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Report 97-53

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ISSN 0922-5641

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# A numerical method to compute the dissolution of second phases in ternary alloys

Fred Vermolen\*, Kees Vuik†

December 4, 1997

## 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. Some results concerning existence, uniqueness, and monotonicity are given. Furthermore, for an unbounded domain an analytical approximation is derived. The main part of this work is the development of a numerical solution method. Finite differences are used on a grid which changes in time. The discretization of the boundary conditions is important to obtain an accurate solution. The resulting nonlinear algebraic system is solved by the Newton-Raphson method. Numerical experiments illustrate the accuracy of the numerical method. The numerical solution is compared with the analytical approximation.

**Keywords:** Stefan problem, moving grid method, stoichiometric particle dissolution, ternary alloy homogenisation

**AMS Subject Classification:** 35R35, 65M06, 80A22

## 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, there are no general models for microstructural changes nor general models for the kinetics of these changes. In the latter cases both the 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.

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To describe this particle dissolution in solid media several physical models for binary alloys have been developed, incorporating the effects of long-distance diffusion [18, 2, 13] and non-equilibrium conditions at the interface [8, 1, 14]. These articles did not cover the technologically important dissolution of stoichiometric multi-component particles in ternary alloys.

The phase transformation element in steel has been studied in [5, 17]. Reiso [11] investigated the dissolution of  $\text{Mg}_2\text{Si}$ -particles in aluminium alloys mainly experimentally. He compared his results to a simple dissolution model valid for dissolution in infinite media. All analyses indicate that the addition of a second alloying element can influence the dissolution kinetics strongly. However, in none of these articles attention was paid to the effect of the particle geometry on the dissolution of particles in ternary alloys. The present article describes the dissolution of spherical and needle shaped particles, a planar medium, a spherical layer of segregation and the combination of a dissolving particle and a dissolving spherical layer of segregation. In many metallurgical situations, the thermal treatment also aims at the dissolution of the segregation layer around the grains. In the articles mentioned, no attention was paid to the impact of all physical parameters on the overall dissolution kinetics.

The present work covers a detailed numerical analysis of a coupled Stefan problem in which two boundaries either move or are fixed. The diffusion equation is solved using a finite difference discretization. The displacement of the boundary is computed with a front-tracking method. The concentration of both chemical elements are linked via the hyperbolic relation between the Dirichlet conditions corresponding to both diffusing elements. The disappearance of a moving boundary is incorporated and modelled by a transition of a Dirichlet condition to a Neumann condition. The calculation can then be continued until complete homogenisation has been reached.

The mathematical model for the dissolution of second phases in ternary alloys is given in Section 2. Some remarks about existence, uniqueness and properties of the solution are given in Section 3. In Section 4 the numerical method is specified. Some properties of the numerical method are investigated in Section 5. In this section also a number of metallurgical applications are solved and properties of their solutions are given.

## 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  $c_B, c_C$  ( $\text{mol}/\text{m}^3$ ) 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 one-dimensional problem. 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 [15], [9] p. 160):

$$\frac{\partial c_p}{\partial t} = \frac{1}{r^a} \frac{\partial}{\partial r} (\mathbb{D}_{p,B} r^a \frac{\partial c_B}{\partial r}) + \frac{1}{r^a} \frac{\partial}{\partial r} (\mathbb{D}_{p,C} r^a \frac{\partial c_C}{\partial r}), \quad r \in \Omega(t), \quad t \in (0, T], \quad p \in \{B, C\}, \quad (1)$$

where  $a$  is a geometric parameter, which equals 0, 1, or 2 for respectively a planar, a cylindrical, or a spherical geometry. Note that  $M_1$  should be non-negative for  $a \neq 0$ . All these geometries occur in metallurgical applications. For simplicity we assume  $\mathbb{D}_{B,C} = \mathbb{D}_{C,B} = 0$ , both species diffuse independently, and that  $\mathbb{D}_{B,B} = \mathbb{D}_B, \mathbb{D}_{C,C} = \mathbb{D}_C$  ( $\text{m}^2/\text{s}$ ) are constant. Hence, the equations given in (1) reduce to:

$$\frac{\partial c_p}{\partial t} = \frac{\mathbb{D}_p}{r^a} \frac{\partial}{\partial r} (r^a \frac{\partial c_p}{\partial r}), \quad r \in \Omega(t), \quad t \in (0, T], \quad p \in \{B, C\}. \quad (2)$$

