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F.J. Vermolen, K. Vuik

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CWI
P.O. Box 94079
1090 GB Amsterdam
The Netherlands

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P.O. Box 94079, 1090 GB Amsterdam (NL)
Kruislaan 413, 1098 SJ Amsterdam (NL)
Telephone +31 20 592 9333
Telefax +31 20 592 4199

A Vector Valued Stefan Problem from Aluminium Industry

Fred Vermolen

CWI

P.O. Box 94079, 1090 GB, Amsterdam, The Netherlands

Kees Vuik

Faculty of Technical Mathematics and Informatics

Delft University of Technology

P.O. Box 5031, 2628 GA, Delft, the Netherlands

ABSTRACT

Dissolution of stoichiometric multi-component particles in ternary alloys is an important process occurring during the heat treatment of as-cast aluminium alloys prior to hot-extrusion. A mathematical model is proposed to describe such a process. In this model an equation is given to determine the position of the particle interface in time, using two diffusion equations which are coupled by nonlinear boundary conditions at the interface. Moreover the well-posedness of the moving boundary problem is investigated using the maximum principle for the parabolic partial differential equation. Furthermore, for an unbounded domain and planar co-ordinates an analytical asymptotic approximation based on self-similarity is derived. This asymptotic approximation gives insight into the well-posedness of the problem.

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1. INTRODUCTION

Heat treatment of metals is often necessary to optimise their mechanical properties both for further processing and for final use. During the heat treatment the metallurgical state of the alloy changes. This change can either involve the phases being present or the morphology of the various phases. Whereas the equilibrium phases can be predicted quite accurately from the thermodynamic models, until recently there are no general models for microstructural changes nor general models for the kinetics of these changes. In the latter cases both initial morphology and the transformation mechanisms have to be specified explicitly. One of these processes that is amenable to modelling is the dissolution of second phase particles in a matrix with a uniform initial composition.

Particle dissolution is modelled as a Stefan Problem: a diffusion problem with a moving boundary. The present work first covers an asymptotic solution of a Stefan problem of a binary alloy. In a binary alloy only one alloying element diffuses and hence determines dissolution. This solution is based on the class of self-similar solutions available for Stefan problems. Using this asymptotic solution a rapid insight is gained into the behaviour of the solutions and into the well-posedness of the model. Moreover, the well-posedness of the problem is investigated using the maximum principle of the parabolic partial differential equation and the overall mass-balance. Subsequently dissolution in ternary alloys is considered. Two

chemical elements diffuse simultaneously and hence determine the rate of the movement of the moving boundary. The diffusion of both the alloying elements is coupled via an hyperbolic relationship between the concentrations at the moving interface.

The mathematical model for the dissolution of second phases in ternary alloys is given in Section 2. Some preliminaries of the well-posedness and a short derivation of a self-similar solution are given in Section 3. For details about the numerical method, we refer to the work of Vermolen and Vuik.

2. A MODEL OF DISSOLUTION IN TERNARY ALLOYS

Consider three chemical species denoted by A , B , and C . We investigate the dissolution of an $A_l B_m C_n$ particle in an $A - B - C$ alloy, where we assume that the concentrations of B and C are small with respect to that of component A . The concentrations of B and C are written as c_B, c_C (mol/m³) respectively. At a given temperature the initial concentrations are equal to c_B^0 and c_C^0 . The concentrations of B and C in the particle are denoted by c_B^{part} and c_C^{part} . The interface concentrations (c_B^{sol} and c_C^{sol}) are variant.

We consider a one-dimensional problem. In this paragraph the model is posed very generally. In the other sections we will use a simplified version of the model. The geometry is given by $\Omega(t) = \{x \in \mathbb{R} | M_1 \leq S_1(t) \leq x \leq S_2(t) \leq M_2\}$, $t \in [0, T]$ where T is an arbitrary positive number. In some applications there is a time t_1 and t_2 such that respectively $S_1(t) = M_1, t \geq t_1$ and $S_2(t) = M_2, t \geq t_2$. For the determination of c_B, c_C we use the multi-component version of Fick's Second Law (see [8], [3] p. 160):

