NUMERICAL SOLUTION OF VECTOR STEFAN PROBLEMS WITH CROSS-DIFFUSION

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Abstract. *A general model for the dissolution of particles in multi-component alloys is proposed and analyzed. The model is based on diffusion equations with cross-terms for the various species, combined with a Stefan condition as the equation of motion of the interface between the particle and diffusant phase. We analyze the existence of solutions of the vector-valued Stefan problem with cross-diffusion for a singular diffusion matrix. Further, we give a self-similar solution of the problem for an unbounded planar domain. This solution is used to check the numerical solution at the early stages. To check the numerical solution at the final stages we present an end-point condition for the interface position and concentrations. Several numerical schemes for the solution of the Stefan problem are proposed and compared. It turns out that diagonalization is usefull for numerical purposes. We stress that in the present paper we only give the main results of the comparison of the various numerical schemes.*

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 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 aluminum extrusion alloys. Although precipitate dissolution and growth are not the only metallurgical processes taking place, these are 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 and growth, many models of various complexity 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. These advanced models cover a range of physical assumptions concerning the dissolution conditions and the initial microstructure. For a review and more physical background we refer to [1]. We remark that the impact of the Gibbs-Thomson effect due to surface tension is disregarded in the present paper. Vermolen et al [1] describe the surface tension effects on the dissolution kinetics of spherical particles.

In this paper we study several numerical methods for a model of particle dissolution and growth in multi-component alloys, i.e. alloys with several alloying elements. The model is based on a vector-valued Stefan problem where the effects of cross-diffusion are taken into account. A self-similarity solution and asymptotic expressions for a one-dimensional geometry are presented in [2]. The present paper is organized as follows: The model equations are introduced first. Subsequently we present some analysis of the equations. This is followed by the main results on stability and efficiency of several numerical methods. For a mathematical justification of the theorems on the numerical analysis we refer to [3]. Some numerical experiments are given and finally the conclusions are presented.

2   MODEL

The vector-valued Stefan problem is based on (cross) diffusion of several chemical species in the domain $\Omega(t)$, which varies with time due to the movement of boundary $S(t)$. This boundary $S(t)$ separates the 'particle' from diffusive phase $\Omega(t)$. In the particle we assume that the composition (stoichiometry) is constant at all the stages of the modelled process. This composition is denoted by c_i^{part} for $i \in \{1, \ldots, n\}$. Furthermore, we assume local equilibrium at the moving interface $S(t)$. Through boundaries, not be-

ing an interface, denoted by $\Gamma(t)$, a no-flux condition is imposed. For more physical justification of the model, we refer to [1].

Mathematically, this all boils down to the following problem for $i \in \{1, \ldots, n\}$:

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{n} D_{ij} \Delta c_j, \text{ for } (x, y) \in \Omega(t), t > 0, \tag{1}$$

$$c_i(x, y, 0) = c_i^0(x, y) \text{ for } (x, y) \in \Omega(0), \tag{2}$$

$$\frac{\partial c_i}{\partial n} = 0, \text{ for } (x, y) \in \Gamma(t), t > 0, \tag{3}$$

$$c_i(x, y, t) = c_i^{\text{sol}}, \text{ for } (x, y) \in S(t), t > 0. \tag{4}$$

The initial position of the interface is known and denoted by $S(0)$. The coefficients, D_{ij}, are the (cross) diffusion coefficients, which are the entries of the diffusion matrix, D. At the moving interface we have

$$(c_1^{\text{sol}})^{m_1} (c_2^{\text{sol}})^{m_2} (...)(c_n^{\text{sol}})^{m_n} = K, \tag{5}$$

where K is known and may depend on time t for an non-isothermal Stefan problem. However, in the present study we take it as a constant. The normal component of the interface velocity is described by

$$\left(c_i^{\text{part}} - c_i^{\text{sol}} \right) v_n = \sum_{j=1}^{n} D_{ij} \frac{\partial c_j}{\partial n} \text{ for } (x, y) \in S(t), t > 0. \tag{6}$$

