

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, 2600 GA Delft, the Netherlands

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 a 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 parabolic partial differential equations. 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.

problem,

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 some phases (as precipitates) being present or the morphology of the various phases (crystal structure). Whereas the equilibrium phases can be predicted quite accurately from thermodynamic models, until recently there were 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. An example of the modelling of dissolution of Mg_2Si -particles in aluminium alloys is described in [15]. The analysis described there is carried out to highlight the influences of the cast-conditions

and temperature-time profile in the furnace in which the alloys are heated.

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 a 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 velocity of the moving boundary. The diffusion of both the alloying elements is coupled via a 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 [13].

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 and c_C (mol/m^3) 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 problem with one spatial variable. 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 $\Omega(t) = \{x \in R | M_1 \leq S_1(t) \leq x \leq S_2(t) \leq M_2\}$, $t \in [0, T]$ where T is a 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 and c_C we use the multi-component version of Fick's Second Law (see [14], [5] p. 160):

$$\frac{\partial c_p}{\partial t} = \frac{D_p}{r^a} \frac{\partial}{\partial r} \left(r^a \frac{\partial c_p}{\partial r} \right), \quad r \in \Omega(t), \quad t \in (0, T], \quad p \in \{B, C\}, \quad (1)$$

where a is a geometric parameter, which equals 0, 1 or 2 for respectively a planar, cylindrical or spherical geometry. D_p denotes the diffusion coefficient in m^2/s of each alloying element ($p \in \{B, C\}$). All these geometries occur in metallurgical applications [7]. Note that M_1 should be non-negative for $a \neq 0$. As initial conditions we use

$$c_p(r, 0) = c_p^0(r), \quad r \in \Omega(0), \quad p \in \{B, C\}, \quad (2)$$

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

$$\frac{\partial c_p}{\partial r}(M_k, t) = 0, \quad \text{for } t \geq t_k, \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (3)$$

On the moving boundaries the following definition is introduced:

$$c_p(S_k(t), t) = c_{p,k}^{sol}(t), \quad t \in [0, T], \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (4)$$

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} and 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: [14]:

$$(c_{B,k}^{sol}(t))^m \cdot (c_{C,k}^{sol}(t))^n = K, \quad k \in \{1, 2\}, \quad (5)$$

where the exponents m and n correspond to the stoichiometric phase $A_l B_m C_n$ and K is some positive number depending on temperature. In this paper we consider an isothermal process, hence K is constant. The balance of B and C atoms and the constant composition of the particle lead to the following equations [8] for the moving boundary positions:

$$(c_p^{part} - c_{p,k}^{sol}(t)) \frac{dS_k}{dt}(t) = D_p \frac{\partial c_p}{\partial r}(S_k(t), t), \quad t \in (0, T], \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (6)$$

Condition (6) implies the following Neumann condition:

$$\frac{D_B}{c_B^{part} - c_{B,k}^{sol}(t)} \frac{\partial c_B}{\partial r}(S_k(t), t) = \frac{D_C}{c_C^{part} - c_{C,k}^{sol}(t)} \frac{\partial c_C}{\partial r}(S_k(t), t), \quad k \in \{1, 2\}. \quad (7)$$

Moving boundary problems of the type given by equations (1), ..., (6) are known as a Stefan problem [3]. 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 (in which there is only one alloying element) (see [14]) and in a ternary alloy. When dissolution or growth of a particle in a binary alloy is considered, only one diffusion equation has to be solved in which the concentration at the interface $S(t)$ is known. When we consider the dissolution or growth in a ternary alloy, in the first place two diffusion equations have to be solved, which are coupled through the conditions (4), (5), and (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. Moreover, in the mathematical model for a ternary alloy an extra non-linearity occurs in equation (5). For a recent book where Stefan problems are considered we refer to [10] (see for instance p. 132 (2.5), (2.9)).

