline{u} = C_1\int_0^\eta e^{-\frac{s^2}{4\lambda}} + D_2$$

By partial integration the integral in the upper equation is computed to yield

$$\overline{v} = \frac{C_1}{2\lambda^2}\left(-\eta\lambda e^{-\frac{\eta^2}{4\lambda}} + \lambda\sqrt{\pi\lambda}erf(\frac{\eta}{2\sqrt{\lambda}})\right) + C_2\sqrt{\pi\lambda}erf(\frac{\eta}{2\sqrt{\lambda}}) + D_1$$

$$\overline{u} = C_1\sqrt{\pi\lambda}erf(\frac{\eta}{2\sqrt{\lambda}}) + D_2$$

The function $\overline{v}$ is monotonous whenever g does not change sign. Furthermore, $\overline{v}$ is monotonous if and only if v is monotonous in space and time. Using the boundary conditions the integration constants can be computed. For the function g then follows

$$g = g(\eta) = \overline{v}' = \left(\frac{1}{2}u^s - v^s - \frac{u^s}{4\lambda^2}\eta^2\right)\frac{e^{-\frac{\eta^2}{4\lambda^2}}}{\sqrt{\pi\lambda}}.$$

The above equation implies that $\overline{v}$ exhibits a (local) interior extreme whenever $\frac{1}{2}u^s - v^s > 0$. We summarize the result in Proposition 3:

Proposition 3 *Consider equations* (12) *for a semi-unbounded domain, supplemented with boundary conditions (BC), then the self-similar solution with $u, v(x,t) = \overline{u}, \overline{v}(\eta)$, $\eta := \dfrac{x}{\sqrt{t}}$ has an interior extreme whenever $\frac{1}{2}u^s - v^s > 0$.*

4   Similarity solutions and asymptotic approximations

In this section we consider the Stefan problem for each component. 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. We showed in [25] (see also Proposition 1) that solutions are not mass-conserving whenever

- $u_i^s < u_i^s < u_i^0$ for a certain $i \in \{1, \ldots, n\}$,

- $u_i^0 < u_i^p < u_i^s$ for a certain $i \in \{1, \ldots, n\}$.

Above conditions are used to reject solutions that are not physically correct. To facilitate the analysis we consider the Stefan problem on an unbounded domain in one Cartesian coordinate:

$$(P_1) \begin{cases} \dfrac{\partial}{\partial t}\underline{u} = \Lambda \dfrac{\partial^2}{\partial r^2}\underline{u} \\[2mm] (\underline{u}^p - \underline{u}^s)\dfrac{dS}{dt} = \Lambda \dfrac{\partial}{\partial r}\underline{u}(S(t),t) \\[2mm] \underline{u}(r,0) = \underline{u}^0, \qquad\qquad\qquad S(0) = S_0, \\[1mm] \underline{u}(S(t),t) = \underline{u}^s. \end{cases}$$

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. For both cases the domain is semi-infinite.

4.1   The exact solution of Neumann for the diagonalizable case

As an 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 [18], one obtains the solution for each component:

$$u_i = u_i^0 + (u_i^0 - u_i^s)\frac{\text{erfc}(\dfrac{r - S_0}{2\sqrt{\lambda_i t}})}{\text{erfc}(\dfrac{k}{2\sqrt{\lambda_i}})}, \qquad \text{for } i \in \{1, \ldots, n\}.$$

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

$$\frac{u_i^0 - u_i^s}{u_i^p - u_i^s} \cdot \sqrt{\frac{\lambda_i}{\pi}} \cdot \frac{e^{-\frac{k^2}{4\lambda_i}}}{\text{erfc}(\frac{k}{2\sqrt{\lambda_i}})} = \frac{k}{2}, \qquad \text{for } i \in \{1, \ldots, n\}.$$

Above equation is 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

$$
(P_2) \begin{cases} \dfrac{u_i^0 - u_i^s}{u_i^p - u_i^s} \cdot \sqrt{\dfrac{\lambda_i}{\pi}} \cdot \dfrac{e^{-\frac{k^2}{4\lambda_i}}}{\text{erfc}(\frac{k}{2\sqrt{\lambda_i}})} = \dfrac{k}{2}, & \text{for } i \in \{1, \ldots, n\}, \\[4mm] (\sum\limits_{j=1}^{n} p_{1j} u_j^s)^{m_1} (\sum\limits_{j=1}^{n} p_{2j} u_j^s)^{m_2} (\ldots)(\sum\limits_{j=1}^{n} p_{nj} u_j^s)^{m_n} = K = K(T). \end{cases}
$$

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 is in general not unique. We apply numerical zero-point methods to obtain the solution. To get insight in the qualitative aspects of the solution, we consider some approximate solutions in the next subsubsection.