The right-hand part of above equations follows from local mass-conservation of the components. Note that if $c_i^{\text{part}} \neq c_i^{\text{sol}}$, then from equation (6) follows

$$\sum_{k=1}^{n} \frac{D_{ik}}{c_i^{\text{part}} - c_i^{\text{sol}}} \frac{\partial c_k}{\partial n} = \sum_{k=1}^{n} \frac{D_{jk}}{c_j^{\text{part}} - c_j^{\text{sol}}} \frac{\partial c_k}{\partial n}, \text{ for } (x, y) \in S(t), t > 0. \tag{7}$$

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 the 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 diffusive phase. We note here that the equations are asymptotically stable if and only if $\Re\{eig(D)\} > 0$. Hence only this case is considered in the present study. For a mathematical overview of Stefan problems we refer to the textbooks of Crank [8], Chadam and Rasmussen [9] and Visintin [10].

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 diagonalization. We end up with a self-similar solution and an expression for the final position of the interface and final concentration profiles.

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 $t > 0$

$$\begin{cases} \dfrac{\partial u}{\partial t} = D\dfrac{\partial^2 u}{\partial x^2}, & x \in (S(t), M), \\[2ex] (u^{\mathrm{part}} - u^{\mathrm{sol}})\dfrac{dS}{dt} = D\dfrac{\partial u}{\partial x}(S(t), t), \\[2ex] u(S(t), t) = u^{\mathrm{sol}}, \\[2ex] \dfrac{\partial u}{\partial n}(M, t) = 0, \\[2ex] u = u^{\mathrm{part}}, & x \in [0, S(t)). \end{cases} \tag{8}$$

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 [11]:

Proposition 1 *Let all concentrations, which are used in problem (8), 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 [11]. 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 diagonalization when the diffusion matrix is singular. For $D = 0$, the one-dimensional version of problem (8) changes into

$$\begin{cases} \dfrac{\partial u}{\partial t} = 0, & x \in (S(t), M) \\[2mm] u(S(t), t) = u^{\mathrm{sol}}, \\[2mm] \dfrac{\partial u}{\partial x}(M, t) = 0, \\[2mm] u = u^{\mathrm{part}}, & x \in [0, S(t)). \end{cases} \tag{9}$$

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 $S(t) < S(\hat{t})$ 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 $S(t) > S(\hat{t})$ 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 [12]) 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. □

Theorem 1 *Let $S(t)$ satisfy smoothness (C) and let the equations in (9) 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 (9) 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 $u^{\text{part}} \neq u^0$. 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 $S(t) > S(\hat{t})$ for all $t \in (0, \tilde{t})$. From Definition 1 follows

$$u^{\text{part}}S(0) + (M - S(0))u^0 = S(\tilde{t})u^{\text{part}} + \int_{S(\tilde{t})}^{S(0)} u(x,t)dx + (M - S(0))u^0, \quad (10)$$

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 (10), changes into

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

Hence $u^{\text{sol}} = u^{\text{part}}$ or $S(\tilde{t}) = S(0)$. Suppose that $u^{\text{sol}} \neq u^{\text{part}}$, then $S(\tilde{t}) = S(0)$ and the first part of the theorem is proven. Further, if $u^{\text{sol}} = u^{\text{part}}$, 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 $u^{\text{part}} \neq u^{\text{sol}}$, otherwise, whenever $u^{\text{part}} = u^{\text{part}}$, the function S is undetermined and hence uniqueness is violated. Similarly, whenever $u^{\text{part}} = u^0$, the solution is undetermined. We state this result in the following corollary:

Corollary 1 *The solution of problem (9) is not uniquely defined when $u^{sol} = u^{part}$ or $u^{part} = u^0$.*

3.2 The 'degenerate' vector-valued Stefan problem

First we consider the planar version with one spatial co-ordinate of the vector-valued Stefan problem, without cross-diffusion, i.e. $D_{ij} = 0$ for $i \neq j$, as defined by equations (1-6). 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 (1-6), 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 relation (6) 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 $\frac{\partial u_j}{\partial x} = 0$ 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 [4])