For generality we specified the Stefan-problem for one, two or three spatial dimensions, we, however, will be concerned with one spatial dimension only in the remainder of the paper.

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 ($M_2 = \infty$). In this section and the following sections, we consider a flat plate with infinite length and width and finite half thickness $S(t)$ which dissolves or grows in an infinite domain. We briefly refer to this flat plate as "the particle". 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. We define the space Q as $Q := \{(r, t) : r \in \Omega(t), t \in (0, T)\}$. We look for solutions of the Stefan problem with the following properties: $S \in C^1(0, T]$ and $c \in C^{2,1}(Q) \cap C(\bar{Q})$. When $c^0(S(0)) \neq c^{sol}(0)$, then c cannot be required to be continuous in $(S(0), 0)$. In these points, we require:

$$\begin{aligned} \min\{c^0(S(0)), c^{sol}(0)\} &= \liminf_{\substack{(r, t) \in Q \\ (r, t) \rightarrow (S(0), 0)}} c(r, t) \leq \\ & \limsup_{\substack{(r, t) \in Q \\ (r, t) \rightarrow (S(0), 0)}} c(r, t) = \max\{c^0(S(0)), c^{sol}(0)\}, \end{aligned} \quad (8)$$

compare FRIEDMAN [4], VUIK (Lemma 2.4., p.18, [12]) proved for $c(r, t)$, being a bounded solution of the diffusion equation in the unbounded domain with the above requirements, that it satisfies a maximum principle. We present this maximum principle for completeness.

Maximum principle

Suppose c satisfies the inequality

$$\frac{\partial^2 c}{\partial r^2} - \frac{\partial c}{\partial t} \geq 0, \quad r \in \Omega(t), \quad t \in (0, T], \quad (9)$$

if there is a local maximum then this 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 $\{(S_1(t), t) : t \in (0, T)\}$ or $\{(S_2(t), t) : t \in (0, T)\}$. If $\frac{\partial c}{\partial \nu}$ denotes the derivative in an outward direction from Q , 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 [6] p. 168, p. 170), by FRIEDMANN for the case of a discontinuity at $r = S(0), t = 0$ (see [4],

p. 40) and by VUIK for an unbounded domain (see [12], p. 18). This principle can also be applied for local minima (and $\frac{\partial c}{\partial \nu} < 0$) when the inequality in (9) 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 [13] some limitations of the vector-valued Stefan problem (1)...(6) are summarised. It appears that the model breaks down when the concentration at the interface equals the concentration in the particle. Moreover in [13] some 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 [9]:appendix 2. The velocity of the interface is given by equation (6) and based on conservation of mass. We formulate conservation of mass by:

$$\int_{S(t)}^{\infty} (c(r, t) - c^0) dr = (c^0 - c^{part}) \cdot (S(t) - S_0) \tag{10}$$

Here we take the quantities c^{sol}, c^{part} and c^0 as known constants. Moreover, we define $c(r, t) = c^{part}$ for $r < S(t)$ and $S(t), S_0 \geq 0$. The above equation is also referred to as the integral formulation of the Stefan condition in an unbounded domain. Note that equation (10) holds under the assumption that $c(r, t) - c^0$ is integrable in the interval $(S(t), \infty)$. Under this assumption and

$$-D \frac{\partial c(r, t)}{\partial r} \rightarrow 0, \text{ as } r \rightarrow \infty \forall t \in (0, T],$$

equation (10) is equivalent to (6).

If we define $\frac{\partial c}{\partial \nu}$ as the derivative in the outward normal direction from Q , it follows from the maximum principle that $(c^{sol} - c^0) \frac{\partial c}{\partial \nu} > 0$. From equation (6), it then follows that

$$v_n(t) (c^{part} - c^{sol}) \cdot \frac{\partial c}{\partial \nu} > 0. \tag{11}$$

on $\{(S(t), t) : t \in (0, T)\}$.