4.2   An asymptotic solution for the diagonalizable case

Suppose that $||\underline{u}^s - \underline{u}^0|| \ll ||\underline{u}^p - \underline{u}^s||$, then the solution of problem (P_2) is approximated by the solution of

$$
(P_3) \begin{cases} k = 2\dfrac{u_i^0 - u_i^s}{u_i^p - u_i^s}\sqrt{\dfrac{\lambda_i}{\pi}}, & \text{for } i \in \{1, \ldots, n\}, \\[4mm] (\sum\limits_{j=1}^{n} p_{1j} u_j^s)^{m_1} (\sum\limits_{j=1}^{n} p_{2j} u_j^s)^{m_2} (\ldots)(\sum\limits_{j=1}^{n} p_{nj} u_j^s)^{m_n} = K = K(T). \end{cases}
$$

Above problem is to be solved using a zero-point method. Suppose that the initial concentrations are zero, then $\underline{u}^0 = \underline{0}$, further we assume that the transformed particle concentration is much larger than the transformed interfacial concentrations, i.e. $u_i^s \ll u_i^p$ for $i \in \{1, \ldots, n\}$, then it follows that the first equation of (P_3) becomes

$$
k \approx 2\frac{u_1^s}{u_1^p}\sqrt{\frac{\lambda_1}{\pi}}. \tag{13}
$$

Hence the equation of motion of the interface becomes

$$
\frac{dS}{dt} \approx -\frac{u_1^s}{u_1^p}\sqrt{\frac{\lambda_1}{\pi t}}. \tag{14}
$$

Further, the following recurrence relation between the transformed interfacial concentrations follows (see also [18], [30] for the derivation):

$$
u_i^s = \frac{u_i^p}{u_1^p}\sqrt{\frac{\lambda_1}{\lambda_i}}u_1^s.
$$

Substitution of above transformed interfacial concentrations into the second equation of (P_3) gives the following real-valued solution

$$u_1^s = \left(\frac{K}{\left(\sum_{j=1}^{n} p_{1j} \frac{u_j^p}{u_1^p} \sqrt{\frac{\lambda_1}{\lambda_j}} \right)^{m_1} \left(\sum_{j=1}^{n} p_{2j} \frac{u_j^p}{u_1^p} \sqrt{\frac{\lambda_1}{\lambda_j}} \right)^{m_2} (\ldots) \left(\sum_{j=1}^{n} p_{nj} \frac{u_j^p}{u_1^p} \sqrt{\frac{\lambda_1}{\lambda_j}} \right)^{m_n}} \right)^{\frac{1}{\mu}},$$

where we defined $\mu := \sum_{j=1}^{n} m_j$. Above expression for the transformed interfacial concentration is substituted into the rate equation for the interface (13). This gives

$$\frac{dS}{dt} = -\frac{1}{u_1^p} \left[\prod_{k=1}^{n} \frac{K}{\left(\sum_{j=1}^{n} \left(p_{kj} \frac{u_j^p}{u_1^p} \sqrt{\frac{\lambda_1}{\lambda_j}} \right) \right)^{m_k}} \right]^{\frac{1}{\mu}} \sqrt{\frac{\lambda_1}{\pi t}}.$$

In above equation we put the factors u_1^p and λ_1 out of the summation and product in the denominator. Furthermore subsequent multiplication of both the denominator and numerator by $\prod_{k=1}^{n} \left(\sqrt{\lambda_k} \right)^{1/\mu}$ gives

$$\frac{dS}{dt} = -\frac{c_{\text{eff}}^{\text{sol}}}{c_{\text{eff}}^{\text{part}}} \sqrt{\frac{D_{\text{eff}}}{\pi t}}, \tag{15}$$

where

$$c_{\text{eff}}^{\text{sol}} = K^{1/\mu}, \ D_{\text{eff}} = \left[\prod_{i=1}^{n} (\lambda_k)^{m_i} \right]^{1/\mu}, \ c_{\text{eff}}^{\text{part}} = \left[\prod_{k=1}^{n} \left(\sum_{j=1}^{n} \left(p_{kj} u_j^p \sqrt{\frac{\lambda_k}{\lambda_j}} \right) \right) \right]^{1/\mu}. \tag{16}$$

Above equation (16) gives the effective interfacial concentration, effective particle concentration and effective diffusivity. These quantities follow in terms of the solubility product, transformed particle concentrations and the eigenvalues and eigenvectors of the diffusion matrix. The differential equation (15) is solved using separation of variables. Dissolution times of the particle can be determined then using known parameters such as the eigenvalues and eigenvectors of the diffusion matrix.