$$\frac{\partial c_p}{\partial t} = \mathbb{D}_p \frac{\partial}{\partial r} \left(r^a \frac{\partial c_p}{\partial r} \right), \quad r \in \Omega(t), \quad t \in (0, T], \quad p \in \{B, C\}, \quad (2.1)$$

where a is a geometric parameter, which equals 0, 1 or 2 for respectively a planar, cylindrical or spherical geometry. All these geometries occur in metallurgical applications. Note that M_1 should be non-negative for $a \neq 0$. As initial conditions we use

$$c_p(r, 0) = c_p^0(r), \quad r \in \Omega(0), \quad p \in \{B, C\}, \quad (2.2)$$

where c_p^0 are given non-negative functions. When a moving boundary becomes fixed, i.e. $S_k(t) = M_k$, we assume that there is no flux through the boundary, so

$$\frac{\partial c_p}{\partial r}(M_k, t) = 0, \quad \text{for } t \geq t_k, \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (2.3)$$

On the moving boundaries the following definition is introduced:

$$c_p(S_k(t), t) = c_{p,k}^{sol}(t), \quad t \in [0, T], \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (2.4)$$

So, six unknown quantities remain: $S_k(t)$, $c_{B,k}^{sol}(t)$, and $c_{C,k}^{sol}(t)$, $k \in \{1, 2\}$. To obtain a unique solution six boundary conditions are necessary. We assume that the particle is stoichiometric, which means that c_A^{part} , c_B^{part} , and c_C^{part} are constant. Using the Gibbs free energy of the stoichiometric compound we get the following coupled Dirichlet condition: [8]:

$$(c_{B,k}^{sol}(t))^m \cdot (c_{C,k}^{sol}(t))^n = K, \quad k \in \{1, 2\}, \quad (2.5)$$

where the exponents m, n correspond to the stoichiometric phase $A_l B_m C_n$ and K is a constant depending on temperature. The balance of B and C atoms and the constant composition of the particle lead to the following equations [5] for the moving boundary positions:

$$(c_p^{part} - c_{p,k}^{sol}(t)) \frac{dS_k(t)}{dt} = \mathbb{D}_p \frac{\partial c_p}{\partial r}(S_k(t), t), \quad t \in (0, T], \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (2.6)$$

Condition (2.6) implies the following Neumann condition:

$$\frac{\mathbb{D}_B}{c_B^{part} - c_{B,k}^{sol}(t)} \frac{\partial c_B}{\partial r}(S_k(t), t) = \frac{\mathbb{D}_C}{c_C^{part} - c_{C,k}^{sol}(t)} \frac{\partial c_C}{\partial r}(S_k(t), t), \quad k \in \{1, 2\}. \quad (2.7)$$

The moving boundary problem given by equations (2.1), ..., (2.6) is known as a Stefan problem [2]. Due to the (non-linear) coupling of the diffusion equations, we refer to it as a vector valued Stefan problem. There are some differences between the dissolution in a binary alloy ([8]) and in a ternary alloy. In the first place, two diffusion equations have to be solved, which are coupled through the conditions (2.4), (2.5), and (2.7) on the moving boundaries. Secondly, the problems are nonlinear due to the balance of atoms on S_1, S_2 , both in the binary and the ternary case. However, in the mathematical model for a ternary alloy an extra non-linearity occurs in equation (2.5). These equations are numerically solved for the concentrations at the interface, c_B^{sol}, c_C^{sol} using a discrete Newton-Raphson scheme where the discretised gradients are used [7]. For a recent book where Stefan problems are considered we refer to [9] (see for instance p. 132 (2.5), (2.9)).

3. PROPERTIES OF THE STEFAN PROBLEM

In this section first the maximum principle is formulated. Using this maximum principle the well-posedness of the Stefan problem is discussed. It is proven that there are Stefan problems for which no solution exists. Finally this section treats an asymptotic solution of a planar Stefan problem in an unbounded domain ($M_2 = \infty$). The properties and solution of the Stefan problem are first discussed for the case of one diffusing element, therefore the subscript for the index of the alloying element is omitted.

3.1 The maximum principle for the diffusion equation

The Stefan problem is formed by the diffusion equation and a displacement equation for one or more moving boundaries. For the diffusion equation it can be proved that the solution satisfies a maximum principle, which we present for completeness.