As initial conditions we use

$$c_p(r, 0) = c_p^0(r), \quad r \in \Omega(0), \quad p \in \{B, C\}, \quad (3)$$

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

$$\frac{\partial c_p}{\partial r}(M_k, t) = 0, \quad \text{for } t \geq t_k, \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (4)$$

On the moving boundaries a Dirichlet boundary condition is used:

$$c_p(S_k(t), t) = c_{p,k,sol}(t), \quad t \in [0, T], \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (5)$$

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 [15]:

$$(c_{B,k,sol}(t))^m \cdot (c_{C,k,sol}(t))^n = K, \quad k \in \{1, 2\}, \quad (6)$$

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 [12] for the moving boundary positions:

$$(c_{p,part} - c_{p,k,sol}(t)) \frac{dS_k}{dt}(t) = \mathbb{D}_p \frac{\partial c_p}{\partial r}(S_k(t), t), \quad t \in (0, T], \quad p \in \{B, C\}, \quad k \in \{1, 2\}. \quad (7)$$

Condition (7) implies

$$\frac{\mathbb{D}_B}{c_{B,part} - c_{B,k,sol}(t)} \frac{\partial c_B}{\partial r}(S_k(t), t) = \frac{\mathbb{D}_C}{c_{C,part} - c_{C,k,sol}(t)} \frac{\partial c_C}{\partial r}(S_k(t), t), \quad k \in \{1, 2\}. \quad (8)$$

The moving boundary problem given by equations (2), ..., (7) is known as a Stefan problem [3]. For a recent book where this type of problems is considered we refer to [16] (see for instance p. 132 (2.5), (2.9)). There are some differences between the dissolution in a binary alloy ([15]) and in a ternary alloy. In the first place, two diffusion equations have to be solved, which are coupled through the conditions (5), (6), 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. However, in the mathematical model for a ternary alloy an extra non-linearity occurs in equation (6).

### 3 Properties of the Stefan problem

After the description of a maximum principle we give some results concerning existence, uniqueness, and monotonicity of solutions of the given Stefan problem. Also an approximate solution is given for the dissolution of a particle in an unbounded domain ( $M_2 = \infty$ ).

#### 3.1 The maximum principle for the diffusion equation

First a few basic principles are formulated, which are used later in this section. 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

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

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 [10] p. 168, p. 170). 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  $t = 0$ .

#### 3.2 Some limitations of the Stefan problem

In this section we consider some artificial problems, in order to investigate the limitations of our mathematical model. In the first example we show that the model breaks down when the concentration at the interface is equal to the particle concentration. From the second example it appears that difficulties occur when the initial concentration is equal to the particle concentration. Then the ternary model should be replaced by a binary model.

The movement of the boundaries  $S_1, S_2$  is given by equation (7). This holds provided  $c_{p,sol} \neq c_{p,part}$ ,  $p \in \{B, C\}$  to prevent a division by zero. If  $\frac{\partial c_p}{\partial r}(S_k(t), t) \neq 0$  then a division by zero would imply an infinite displacement. Such a situation can occur, for example, when we have an initial concentration profile in which  $c_p^0(r) < c_{p,part}$  for  $r \in (S_1(0), (S_1(0) + S_2(0))/2)$  and  $c_p^0(r) > c_{p,part}$  for  $r \in ((S_1(0) + S_2(0))/2, S_2(0))$ . Simulations have shown that then possibly  $c_{p,sol}$  converges to  $c_{p,part}$ , causing a division by zero when computing the displacement of the boundary.