4.3 The exact solution of Neumann for the non-diagonalizable case

We deal with a ternary example, where $n = 2$, higher order examples can be treated similarly. When the matrix D is not diagonalizable then we use a Jordan decomposition. For $D \in \mathbb{R}^{2 \times 2}$ 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

$$\begin{cases} \dfrac{\partial u_1}{\partial t} = \lambda \dfrac{\partial^2 u_1}{\partial x^2} + \dfrac{\partial^2 u_2}{\partial x^2} \\[4mm] \dfrac{\partial u_2}{\partial t} = \lambda \dfrac{\partial^2 u_2}{\partial x^2} \end{cases} \tag{17}$$

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 $\eta := \dfrac{x - S_0}{\sqrt{t}}$, then a similar procedure as in Section 3.4. the following is obtained:

$$\overline{u}_1 = \frac{C_1}{2\lambda^2}\left(-\eta\lambda e^{-\frac{\eta^2}{4\lambda}} + \lambda\sqrt{\pi\lambda}erf(\frac{\eta}{2\sqrt{\lambda}}) \right) + C_2\sqrt{\pi\lambda}erf(\frac{\eta}{2\sqrt{\lambda}}) + D_1$$

$$\overline{u}_2 = C_1\sqrt{\pi\lambda}erf(\frac{\eta}{2\sqrt{\lambda}}) + D_2$$

Again we use the trial solution $S = S_0 + k\sqrt{t}$, a combination with the boundary conditions delivers

$$C_1 = \frac{u_2^0 - u_2^s}{\sqrt{\pi\lambda}erfc(\frac{k}{2\sqrt{\lambda}})}, \qquad\qquad\qquad D_2 = u_2^0 - C_1\sqrt{\pi\lambda}$$

$$C_2 = \frac{1}{\sqrt{\pi\lambda}}\left\{ \frac{u_1^0 - u_1^s}{erfc(\frac{k}{2\sqrt{\lambda}})} - \frac{C_1}{2}\left(\sqrt{\frac{\pi}{\lambda}} + \frac{k}{\lambda}\frac{e^{-\frac{k^2}{4\lambda}}}{erfc(\frac{k}{2\sqrt{\lambda}})} \right) \right\}, \quad D_1 = u_1^0 - \sqrt{\pi\lambda}C_2 - \frac{C_1}{2}\sqrt{\frac{\pi}{\lambda}}.$$

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 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:

$$(u_2^p - u_2^s)\frac{k}{2\sqrt{\lambda}} = \frac{u_2^0 - u_2^s}{erfc(\frac{k}{2\sqrt{\lambda}})}\sqrt{\frac{1}{\pi}} \cdot e^{-\frac{k^2}{4\lambda}}$$

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

$$(p_{11}u_1^s + p_{12}u_2^s)^{m_1} (p_{21}u_1^s + p_{22}u_2^s)^{m_2} = K. \tag{18}$$

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. In the next subsection we will consider some

approximations of the solution of the above equations.

4.4 An asymptotic solution for the non-diagonalizable case

Suppose $|u_2^s - u_2^0| \ll |u_2^p - u_2^s|$, then $k \to 0$ and hence $\dfrac{\mathrm{e}^{-\frac{k^2}{4\lambda}}}{erfc(\frac{k}{2\sqrt{\lambda}})} \to 1$. The above equations (18) tend to the following expressions:

$$\frac{k}{2\sqrt{\lambda}} = \sqrt{\frac{1}{\pi}} \frac{u_2^0 - u_2^s}{u_2^p - u_2^s}$$

$$\frac{k}{2\sqrt{\lambda}} = \sqrt{\frac{1}{\pi}} \left\{ \frac{u_1^0 - u_1^s}{u_1^p - u_1^s} + \frac{u_2^0 - u_2^s}{2\lambda(u_1^p - u_1^s)} \right\} \tag{19}$$