Maximum principle

Suppose c satisfies the inequality

$$\frac{\partial^2 c}{\partial r^2} - \frac{\partial c}{\partial t} \geq 0, \quad r \in \Omega(t), \quad t \in (0, T], \quad (3.1)$$

then a local maximum has to occur at one or both of the sides S_1, S_2 (the moving boundaries), or at $t = 0$ (the initial condition). Suppose that a local maximum occurs at the point P on S_1 , or S_2 . If $\frac{\partial}{\partial \nu}$ denotes the derivative in an outward direction from $\Omega(t)$, then $\frac{\partial c}{\partial \nu} > 0$ at P .

This statement is referred to as the maximum principle and has been proved by Protter and Weinberger for a general parabolic operator (see [4] p. 168, p. 170). This principle can also be applied for local minima (and $\frac{\partial c}{\partial \nu} < 0$) when the inequality in (3.1) is reversed. The principle

thus requires the global extremes of a solution to the diffusion equation to occur either at the boundaries S_1, S_2 , or at $t = 0$.

In [7] some limitations of the vector valued Stefan problem (2.1)...(2.6) are summarised. It appears that the model breaks down when the concentration at the interface equals the concentration in the particle. Moreover in [7] the monotonicity properties are described as well.

3.2 Well and Ill-posed one-dimensional Stefan problems describing particle dissolution or growth

In this subsection it is proven that for some one-dimensional Stefan problems no solutions exist. We consider a planar Stefan problem in an unbounded domain. For a bounded problem the proofs have been given in [6]:appendix 2. The velocity of the interface is given by equation (2.6) and based on mass conservation. With mass conservation we here mean that the total mass is constant. Here we take the quantities c^{sol} , c^{part} and c^0 constant. The integral form of the Stefan condition, in an unbounded domain, is given by:

$$\int_0^\infty (c(r, t) - c^0) dr = (c^{part} - c^0) S(t) + \int_{S(t)}^\infty (c(r, t) - c^0) dr = (c^{part} - c^0) S_0 \quad (3.2)$$

The above equation states that the total mass is constant. It can be proven easily by differentiation that equation (3.2) and equation (2.6) are equivalent for the case that the total mass is constant. For this case the concentration at infinity is constant and the concentration gradient is equal to zero there. For the case that the total mass is constant the Stefan problem is well-posed.

If we define $\frac{\partial c}{\partial \nu}$ as the spatial derivative in the direction of the outward normal from $\Omega(t)$, it follows from the maximum principle that $(c^{sol} - c^0) * \frac{\partial c}{\partial \nu} > 0$. From equation (2.6), it then follows that

$$v_n(t) * (c^{part} - c^{sol}) \cdot \frac{\partial c}{\partial \nu} > 0. \quad (3.3)$$

In which we define $v_n(t)$ as the velocity of the moving boundary in the outward normal from $\Omega(t)$. In the remaining part of this subsection it will be shown by contradiction that for some Stefan-problems no solutions, satisfying the total mass balance, exist. The following proposition formulates the existence of the solution for the case of a one-dimensional unbounded domain:

Proposition 1 The problem as constituted as the Stefan problem has no solution if

$$(c^{part} - c^0) * (c^{part} - c^{sol}) < 0.$$

Proof

Suppose that a solution exists for the Stefan problem with $(c^{part} - c^0) * (c^{part} - c^{sol}) < 0$. We then have $(c^0 < c^{part} < c^{sol})$ or $(c^{sol} < c^{part} < c^0)$.

First we consider the case that $c^0 < c^{part} < c^{sol}$. From equation (3.3) and $(c^{sol} - c^0) * \frac{\partial c}{\partial \nu} > 0$, follows that $v_n(t) < 0$ and thus $\frac{dS(t)}{dt} > 0$. Considering $t = 0$, we have for the global mass difference:

$$\int_0^\infty (c(r, 0) - c^0) dr = S_0(c^{part} - c^0).$$

For $t > 0$, we have for the global mass difference:

$$\begin{aligned} \int_0^\infty (c(r, t) - c^0) dr &= S(t) * (c^{part} - c^0) + \int_{S(t)}^\infty (c(r, t) - c^0) dr = \\ &= S_0(c^{part} - c^0) + (S(t) - S_0)(c^{part} - c^0) + \int_{S(t)}^\infty (c(r, t) - c^0) dr = \\ &= S_0(c^{part} - c^0) + \int_{S_0}^\infty (c(r, t) - c^0) dr. \end{aligned}$$