We consider the following planar problem:  $c_C^0 = 0$ ,  $c_B^0 = c_{B,part}$ ,  $S_2(t) = M_2$ , and for simplicity equation (4) is replaced by

$$c_p(M_2, t) = c_p^0, \quad p \in \{B, C\}. \quad (10)$$

Suppose that  $S_1, c_B$ , and  $c_C$  are a solution of the Stefan problem, where  $0 \leq c_{C,sol}(t) \leq c_{C,part}$ . Then we have the following result:

**Proposition**

There is no  $\hat{t} > 0$  such that  $S_1(t)$  is monotone on  $[0, \hat{t}]$ , unless  $c_{B,sol}(\hat{t}) = c_{B,part}$ .

**Proof**

Suppose there is a  $\hat{t} > 0$  such that  $\frac{dS_1}{dt} \geq 0, t \in [0, \hat{t}]$ . This assumption together with the inequality  $c_{C,sol}(t) \leq c_{C,part}$ , and equation (7) imply that  $\frac{\partial c_C}{\partial r}(S_1(t), t) \geq 0, t \in [0, \hat{t}]$ . Equation (6) implies that  $c_{C,sol}(t) \neq 0$ . From the maximum principle it follows that the maximum occurs at  $S_1$ . However at such a point the inequality  $\frac{\partial c_C}{\partial r}(S_1(t), t) < 0$  holds. This leads to a contradiction.

Now we assume that there is a  $\hat{t} > 0$  such that  $\frac{dS_1}{dt} \leq 0, t \in [0, \hat{t}]$ . When there is a  $\tilde{t} \in [0, \hat{t}]$  such that  $c_{B,sol}(\tilde{t}) > c_{B,part}$ , equation (7) implies that  $\frac{\partial c_C}{\partial r}(S_1(\tilde{t}), \tilde{t}) \geq 0$ . Using the maximum principle as before, we again obtain a contradiction. In the same way it can be proved that  $c_{B,sol}(\tilde{t}) < c_{B,part}$  is impossible.  $\square$

This proposition implies that the only physically acceptable solution occurs when  $c_{B,sol}(t) = c_{B,part}$ . In this case we are faced with a division by zero when computing the displacement of the boundary. However, due to the maximum principle  $c_B(r, t) = c_{B,part} = c_B^0$ , so  $\frac{\partial c_B}{\partial r}(S_1(t), t) = 0$ . Hence we are faced with a zero-by-zero division. From a thermodynamic point of view it is reasonable that for this case there is no change of the concentration profile in the matrix. The boundary conditions are coupled via equation (6). The solution for this situation can be obtained using the solution of the concentration profile of the element  $C$  only. We are thus faced with a binary diffusion problem, in which the interfacial concentration of element  $C$  is then determined by the concentration of element  $B$  by equation (6).

### 3.3 Monotonicity properties

Consider the solution of the Stefan problem:  $S_1, c_B$ , and  $c_C$ , where  $S_2 = M_2$  and equation (4) replaced by (10). We assume that  $c_B^0 < c_{B,part}$ . Suppose that at some time,  $t_1$ ,  $c_B(S_1(t_1), t_1) < c_{B,part}$  and at a later time,  $t_3 > t_1$ , we would have  $c_B(S_1(t_3), t_3) > c_{B,part}$ . From the continuity of  $c_B(S_1(t), t)$ , it follows that for some time,  $t_2$ , such that  $t_1 < t_2 < t_3$ ,  $c_B(S_1(t), t) < c_{B,part}$ ,  $t \in [t_1, t_2)$ , and  $c_B(S_1(t_2), t_2) = c_{B,part}$ . According to equation (7),  $\frac{\partial c_B}{\partial r}(S_1(t_2), t_2) = 0$ . This violates the maximum principle. A similar situation can be analysed for  $c_B^0 > c_{B,part}$ , and  $c_B(S_1(t_1), t_1) > c_{B,part}$ . From this it can be concluded that the sign of  $c_p(S_k(t), t) - c_{p,part}$  does not change with time, provided this sign is equal to the sign of  $c_p^0(r) - c_{p,part}$  for all  $r$ .