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

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 (5) using the above values for u_j^{sol}, $j \in \{2, \ldots, n\}$. Further from relation (5) 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 $\frac{\partial u_1}{\partial x} = 0$, 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 equations (1-6). If the values of $\{u_2^{\text{sol}}, \ldots, u_n^{\text{sol}}\}$ are such that $\frac{dS}{dt} \leq 0$ (see [11]), 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

$$\frac{\partial}{\partial t}\underline{c} = D\Delta\underline{c}. \tag{11}$$

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:

$$(\underline{c}^p - \underline{c}^s)\frac{dS}{dt} = D\frac{\partial\underline{c}}{\partial n}, \text{ for } (x,y) \in S(t).$$

Here n represent the unit outward normal vector.

To analyze equation (11) 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 [5] or Golub and Van Loan [6] 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.(11) gives

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

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

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In the above relations we assume that D is a constant matrix. Further, it is easily shown for this case that D and the operator Δ commute. 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

$$\frac{\partial}{\partial t}\underline{u} = \Lambda\Delta\underline{u}$$

$$(\underline{u}^p - \underline{u}^s)\frac{dS}{dt} = \Lambda\frac{\partial\underline{u}}{\partial n}, \text{ for } (x,y) \in S(t). \tag{12}$$

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 (4) changes into

$$(\sum_{j=1}^{n} p_{1j}u_j^s)^{m_1}(\sum_{j=1}^{n} p_{2j}u_j^s)^{m_2}(\ldots)(\sum_{j=1}^{n} p_{nj}u_j^s)^{m_n} = K = K(T). \tag{13}$$

Although this condition becomes more complicated, the analysis is facilitated using the diagonalization 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

$$\frac{\partial u_i}{\partial t} = -\mu\Delta u_i, \text{ with } \mu := -\lambda < 0, \text{ for } x \in \Omega(t), t > 0.$$

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

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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 (12) and (13), 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 $j \in \{2, \ldots, n\}$. $\qquad \square$

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. We remark that complex eigenvalues of the diffusion matrix is a topic of current reseach. For the non-moving interface it is required that the eigenvalues of the diffusion matrix have a positive real part for asymptotic stability. We note that the eigenvalues of the overall diffusion system follow from a product of the eigenvalues of the diffusion matrix and the eigenvalues of the Laplacian.

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   A self similar solution for $\mathbb{R}^1$

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. To facilitate the analysis we consider the Stefan problem on an unbounded domain where $a = 0$ (planar case) in one co-ordinate:

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

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Here we only deal with the diagonalizable case where we consider an exact solution for the infinite half plane. A self-similar solution, where the boundaries do not move, can be found in the book of Glicksman [7], chapters 23 and 24.

As a trial solution of (P_1) we look for solutions where 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 [11], one obtains the solution for each component:

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

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

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

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

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

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 the solution.

As a test problem we consider the following configuration:

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

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

From the above problem it follows that $c_1^{\text{sol}} = 1.1885$ (dissolution) or $c_1^{\text{sol}} = -1.193$ (growth). Since we are interested in non-negative concentrations only, we reject the

second case, i.e. we have $c_1^{\text{sol}} = 1.1885$. The constant interface concentrations are indeed a solution of the planar semi-infinite case. For the spherical semi-infinite case the interface concentration is not constant. In the next section we show that for a finite cell radius in a planar configuration the interface concentrations are no longer constant either.

Some asymptotic solutions are derived and treated in [2]. Further, in that paper we present the self-similar solutions for the case of the non-diagonalizable diffusion matrix as well.