As an approximation we set $u_i^0 \approx 0$ and $u_i^p \gg u_i^s$, then the above equation change into

$$k = -2\sqrt{\frac{\lambda}{\pi}} \frac{u_2^s}{u_2^p}$$

$$k = -2\sqrt{\frac{\lambda}{\pi}} \left\{ \frac{u_1^s}{u_1^p} + \frac{u_2^s}{2u_1^p \lambda} \right\} \tag{20}$$

From the above equations, we obtain the following relation between u_1^s and u_2^s:

$$u_2^s = \frac{u_2^p}{(u_1^p - \frac{u_2^p}{2\lambda})} u_1^s, \text{ for } u_1^p - \frac{u_2^p}{2\lambda} \neq 0.$$

The above expression is substituted into the third equation, which links u_1^s and u_2^s, to obtain a value for u_1^s. Using this value u_2^s can be computed and subsequently we can compute the interface rate coefficient k. The interface movement can then be determined. Note from the above equation that the expression for the interfacial concentrations and effective diffusion coefficient is less simple than for the case in which there is no cross-diffusion.

5 Numerical experiments

As a numerical experiment we show the computation of the dissolution of a planar phase for the case that the diffusion matrix is diagonalizable. The used numerical scheme is similar to the scheme for multi-component dissolution as described in [18] where a Finite difference method is used for the concentrations and a discrete Newton method for the determination of the interfacial concentrations. For the diagonalizable case the only difference is the change of the hyperbolic relation between the solubilities changes when using the so-called transformed concentrations. Furthermore, we compare the computed numerical solutions with the self-
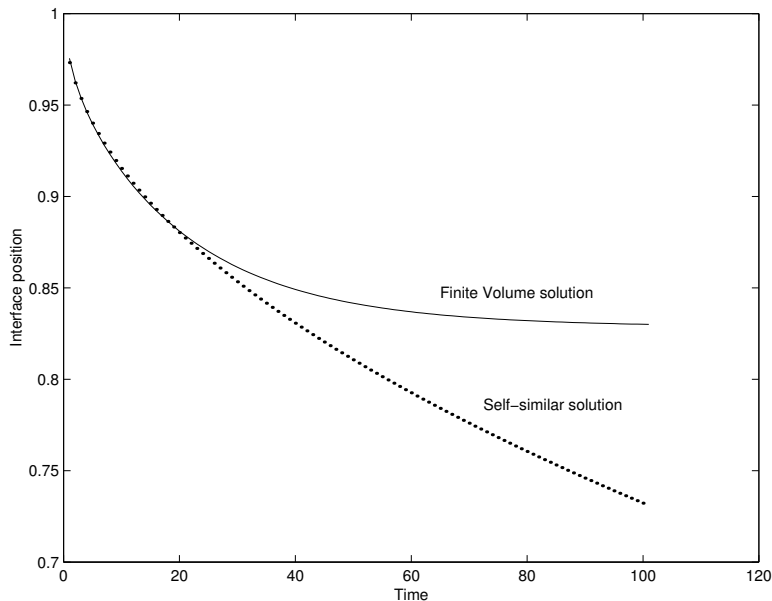
Figure 1: The interfacial position as a function of time. The dotted curve corresponds to self-similar solution and the other curve corresponds to the numerical approach.

similar solution as developed in Section 4. As input-data we used

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

$$D = \begin{pmatrix} 1 & -1/2 \\ 1/4 & 2 \end{pmatrix}, \qquad K = 1.$$

The above matrix is diagonalizable. In Figure 1 we plot the interface as a function of time for the self-similar solution and numerical solution. As to be expected the solutions co-incide for small times and start to deviate for later stages. From Figure 1 it is concluded that the numerical scheme is also applicable for cross-diffusion. Numerical computations with cross-diffusion for the case where the diffusion matrix is not diagonalizable remain to be done. We further show the interface position as a function of time for the self-similar (exact) solution and the quasi-binary approach in Figure 2. It can be seen that the quasi-binary approach is very accurate for this case.