From the maximum principle, it follows that $c(r, t) > c^0$, it is then clear that

$$S_0(c^{part} - c^0) + \int_{S_0}^\infty (c(r, t) - c^0) dr > S_0(c^{part} - c^0).$$

This implies that equations (2.6) and (3.2) are not equivalent. The Stefan problem with $(c^0 < c^{part} < c^{sol})$ does not have a solution and is therefore ill-posed.

A similar proof can be given to show that for the case $(c^{sol} < c^{part} < c^0)$ no solution exists either. We then can show that

$$S(t)(c^{part} - c^0) + \int_{S(t)}^\infty (c(r, t) - c^0) dr < S_0(c^{part} - c^0). \quad \square$$

This proposition can also be given and proven in the same way for a similar more-dimensional Stefan-problem.

If we have $(c^{part} - c^0) * (c^{part} - c^{sol}) > 0$, we either have $(c^{part} < c^0) \wedge (c^{part} < c^{sol})$ or $(c^{part} > c^0) \wedge (c^{part} > c^{sol})$. Then it can be proven in a similar way that it is possible to conserve the mass and the Stefan problem is well posed. Furthermore, it appears that we will have dissolution, i.e. $\frac{dS(t)}{dt} < 0$, if $(c^{sol} - c^0)(c^{sol} - c^{part}) < 0$ and contrarily for the other well-posed problems, we will have growth.

The above mentioned concepts of well- and ill-posedness of the Stefan-problem will be used in the next sections when the solution of the vector valued Stefan-problem may not be unique.

3.3 An asymptotic solution to a planar Stefan problem

Consider a planar particle that is dissolving in an infinite matrix. The diffusion is then given by:

$$\frac{\partial c}{\partial t} = \mathbb{D} \frac{\partial^2 c}{\partial x^2}.$$

The condition at the interface is given by:

$$c(S(t), t) = c^{sol}.$$

At infinity and for $t = 0$:

$$c(r, 0) = c^0, \quad c(\infty, t) = c^0, \quad S(0) = S_0,$$

where c^{sol} and c^0 are given constants.

We look for a self-similar solution given by [10]:

$$\tilde{c}(r, t) = \alpha * \operatorname{erfc} \left(\frac{r - S_0}{2\sqrt{\mathbb{D}t}} \right) + \beta. \quad (3.4)$$

It can be seen that this function satisfies the diffusion equation. We look for solutions of the moving boundary problem with the following form:

$$S(t) = S_0 + k\sqrt{t}.$$

To satisfy the boundary conditions, we obtain for α and β :

$$\alpha = \frac{c^0 - c^{sol}}{\operatorname{erfc} \left(\frac{k}{2\sqrt{\mathbb{D}}} \right)}, \quad \beta = c^0.$$

Combination of (3.4) with (2.6) and the square-root like solutions of the free boundary position $S(t)$, yields the following equation to be solved for k :

$$\frac{k}{2\sqrt{\mathbb{D}}} = \frac{(c^0 - c^{sol})}{(c^{part} - c^{sol})} \frac{1}{\sqrt{\pi}} * \frac{\exp \left(-\frac{k^2}{4\mathbb{D}} \right)}{\operatorname{erfc} \left(\frac{k}{2\sqrt{\mathbb{D}}} \right)}. \quad (3.5)$$

In the above equation it can be seen that both sides are functions of the parameter $\lambda := \frac{k}{2\sqrt{\mathbb{D}}}$. For the right hand side, we have the following two limits: $\lim_{\lambda \rightarrow 0} \frac{e^{-\lambda^2}}{\operatorname{erfc}(\lambda)} = 1$ and $\lim_{\lambda \rightarrow \infty} \frac{e^{-\lambda^2}}{\operatorname{erfc}(\lambda)*\lambda} = \sqrt{\pi}$. Defining $A := \frac{c^0 - c^{sol}}{c^{part} - c^{sol}} \frac{1}{\sqrt{\pi}}$, we can re-arrange equation (3.5) into:

$$\frac{\lambda}{A} = \frac{\exp(-\lambda^2)}{\operatorname{erfc}(\lambda)}. \quad (3.6)$$