We here 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

$$(c^{part} - c^0) (c^{part} - c^{sol}) \leq 0 \text{ and } c^{sol} \neq c^0.$$

PROOF

We assume that $c^{sol} \neq c^0$, the maximum principle states that:

$$(c^{sol} - c^0) \cdot \frac{\partial c}{\partial \nu} > 0, \quad (12)$$

on $\{(S(t), t) : t \in (0, T]\}$, where $\frac{\partial}{\partial \nu}$ denotes the derivative in the outward normal direction from Q . One can write the normal on the moving boundary $\{(S(t), t) : t \in (0, T]\}$ in Q as a scalar multiple of $(-1, S'(t))$, which gives:

$$\frac{\partial c}{\partial \nu} = \underline{\nu} \cdot \nabla_Q c = (-1, S'(t)) \cdot \left(\frac{\partial c}{\partial r}, \frac{\partial c}{\partial t} \right). \quad (13)$$

In which the operator $\nabla_Q := \left(\frac{\partial}{\partial r}, \frac{\partial}{\partial t} \right)$. Substitution of (13) into (12) gives:

$$(c^{sol} - c^0) \left\{ -\frac{\partial c(S(t), t)}{\partial r} + S'(t) \frac{\partial c(S(t), t)}{\partial t} \right\} > 0. \quad (14)$$

For $c(S(t), t) = c^{sol}$, we have for the time derivative:

$$0 = \frac{dc(S(t), t)}{dt} = S'(t) \frac{\partial c(S(t), t)}{\partial r} + \frac{\partial c(S(t), t)}{\partial t}, \quad \forall t \in (0, T]. \quad (15)$$

Combination of equations (15) and (6) to eliminate $\frac{\partial c}{\partial r}$ and $\frac{\partial c}{\partial t}$ yields:

$$\frac{1}{D} (c^{sol} - c^0) (c^{sol} - c^{part}) S'(t) [1 + S'(t)^2] > 0, \quad \forall t \in (0, T]. \quad (16)$$

Hence:

$$(c^{sol} - c^0) (c^{sol} - c^{part}) S'(t) > 0, \quad \forall t \in (0, T]. \quad (17)$$

Integration of the above expression in t , yields:

$$(c^{sol} - c^0) (c^{sol} - c^{part}) (S(t) - s_0) > 0, \quad \forall t \in (0, T]. \quad (18)$$

From the maximum principle follows

$$(c^{sol} - c^0) \int_{S(t)}^{\infty} (c(r, t) - c^0) dr > 0, \quad (19)$$

which can be written as (by using (10)):

$$(c^{sol} - c^0) (c^0 - c^{part}) (S(t) - S_0) > 0, \quad \forall t \in (0, T]. \quad (20)$$

Combination of (18) and (20) yields:

$$(c^0 - c^{part}) (c^{sol} - c^{part}) (c^{sol} - c^0)^2 (S(t) - S_0)^2 > 0,$$

which implies that if $c^{sol} \neq c^0$ the problem has a solution if

$$(c^0 - c^{part})(c^{sol} - c^{part}) > 0, \quad \forall t \in (0, T].$$

Hence if $(c^0 - c^{part})(c^{sol} - c^{part}) \leq 0$ then the Stefan problem has no solution. \square

Moreover, if $(c^{sol} - c^0)(c^{sol} - c^{part}) > 0$ then $S'(t) > 0, \forall t \in (0, T]$. Whereas if $(c^{sol} - c^0)(c^{sol} - c^{part}) < 0$ then $S'(t) < 0, \forall t \in (0, T]$.