3.5 The final state

For simplicity we consider one spatial co-ordinate only where $x \in [0, M]$ for $M > 0$, i.e. the cell radius is finite. For the scalar Stefan problem it can be shown by use of the maximum principle of the diffusion equation [4] that for a constant interface concentration the interface position is monotonic in time. Further, the final stage gives the final interface position, where S^f ranges from 0 till M, i.e. $S^f \in [0, M)$. This follows from the fact that if $S^f = M$ for $c^{\text{part}} \neq c^0$ then mass would not be conserved, i.e. $\frac{d}{dt} \int_0^M c(x, t) dx \neq 0$, which we reject as a physical solution. We assume here that the solution of the vector-valued Stefan problem is monotonic and conserves mass in the sense of Definition 2, hence there exists a $S^f \in [0, M)$. Hence concentration gradients vanish as $S(t) \to S^f$ ($t \to \infty$). This implies that as $S \to S^f \neq 0$ the concentration between S^f and M tends to a limit for each chemical element, i.e. there exists c_i^f for all $i \in \{1, \dots, n\}$ such that $c(x, t) \to c_i^f$ as $t \to \infty$. If $S^f = 0$ then a homogeneous Neumann condition for all concentrations arises. Whereas, if $S^f > 0$ then the final stage concentrations should satisfy hyperbolic relationship, i.e. $f(c_1^f, \dots, c_n^f) = (c_1^f)^{m_1}(c_2^f)^{m_2}(\dots)(c_n^f)^{m_n} - K = 0$. We summarize this in the following problem:

$$(P_F) \left[\begin{array}{l} \text{Find } c_1^f, \dots, c_n^f \text{ and } S^f \text{ such that} \\[2mm] \begin{cases} c_i^{\text{part}} S^f + c_i^f (M - S^f) = c_i^{\text{part}} S_0 + c_i^0 (M - S_0) \text{ for } i \in \{1, \dots, n\}, \quad (14) \\[3mm] f(c_1^f, \dots, c_n^f) = (c_1^f)^{m_1}(c_2^f)^{m_2}(\dots)(c_n^f)^{m_n} - K = 0. \end{cases} \end{array} \right.$$

The above problem applies for the case $S^f > 0$. For the case that $S^f = 0$ then the condition $f(c_1^f, \dots, c_n^f) = 0$ is dropped to avoid inconsistency. Further, we observe that the final concentrations do not depend on the coefficients in the diffusion matrix.

The above insight is used to check whether the numerical solution conserves mass. Of course existence and uniqueness are important items here. We illustrate the above concepts with the following example:

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

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

Further, $S_0 = 0.1$ and $M = 1$. Then from problem (P_F) follows that the final interface position is given by $S^f = 0.0816$ or $S_f = 1.176$ with respectively $c_1^f = 1 = c_2^f$ or $c_1^f = -1 = c_2^f$, which both satisfy problem (P_F). For physical reasons we assume that the concentrations are non-negative and hence the second solution is rejected, i.e. $S^f = 0.0816$. This means that the particle dissolves partly. Similar considerations can be written for more general geometries. Further, we observe that if for our particular choice of diffusion matrix D the interface concentrations are not constant at all stages of the dissolution process (see the preceding subsection). We further remark that this is still subject to research and hence the conclusions in this subsection are preliminary.

4   NUMERICAL METHOD

In general situations we are not able to give an analytical solution for the vector-valued Stefan problem with cross-diffusion and hence a numerical method is used. The Stefan problem considered in this paper contains two difficulties:

- the computation of the moving interface;

- the occurrence of the cross-diffusion terms.

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. For a survey of other methods, such as the phase field method and the level-set method, we refer to [14, 15, 16, 17]. We stress that this selection of references is far from complete.

A complete description of the numerical method to solve the vector-valued Stefan problem is given in [3]. There, the numerical treatment of the movement of the interface position is described as well. Further, there the solution of the non-linear problem by means of the Picard or quasi-Newton method is presented as well. Basically, in that paper roughly two strategies are compared: diagonalization of the diffusion matrix to decouple the diffusion equations due to the various species and a direct solution procedure, which does not make use of the decoupling. In this section we state the main result concerning the direct approach in which no diagonalization is used. Here we distinguish two schemes: The IMEX scheme and the (fully) implicit scheme (Euler backward). In the IMEX scheme a decoupling of the diffusion matrix is made: the main diagonal components are subject to an implicit treatment, whereas the other coefficients are dealt with explicitly (i.e. at the preceding time-step). In the implicit scheme the discretization from all the entries of the diffusion matrix are treated implicitly. We remark that the eigenvalues of the overall discretized follow from the fact that the overall discretization operator is a Knonecker product of the diffusion matrix and the discretized Laplacian. Then, the eigenvalues of the overall discretization are given by the product of the eigenvalues of the diffusion matrix and the eigenvalues of the discretized Laplacian.