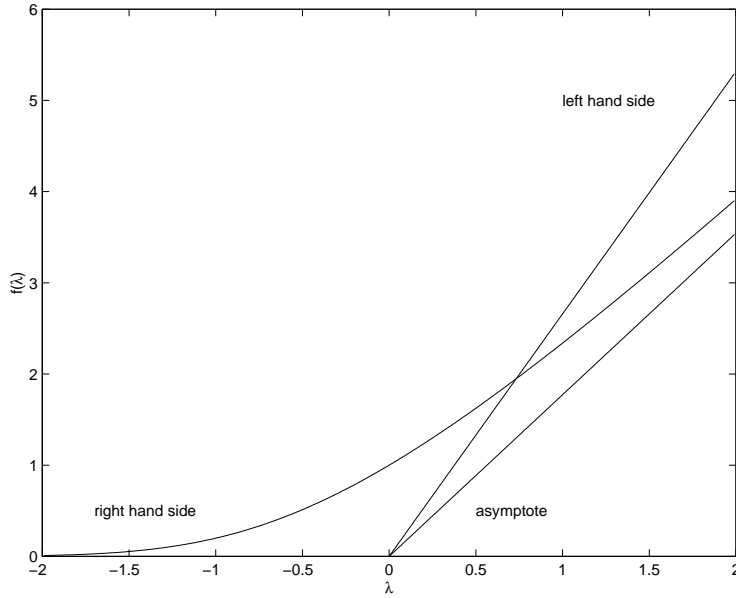


Figure 1: A graph of both sides of equation (3.6).

Solutions of this equation can be found numerically. Figure 1 displays the graph of both sides of equation (3.6). The solution is given by the intersection of the curve and the straight line from respectively the right- and left hand side of equation (3.6). The most right straight line corresponds to the asymptote $f(\lambda) = \sqrt{\pi} * \lambda$. It can be observed that for $A \approx 0$, the solution is $\frac{\lambda}{A} \approx 1$. From the limit to ∞ , it can be observed that for $0 < \frac{1}{A} < \sqrt{\pi}$, or $A > \frac{1}{\sqrt{\pi}}$ no solution exists. $A > \frac{1}{\sqrt{\pi}}$ corresponds to $\frac{c^0 - c^{sol}}{c^{part} - c^{sol}} > 1$, it can be seen that this exactly corresponds to the condition $(c^{part} - c^0) * (c^{part} - c^{sol}) < 0$ (see proposition). From this may also be observed that if a solution of this planar unbounded Stefan problem exists, the self-similar solution is unique.

Using $\frac{\lambda}{A} \approx 1$, it can be seen that k can be approximated by, for $|\frac{(c^0 - c^{sol})}{(c^{part} - c^{sol})}|$ sufficiently small:

$$k = 2 \frac{(c^0 - c^{sol})}{(c^{part} - c^{sol})} * \sqrt{\frac{\mathbb{D}}{\pi}} \quad (3.7)$$

Equation (3.7) is the same solution as we would obtain from a (inverse) Laplace transform of the diffusion equation [11], [1]. The velocity of the moving boundary can then be approximated by:

$$\frac{dS(t)}{dt} = - \frac{(c^{sol} - c^0)}{(c^{part} - c^{sol})} * \sqrt{\frac{\mathbb{D}}{\pi t}} \quad (3.8)$$

This (approximate) solution will be used in the remainder of the present paper as a fast approximate solution of the vector valued Stefan problem. It is also noted that this solution would be obtained if the interface would be stationary, i.e. not moving.