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. In real world aluminium alloys the following two cases take place: $c^{sol} < c^0 < c^{part}$ and $c^0 < c^{sol} < c^{part}$. Physically, diffusion involves transport of atoms from areas with high concentrations to areas with low concentrations. Hence, if for instance $c^{sol} < c^0 < c^{part}$, then the transport of atoms in $\Omega(t)$ proceeds towards the particle. For thermodynamic reasons the concentration at the moving boundary (i.e. $c(S(t), t) = c^{sol}$) has to remain constant and hence the atoms will cross the free boundary and hence the particle will grow. On the contrary, the case $c^{sol} > c^0$ means that the atoms in the particle will jump over the moving boundary. This leads to an increase of the interface concentration up to c^{sol} and diffusion will start from the particle. Since the particle concentration, c^{part} is fixed, the particle will dissolve. The case that $c^{part} < c^0 < c^{sol}$ occurs in phase-transformations in some steel alloys: Near the particle (but outside, i.e. at $r > S(t)$), a transition of the crystal structure occurs to the structure as in the particle, which causes a movement of the boundary. Due to this crystal structure, the atoms cross the moving boundary and the concentration at the moving boundary is increased up to c^{sol} . Diffusion will then take place from the particle. In this model the evolution of the concentration at the moving boundary is assumed to be infinitely fast, i.e. the concentration at the moving boundary equals c^{sol} immediately. Experimental observations for Al-Si- alloys confirmed this [11]. It can be seen that if $(c^{part} - c^0) \cdot (c^{part} - c^{sol}) < 0$, physically the mass balance would be violated.

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. Some of the concepts of the derivation of the solution has been described by CARSLAW and JAEGER [2]. Nevertheless, for completeness we present the derivation in this paper. Later in this section, we will need some insights from this. The diffusion is then given by:

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

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 [16]:

$$\tilde{c}(r, t) = \alpha \cdot \operatorname{erfc}\left(\frac{r - S_0}{2\sqrt{Dt}}\right) + \beta. \quad (21)$$

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 :

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

Combination of (21) with (6) and the square-root like solutions of the free boundary position $S(t)$, yields the following equation to be solved for k :

$$\frac{k}{2\sqrt{D}} = \frac{(c^0 - c^{sol})}{(c^{part} - c^{sol})} \frac{1}{\sqrt{\pi}} \frac{\exp\left(-\frac{k^2}{4D}\right)}{\operatorname{erfc}\left(\frac{k}{2\sqrt{D}}\right)}. \quad (22)$$

In the above equation it can be seen that both sides are functions of the parameter $\lambda := \frac{k}{2\sqrt{D}}$. For the right hand side, we have the following: For $\lambda = 0$, $\frac{e^{-\lambda^2}}{\operatorname{erfc}(\lambda)} = 1$ 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 (22) into:

$$\frac{\lambda}{A} = \frac{\exp(-\lambda^2)}{\operatorname{erfc}(\lambda)}. \quad (23)$$

Solutions of this equation can be found numerically. Figure 1 displays the graph of both sides of equation (23). The solution is given by the intersection of the curve and the straight line from respectively the right- and left hand side of equation (23) (compare [2], section 11.2.II). 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

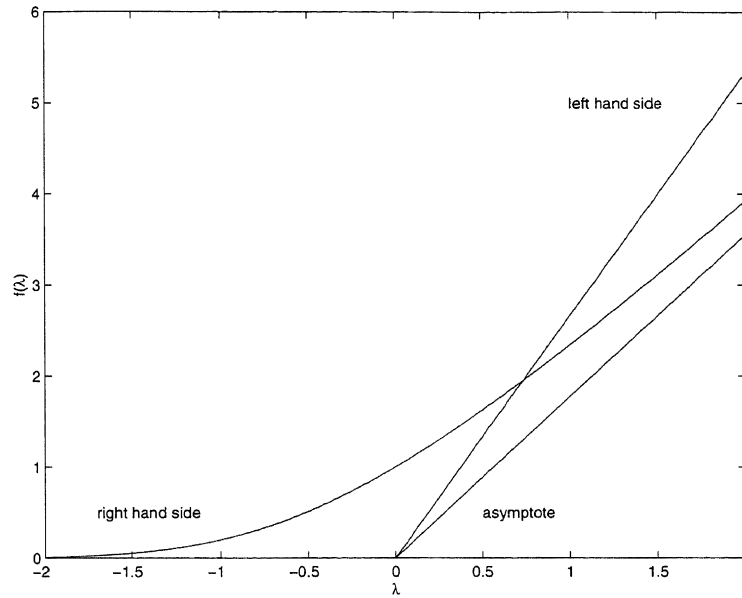


FIGURE 1. A graph of both sides of equation (23).