In [3] we prove the following stability properties of the methods for a 2×2 diffusion matrix.

Theorem 5 *Consider the time integration of equation (1), and let λ be an eigenvalue of the discretized Laplace operator whose eigenvalues are all negative, $D \in \mathbb{R}^{2 \times 2}$ and $D_{11}, D_{22} > 0$, and let $\Re(eig(D)) > 0$, then;*

1. *The explicit time integration is stable if*

$$\Delta t < \frac{2\Re(eig(D))}{|\lambda||eig(D)|^2}.$$

2. *The implicit time-integration is unconditionally stable and super stable.*

3. *If $0 < |D_{12}D_{21}| < D_{11}D_{22}$ then the IMEX time-integration, given in eq. (??), is unconditionally stable and super stable. If $|D_{12}D_{21}| > D_{11}D_{22}$ then the IMEX time-integration is stable if*

$$|\lambda|\Delta t < -\frac{D_{11} + D_{22}}{D_{11}D_{22} + D_{12}D_{21}} \ if \ D_{12}D_{21} < 0,$$

and

$$|\lambda|\Delta t < \frac{D_{11} + D_{22} + \sqrt{(D_{11} + D_{22})^2 + 4(D_{12}D_{21} - D_{11}D_{22})}}{D_{12}D_{21} - D_{11}D_{22}} \ if \ D_{12}D_{21} > 0.$$

As consequences of the above assertion one can easily prove the following statements:

Corollary 2 *Let all hypotheses in Theorem 5 be satisfied, then*

1. *For all discretizations with a symmetric matrix, Theorem 5 holds.*

2. *A consequence of Theorem 5 is that the IMEX time integration is unconditionally stable if the diffusion matrix is diagonally dominant and if the discretized Laplacian is symmetric.*

Numerical experiments reveal that the derived criterion in Theorem 5 is sharp. In [3] the above assertion is also extended to the Finite Element method.

In [3] it is motivated that the solution of the large system of linear equations for the implicit method is less efficient than for the IMEX method for several arrangements of the unknowns. There also some experimentally determined computation times are given.

We finish here with a numerical experiment showing that at the early stages the numerically obtained interface position co-incides well with the interface position from the analytical solution for an unbounded domain. Further as the interface moves towards its final position, we see in Figure 1 that the numerically obtained interface position tends to its asymptotic value, which is derived in the Section 3. For the calculations we use the configuration of Section 3.4.

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5 CONCLUSIONS

A model, based on a vector-valued Stefan problem, has been analyzed to predict dissolution or growth 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 or a Jordan decomposition if necessary the vector-valued Stefan problem with cross-diffusion is transformed into a vector-valued Stefan problem where the cross-terms vanish or at least as much as possible (for the Jordan decomposition). 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. For the case that the diffusion matrix is singular, it is shown that the solution is not unique. Further, some expressions for an end state for the interface position and concentrations are derived, which are used to demonstrate that the interface concentrations are not constant during the dissolution or growth process when a bounded planar computational domain is considered.

We summarize the results of several analyzed numerical methods for the cross-diffusion problem with a moving interface. The Euler Backward time integration method is unconditionally stable. A drawback is the long computation time needed to solve the large system of linear equations from the spatial discretization. A stability criterion for some cases of the IMEX method is given. The computation times are smaller than for the fully implicit method. If diagonalization is used then the IMEX and Euler Backward time-integration methods are equivalent combining the advantages of stability and efficiency. Therefore we recommend the use of the diagonalization argument if the coefficients of D are constant.