We show the curve for the concentration profile for a case where the diffusion matrix is not diagonalizable (see Figure 3 and Figure 4) for subsequent times. It is clear that one of the concentrations is not monotonous, see Proposition 3. The data-set that we used is given by:

$$\underline{c}^0 = (0,0)^T, \qquad \underline{c}^{\mathrm{part}} = (100,50)^T,$$

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

Further, the interfacial position is plotted in Figure 5. We show the results for the exact solution, see Section 4.3. and the results for the asymptotic approximation (i.e. the quasi-binary approach), see Section 4.4. It can be seen that the curves co-incide well and hence for
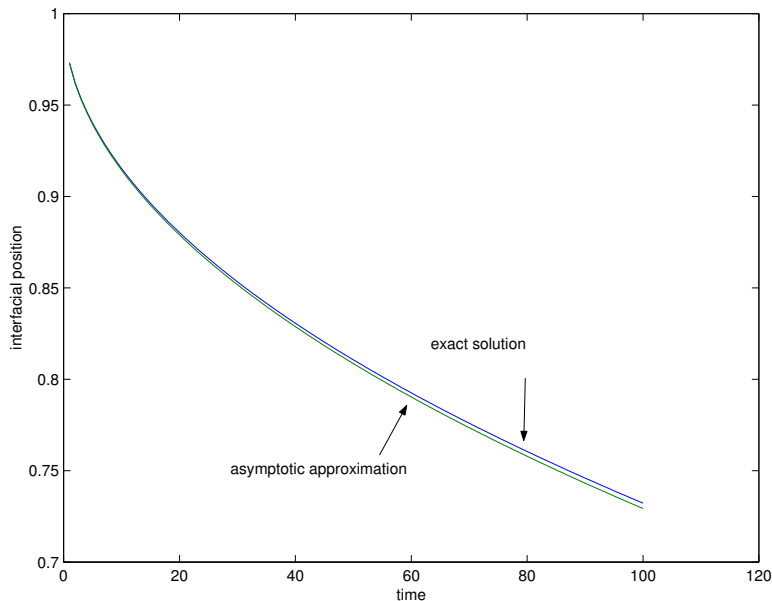
Figure 2: The interfacial position as a function of time for the same dataset as in Figure 1 for the exact self-similar solution and the asymptotic approximation (quasi binary approach).

this case the asymptotic approach is accurate.

6   Conclusions

A model, based on a vector-valued Stefan problem, has been developed to predict dissolution kinetics of stoichiometric particles in multi-component alloys. Cross-diffusion of the alloying elements is taken into account, which gives a strong coupling of the differential equations. Using a diagonalization argument the vector-valued Stefan problem with cross-diffusion is transformed into a vector-valued Stefan problem where the cross-terms vanish whenever the diffusion matrix is diagonalizable. For the diagonalizable case the numerical solution procedure, which is used for modelling particle dissolution / growth when no cross-diffusion is taken account, can be used. When the diffusion matrix is not diagonalizable, the Jordan decomposition is used to facilitate the analysis. Well-known mathematical implications, concerning mass-conservation of the Stefan problem and self-similarity solutions can be recovered now also for the case of cross-diffusion. The hyperbolic relation between the interfacial concentrations becomes more complicated, however, since the eigenvectors of the diffusion matrix have to be taken into account as well. In spite of this complication, the vector-valued Stefan problem can be approximated by a quasi-binary in a similar way as for the case in which no cross-diffusion is taken into account for the vector-valued Stefan problem. Similar as in the case of no cross-diffusion we obtain expressions for the effective interfacial concentration, particle concentration and effective diffusion coefficient. For the case that the diffusion matrix is singular, it is shown that the solution is not unique. Furthermore, the case of a non-diagonalizable diffusion matrix is analyzed.

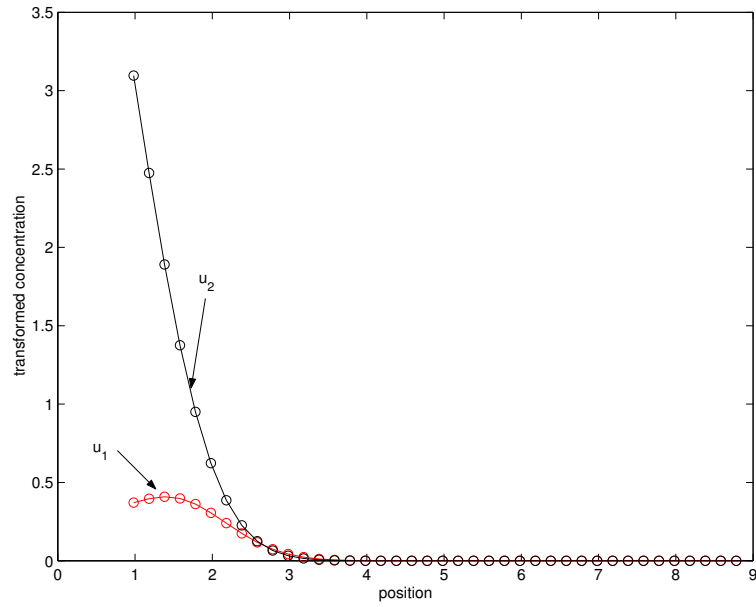Still the following remains to be done:

Figure 3: The concentration profiles for consecutive times in the α-rich phase for two alloying elements where the diffusion matrix is not diagonalizable. The concentration of element 1 is not monotonous.
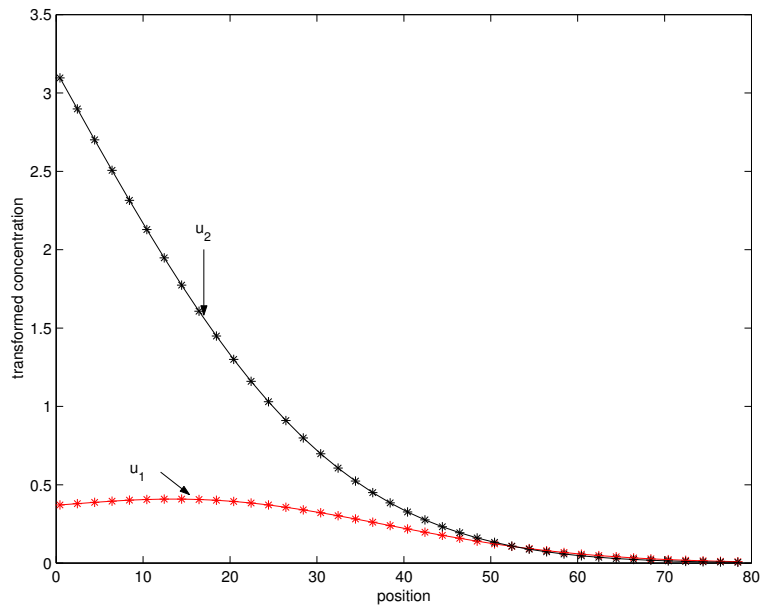

Figure 4: The concentration profiles for consecutive times in the α-rich phase for two alloying elements where the diffusion matrix is not diagonalizable. The concentration of element 1 is not monotonous.
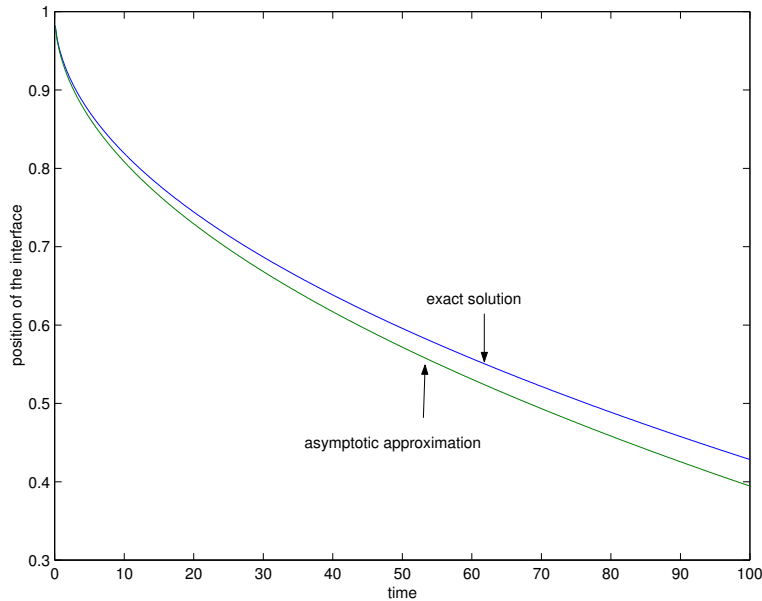
Figure 5: The interface position as a function of time for the case that the diffusion matrix is not diagonalizable. The exact- and asymptotic solution are shown.

1. We want to include the other geometries as well in the analysis.

2. Some numerical calculations for the case of a non-diagonalizable diffusion matrix will be done.

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