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 a self-similar solution of this planar unbounded Stefan problem exists, and, it is unique in the considered class of self-similar solutions.

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:

$$k = 2 \frac{(c^0 - c^{sol})}{(c^{part} - c^{sol})} \sqrt{\frac{D}{\pi}} \tag{24}$$

Approximation (24) is the same solution as we would obtain from a (inverse) Laplace transform of the diffusion equation [1, 17]. The velocity of the moving boundary can then be approximated by:

$$\frac{dS(t)}{dt} = - \frac{(c^{sol} - c^0)}{(c^{part} - c^{sol})} \sqrt{\frac{D}{\pi t}} \tag{25}$$

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 fulfil the requirement as stated by equation (7), and using (25) it follows that:

$$\frac{\hat{c}_B^{sol} - c_B^0}{c_B^{part} - \hat{c}_B^{sol}} \sqrt{\frac{D_B}{\pi t}} = \frac{\hat{c}_C^{sol} - c_C^0}{c_C^{part} - \hat{c}_C^{sol}} \sqrt{\frac{D_C}{\pi t}}. \quad (26)$$

In which c_B^{sol} and c_C^{sol} here are constants to be determined. Using equation (5) as the relation between the concentrations at the interface S and substitution this into equation (26), one obtains:

$$\frac{\hat{c}_B^{sol} - c_B^0}{c_B^{part} - \hat{c}_B^{sol}} \sqrt{\frac{D_B}{D_C}} = \frac{(K(\hat{c}_B^{sol})^n)^{1/m} - c_C^0}{c_C^{part} - (K(\hat{c}_B^{sol})^n)^{1/m}}. \quad (27)$$

This approximation gives rapid insight. It can be shown that equation (27) holds for all K as long as $|\frac{c^0 - c^{sol}}{c^{part} - c^{sol}}|$ is small enough (see Figure 1). However, we formally have to solve the following non-linear system (using the definitions $\lambda_p := \frac{k}{2\sqrt{D_p}}$, and $A_p := \frac{c_p^0 - c_p^{sol}}{c_p^{part} - c_p^{sol}} \frac{1}{\sqrt{\pi}}$, $p \in \{B, C\}$):

$$\frac{\lambda_B}{A_B} = \frac{\exp(-\lambda_B^2)}{\operatorname{erfc}(\lambda_B)}, \quad \frac{\lambda_C}{A_C} = \frac{\exp(-\lambda_C^2)}{\operatorname{erfc}(\lambda_C)}, \quad (c_B^{sol})^n (c_C^{sol})^m = K. \quad (28)$$

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 (27) and (28) are respectively referred to as the approximate and exact solution of the vector-valued Stefan problem.

Note that the constructed solution is such that the interfacial concentrations are constant in time. Applying a similar approach to a spherical geometry, it is shown in [14] that this need not be the case for spherical geometry. The variation of the interfacial concentration with time is then most significant at the early stages. Moreover, finite difference simulations showed that the interface concentration is not constant either for axial symmetry and for the planar particle in a bounded domain.