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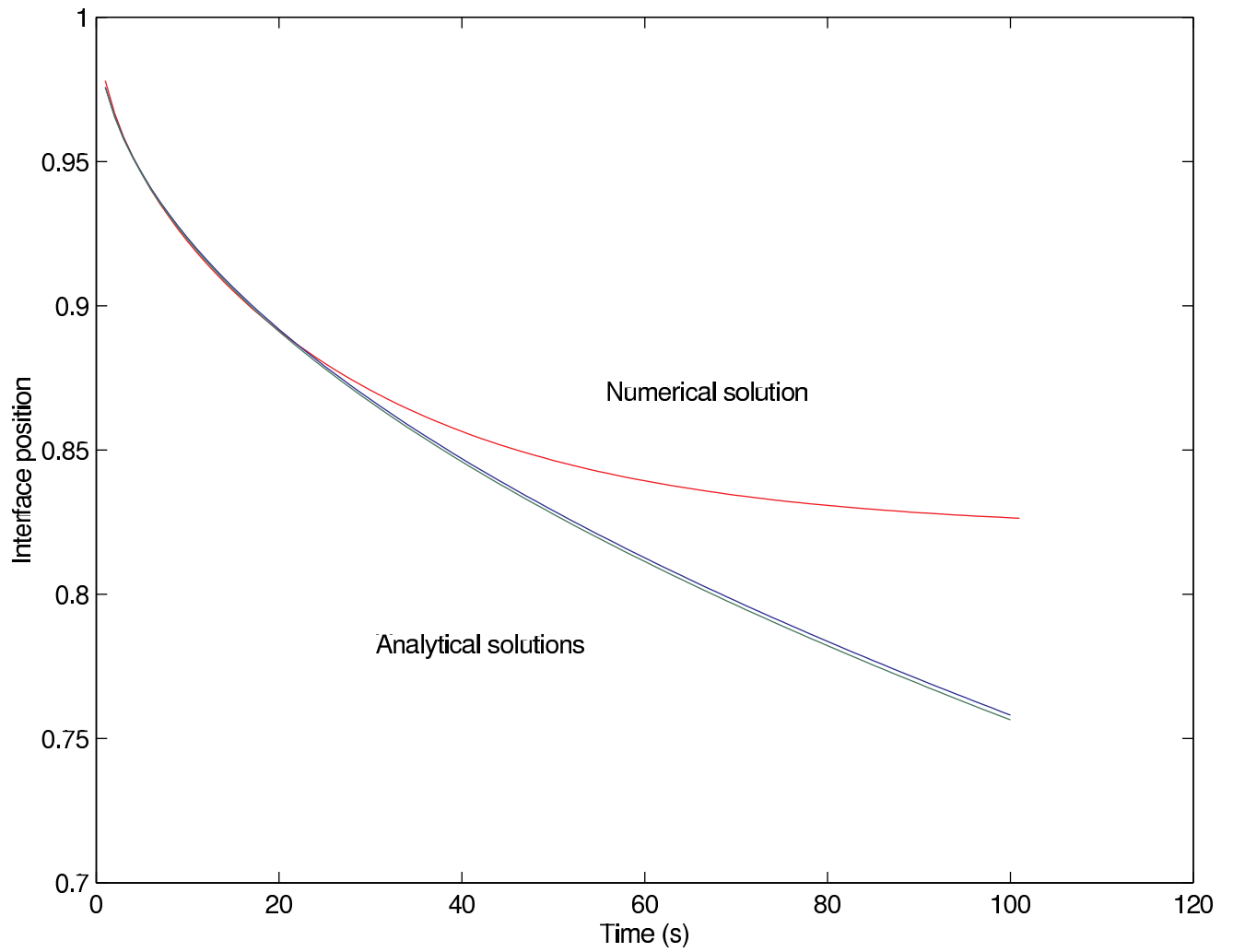
Figure 1: The interface position as a function of time. The dotted curve corresponds to the self-similar solution and the solid curve to the numerical approach.