4. SOLUTIONS OF THE VECTOR-VALUED STEFAN PROBLEM

Combination of both components to fulfill the requirement as stated by equation (2.7), and using (3.8) it follows that:

$$\frac{\hat{c}_B^{sol} - c_B^0}{c_B^{part} - \hat{c}_B^{sol}} * \sqrt{\frac{\mathbb{D}_B}{\pi t}} = \frac{\hat{c}_C^{sol} - c_C^0}{c_C^{part} - \hat{c}_C^{sol}} * \sqrt{\frac{\mathbb{D}_C}{\pi t}}. \quad (4.1)$$

Using equation (2.5) as the relation between the concentrations at the interface S and substitution this into equation (4.1), one obtains:

$$\frac{\hat{c}_B^{sol} - c_B^0}{c_B^{part} - \hat{c}_B^{sol}} * \sqrt{\frac{\mathbb{D}_B}{\mathbb{D}_C}} = \frac{(K/\hat{c}_B^{sol})^{1/m} - c_C^0}{c_C^{part} - (K/\hat{c}_B^{sol})^{1/m}}. \quad (4.2)$$

This approximation gives rapid insight. It can be shown that equation (4.2) holds for all K as long as $|\frac{c_p^0 - c_p^{sol}}{c_p^{part} - c_p^{sol}}|$ is small enough (see Figure 1).

However, we formally have to solve the following non-linear system (using the definitions

$$\lambda_p := \frac{k}{2\sqrt{D_p}}, \text{ and } A_p := \frac{c_p^0 - c_p^{sol}}{c_p^{part} - c_p^{sol}} \frac{1}{\sqrt{\pi}}, p \in \{B, C\}:$$

$$\frac{\lambda_B}{A_B} = \frac{\exp(-\lambda_B^2)}{\operatorname{erfc}(\lambda_B)}, \quad \frac{\lambda_C}{A_C} = \frac{\exp(-\lambda_C^2)}{\operatorname{erfc}(\lambda_C)}, \quad (c_B^{sol})^n (c_C^{sol})^m = K. \quad (4.3)$$

The solution of this system gives then values for k , c_B^{sol} and c_C^{sol} . The solutions for (c_B^{sol}, c_C^{sol}) from equations (4.2) and (4.3) are respectively referred to as the approximate and exact solution of the vector valued Stefan problem. It turns out that the interfacial concentration is constant in time. This is a characteristic property of the planar Stefan-problem. It is shown in [8] that the interfacial concentration is not constant in time for different, curved geometries. The variation of the interfacial concentration with time is then most significant at the early stages.

For the case of a particle stoichiometry BC , i.e. $n = m$, equation (4.2) results into a simple quadratic equation. If $(c_C^0 - c_C^{part} * \sqrt{\frac{\mathbb{D}_B}{\mathbb{D}_C}}) * (c_B^{part} - c_B^0 * \sqrt{\frac{\mathbb{D}_B}{\mathbb{D}_C}}) < 0$ then there is only one root for which the inequality $\hat{c}_{B,sol} > 0$ holds. If however, $(c_C^0 - c_C^{part} * \sqrt{\frac{\mathbb{D}_B}{\mathbb{D}_C}}) * (c_B^{part} - c_B^0 * \sqrt{\frac{\mathbb{D}_B}{\mathbb{D}_C}}) > 0$ and the discriminant is positive then we have to keep in mind that the roots have to meet the requirement that the Stefan problem is not ill-posed, i.e. we may not have $0 \leq c_p^0 < c_p^{part} < c_p^{sol}$ or $0 < c_p^{sol} < c_p^{part} < c_p^0$, $p \in \{B, C\}$. A root that does not satisfy this requirement is rejected. It should be noted that the system (equation (4.3)) does not admit solutions that are not mass-conserving. In the next section the accuracy of the approximate solution is investigated.

It appeared from numerical experiments that one of the solutions may be unstable. This instability depends on the formulation of the numerical problem and is hence a numerical instability [7]. For higher orders (different stoichiometries) it is very hard to state any general remarks about the solution. For the practical cases considered so far, it was found that there was only one real solution larger than zero.