For the case of a particle stoichiometry BC , i.e. $n = m$, equation (27) results into a simple quadratic equation. If $(c_C^0 - c_C^{part} \sqrt{\frac{D_B}{D_C}})(c_B^{part} - c_B^0 \sqrt{\frac{D_B}{D_C}}) < 0$ then there is only one root for which the inequality $\hat{c}_{B,sol} > 0$ holds. If however, $(c_C^0 - c_C^{part} \sqrt{\frac{D_B}{D_C}}) * (c_B^{part} - c_B^0 \sqrt{\frac{D_B}{D_C}}) > 0$ and the discriminant is positive then we have to keep in mind that the roots (c_B^{sol}, c_C^{sol}) have to be such that $not\ 0 \leq c_p^0 < c_p^{part} < c_p^{sol}$ and $not\ 0 < c_p^{sol} < c_p^{part} < c_p^0$, $p \in \{B, C\}$. A root that does not satisfy this requirement is rejected (see proposition). The global mass balance would not be satisfied then. It should be noted that the system (equation (28)) 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

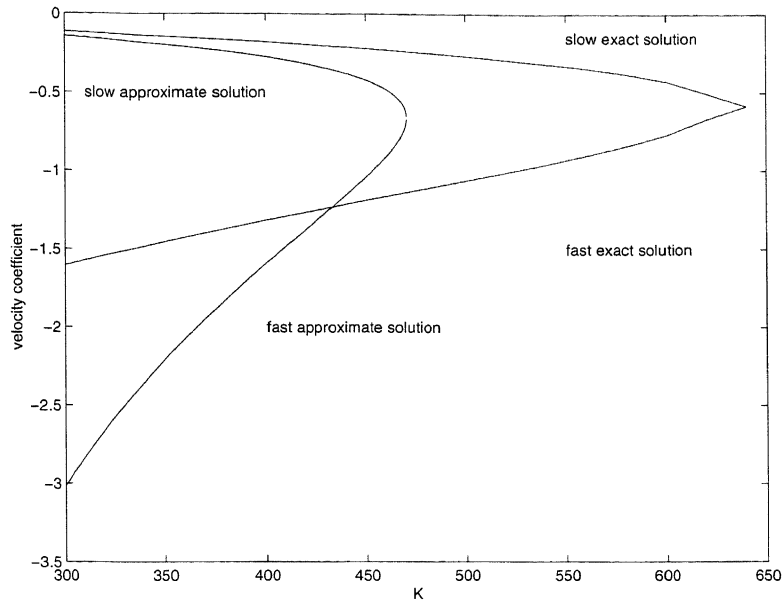


FIGURE 2. Interface velocity for various values of K .

is hence a numerical instability [13]. 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 solution which yielded a pair c_B^{sol} and c_C^{sol} both of which 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-valued Stefan problem and of the accuracy of the approximate solution, we consider the following example: $(c_B^{part}, c_C^{part}) = (50, 1)$ $(c_B^0, c_C^0) = (2, 30)$ and $D_C = 2 * D_B = 2 * 10^{-13} m^2/s$ and the value of K is varied. The interface conditions have been calculated using equation (27). Subsequently, the interface velocity is computed using equation (6).

Figure 2 shows the interface velocity coefficient $\frac{dS(t)}{dt} * \sqrt{\frac{t}{D_B}}$ 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 $0 < K < 50$ (not shown in the figure) the discriminant, resulting from approximation (27) is positive and hence two solutions are obtained. This holds for both the approximate- and exact solution. Also the difference between the approximate and exact solution tends to zero as K decreases. This is due to

the fact that for this case A_p is small enough (typically of the order (0.01,0.1)). After solving approximation (27), the fast approximate solution gives roots such that $(c_p^{part} - c_p^0)(c_p^{part} - c_p^{sol}) < 0$. Whereas the velocity coefficient corresponding to the fast root of the 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 $K = 50$, one obtains one root which gives a division by zero in approximation (27). For $K > 50$ two positive roots for c_B^{sol} are obtained. Both solutions then have a negative velocity, so the particle dissolves. For $K > 350$ it can be observed in Figure 2 that 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 a uniform and constant composition and consisting of two alloying elements. Some results of existence and uniqueness of the solution are 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 of mass conservation.