### 3.4 An approximate solution

For the case that diffusion takes place in an infinite medium with spherical symmetry near a spherical particle, the Laplace transform can be used to solve the problem. The diffusion equation for spherical symmetry determines the transport of matter:

$$\frac{\partial c_p}{\partial t} = \frac{D_p}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial c_p}{\partial r}), \quad p \in \{B, C\}.$$

The condition at the interface is given by:

$$c_p(S_1(t), t) = c_{p,sol}(t).$$

At infinity and for  $t = 0$ :

$$c_p(r, 0) = c_p^0, \quad c_p(\infty, t) = c_p^0,$$

where  $c_p^0$  are given constants. We approximate the function  $c_{p,sol}(t)$  by a constant value  $\hat{c}_{p,sol}$ . By means of the (inverse) Laplace transform an approximate solution [18] is given by:

$$\tilde{c}_p(r, t) = c_p^0 + (\hat{c}_{p,sol} - c_p^0) * \frac{S_1(t)}{r} * \text{Erfc} \left( \frac{r - S_1(t)}{2\sqrt{\mathbb{D}_p t}} \right). \quad (11)$$

This approximation is exact when  $S_1(t)$  is constant. So we assume that the difference between the exact solution and the approximation is small as long as  $S_1(t)$  is a slowly varying function. Substitution of  $\tilde{c}_p$  into equation (7), yields:

$$\frac{dS_1(t)}{dt} = -\frac{\hat{c}_{p,sol} - c_p^0}{c_{p,part} - c_{p,sol}} * \left( \frac{\mathbb{D}_p}{S_1(t)} + \sqrt{\frac{\mathbb{D}_p}{\pi t}} \right). \quad (12)$$

Combination of both components to full fill the requirement as stated by equation (8), it follows that:

$$\frac{\hat{c}_{B,sol} - c_B^0}{c_{B,part} - \hat{c}_{B,sol}} * \left( \frac{\mathbb{D}_B}{S_1(t)} + \sqrt{\frac{\mathbb{D}_B}{\pi t}} \right) = \frac{\hat{c}_{C,sol} - c_C^0}{c_{C,part} - \hat{c}_{C,sol}} * \left( \frac{\mathbb{D}_C}{S_1(t)} + \sqrt{\frac{\mathbb{D}_C}{\pi t}} \right). \quad (13)$$

Using equation (6) as the relation between the concentrations at the interface  $S_1$ , it follows that for  $t \downarrow 0$ :

$$\frac{\hat{c}_{B,sol} - c_B^0}{c_{B,part} - \hat{c}_{B,sol}} * \sqrt{\frac{\mathbb{D}_B}{\mathbb{D}_C}} = \frac{(K/\hat{c}_{B,sol}^n)^{1/m} - c_C^0}{c_{C,part} - (K/\hat{c}_{B,sol}^n)^{1/m}}. \quad (14)$$

As has been remarked before, it has been assumed that the interfacial concentration is constant in time. The variation of the interfacial concentration with time is most significant at the early stages: the interfacial concentrations then change from  $c_p^0$  to  $\hat{c}_{p,sol}$ . In the later stages, the interfacial concentrations will vary less with time and the above used approximation may be more accurate. As the diffusion of the chemical elements proceeds, the elements reach the other boundary. Then, an accumulation of atoms occurs there. However, this analytical model does not incorporate this effect since it is assumed that the domain in which the elements diffuse is infinite. Therefore at the later stages this approximation will become less accurate as well.

For the case of a particle stoichiometry  $BC$ , i.e.  $n = m$ , a quadratic equation results from equation (14). 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 degenerate, 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. In case of the existence of two real positive roots such that the problem is not degenerate the model cannot be used reliably. It appeared from numerical experiments that the solutions are unstable then. For higher orders (different stoichiometries) it is very hard to state any general remarks about the solution. For the cases considered so far, it was found that there was only one real solution larger than zero.