5. AN EXAMPLE OF NON-UNIQUENESS OF THE VECTOR-VALUED STEFAN PROBLEM

To get some insight into the non-uniqueness of the solution of the vector-value Stefan problem and of the accuracy of the approximate solution, we consider the following example:

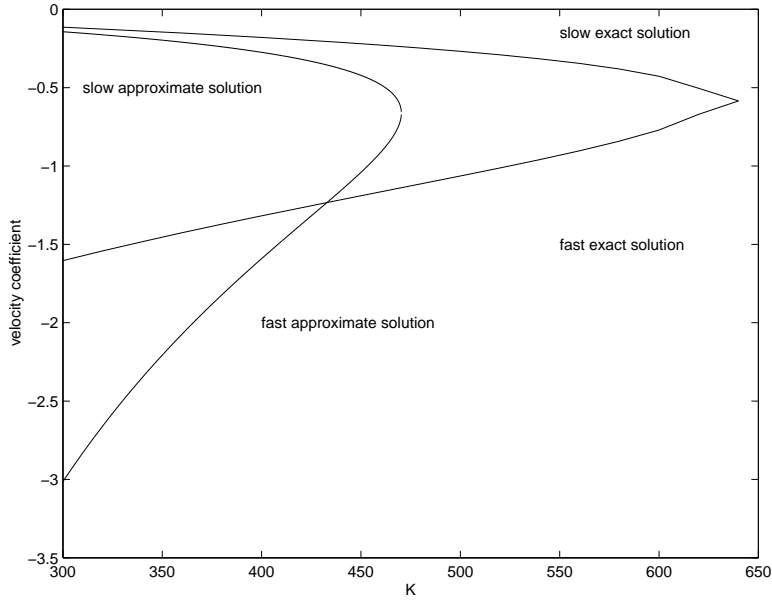


Figure 2: Interface velocity for various values of K .

$(c_B^{part}, c_C^{part}) = (50, 1)$ $(c_B^0, c_C^0) = (2, 30)$ and $\mathbb{D}_C = 2 * \mathbb{D}_B = 2 * 10^{-13} m^2/s$ and the value of K is varied. The interface conditions have been calculated using equation (4.2). Subsequently, the interface velocity is computed using equation (2.6).

Figure 2 shows the interface velocity coefficient $\frac{dS(t)}{dt} * \sqrt{\frac{t}{\mathbb{D}_B}}$ as a function of K for $K \in (300, 650)$ for the approximate and exact solution of the vector valued Stefan problem. It can be seen that there is a fast and a slow solution. The solution above and beneath are respectively referred to the slow and the fast solution.

For $0 < K < 50$, it can be seen that the discriminant, resulting from equation (4.2) is positive and hence two solutions are obtained. This is observed for both the approximate- and exact solution. It is also observed that for lower values of K the slow solution of the approximate and exact solution converge to each other. This is due to the fact that for this case A_p is small enough (typically of the order (0.01,0.1)). The fast approximate solution gives an ill-posed Stefan problem. Whereas the fast exact solution diverges to $-\infty$, corresponding to $c_p^{sol} > 100$, for some $p \in \{B, C\}$. For this case the fast solution is rejected, the solution can then be regarded as unique. For $K = 50$, it may be seen that one obtains one root corresponding to a division by zero. For $K > 50$ two positive roots for c_B^{sol} are obtained. Both solutions then have a negative velocity, so the particle dissolves. It can be observed that for $K > 350$ the approximate and exact solution start to deviate significantly for the slow solution as well. We then obtain larger values of the parameters A_B and A_C for the slow solution too. The values of A_B and A_C for the fast solution are already very large (typically in the order of (-1,-200)). This analysis gives some insight into uniqueness of the solution of the vector valued Stefan problem and on the accuracy of the approximate solution.

6. CONCLUSIONS

A mathematical model is given to describe the dissolution of particles of constant composition and consisting of two alloying elements. Some results of existence and uniqueness of the solution is given. Moreover, it is shown that some Stefan-problems are ill-posed since their solutions may satisfy the Stefan-problem, but they do not satisfy the condition that the total mass is constant.

The solution proposed here is only valid in an unbounded domain, but gives a rapid estimate of the dissolution time of plate-like particles. The solution for the plate in an unbounded domain can be used as a starting solution in the discrete Newton iteration scheme necessary for the computation of the free boundary concentrations.

The accuracy of an approximate solution is analysed. It has turned out that the approximate solution can be used reliably if $|\frac{c_p^0 - c_p^{sol}}{c_p^{part} - c_p^{sol}}| \ll 1$, $p \in \{B, C\}$.

An open question remains concerning a generalisation to different stoichiometries (i.e. $m \neq n$). More research is needed at this point.

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