The solution proposed here is only valid in an unbounded domain, but gives some qualitative insight into the dissolution time of plate-like particles, which then can be obtained without the use of a finite difference discretisation routine or a numerical routine to solve the non-linear system given in 28, which needs some programming. The solution for the plate in an unbounded domain can be used as a starting solution in a discrete Newton iteration scheme necessary for the computation of the moving boundary concentrations.

The accuracy of an approximate solution is analysed. It has turned out that the approximate solution does not differ significantly from the exact solution if $|\frac{c_p^0 - c_p^{sol}}{c_p^{part} - c_p^{sol}}| \ll 1$, $p \in \{B, C\}$ (only then the approximate solution is accurate).

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

ACKNOWLEDGEMENT

Part of the work done for this paper by the first author, has been done at the Delft University of Technology at the laboratory for Materials Science in the group of prof.dr.ir. S. Van der Zwaag. Moreover, the authors thank the referee for the helpful suggestions.

REFERENCES

1. H.B. AARON, G.R. KOTLER, 1971, Second phase dissolution. *Metallurgical Transactions*, 2:393–407.
2. H.S. CARSLAW, J.C. JAEGER, 1959, *Conduction of heat in solids*. 2nd ed. Clarendon Press, Oxford.
3. J. CRANK, 1984, *Free and Moving Boundary Problems*. Clarendon Press, Oxford.
4. A. FRIEDMAN, 1964, *Partial differential equations of parabolic type*. Prentice-Hall, INC, Englewood Cliffs, N.J..
5. R.L. PARKER, 1970, Crystal growth mechanisms: energetics, kinetics and transport. *Solid State Physics*, 25: 152–298.
6. M.H. PROTTER, H.F. WEINBERGER, 1967, *Maximum Principles in Differential Equations*. Prentice-Hall, Englewood Cliffs.
7. O. REISO, N. RYUM, J. STRID, 1993, Melting and dissolution of secondary phase particles in AlMgSi-alloys. *Met. Trans. A*, 24A: 2629–2641.
8. GUUS SEGAL, KEES VUIK, FRED VERMOLEN, 1998, A conserving discretization for the free boundary in a two-dimensional Stefan problem. *J. Comp. Phys.*, 141: 1–21.
9. FRED VERMOLEN, 1998. *Mathematical models for particle dissolution in extrudable aluminium alloys*. Delft University Press, Delft. Thesis.
10. A. VISINTIN, 1996. *Models of Phase Transitions*. Progress in Nonlinear Differential Equations and Their Application: 28. Birkhäuser, Boston.
11. FRED VERMOLEN, MICHEL SLABBEKOORN, SYBRAND VAN DER ZWAAG, 1997, The apparent activation energy for the dissolution of spherical si-particles in alsi-alloys. *Journal of Materials Science and Engineering*, A231: 80–89.
12. C. VUIK, 1993, *The solution of a one-dimensional Stefan problem*. 90. CWI-tract, CWI-Amsterdam.
13. FRED VERMOLEN, KEES VUIK, 1998, A numerical method to compute the dissolution of second phases in ternary alloys. *Journal of computational and applied mathematics*, 93: 123–143.
14. FRED VERMOLEN, KEES VUIK, SYBRAND VAN DER ZWAAG, 1998, The dissolution of a stoichiometric second phase in ternary alloys: a numerical analysis. *Materials Science and Engineering A*, A246: 93–103.
15. FRED VERMOLEN, KEES VUIK, SYBRAND VAN DER ZWAAG, 1998, A mathematical model for the dissolution kinetics of mg_2si -phases in al-mg-si-alloys during homogenisation under industrial conditions. *Journal of Materials Science and Engineering*, accepted, to appear.
16. H. WEBER, 1901, *Die partiellen Differential-Gleichungen der mathematischen Physik II*. Vieweg, Braunschweig.
17. M.J. WHELAN, 1969, On the kinetics of particle dissolution. *Metal Science Journal*, 3: 95–97.