## 4 The numerical method

Various numerical methods are known to solve Stefan problems. In Crank [3] the following types of method are distinguished: front-tracking, front-fixing, and fixed-domain methods. The latter two methods can only be used when the concentration on the interface is a constant. We choose a front-tracking method to solve our problem numerically, because in this problem the concentrations on the time-dependent boundaries are variable. We use the front-tracking method of Murray and Landis [7]. First an outline of the numerical method is given. Thereafter each part is described in more detail.

The equations are solved with a finite difference method in the  $r$  and  $t$ -direction. A characteristic feature of a front-tracking method is that the interface positions are nodal points in every time-step. So, the position of the grid points depends on time. An outline of the algorithm is:

1. Compute the concentration profiles solving the nonlinear problem given by (2), ..., (6), (8),
2. Predict the positions of  $S_1$  and  $S_2$  at the new time-step:  $S_1(t + \Delta t)$  and  $S_2(t + \Delta t)$ ,
3. Redistribute the grid such that  $S_1(t + \Delta t)$  and  $S_2(t + \Delta t)$  are nodal points,
4. Return to step 1.

We introduce the following notation: the time-step is  $\Delta t = T/N_T$ , and the positions of the interfaces are denoted by  $S_k^j = S_k(j\Delta t)$ ,  $k \in \{1, 2\}$ . The step-size in the space direction is  $\Delta r^j = \frac{S_2^j - S_1^j}{N}$ , and  $r_i^j = S_1^j + i\Delta r^j$ ,  $i \in \{0, \dots, N\}$ . In some expressions  $r_{i\pm\frac{1}{2}}^j$  is used, which is equal to  $S_1^j + (i \pm \frac{1}{2})\Delta r^j$ . Finally, the concentration  $c_k(r_i^j, j\Delta t)$  is approximated by  $c_{k,i}^j$ ,  $k \in \{B, C\}$ . In the remainder of this section we give a detailed description of the various parts of our algorithm. In this paper we explain the method for an equidistant grid. In practice one can save much computation time when the grid is refined in the neighbourhood of the moving boundaries.

### Discretization of the interior region

In this paragraph we use the symbols  $c$  and  $\mathbb{D}$  instead of  $c_B, c_C, \mathbb{D}_B$ , or  $\mathbb{D}_C$ . We suppose that  $S_k^{j+1}$  and  $c_i^j$  are given. The concentration on the new time-step satisfies the following equation:

$$\frac{c_i^{j+1}}{\mathbb{D}\Delta t} + \{[(r_{i+\frac{1}{2}}^{j+1})^a + (r_{i-\frac{1}{2}}^{j+1})^a]c_i^{j+1} - (r_{i-\frac{1}{2}}^{j+1})^a c_{i-1}^{j+1} - (r_{i+\frac{1}{2}}^{j+1})^a c_{i+1}^{j+1}\} / \{(r_i^{j+1})^a (\Delta r^{j+1})^2\} = \frac{1}{\mathbb{D}\Delta t} \{c_i^j + \frac{c_{i+1}^j - c_{i-1}^j}{2\Delta r^j} (r_i^{j+1} - r_i^j)\}, \quad i = 1, \dots, N-1. \quad (15)$$

In this formula central differences are used to discretize the term  $\frac{1}{r^a} \frac{\partial}{\partial r} (r^a \frac{\partial c}{\partial r})$ . The final term is caused by the changing mesh. The value of  $c_i^j$  is given in the point  $(r_i^j, j\Delta t)$ . However, for the time derivative it is necessary to evaluate  $c_i^j$  at  $(r_i^{j+1}, j\Delta t)$ . Linear interpolation is used to approximate this value:

$$c_i^j(r_i^{j+1}, j\Delta t) \simeq c_i^j + \left(\frac{\partial c}{\partial r}\right)_i^j (r_i^{j+1} - r_i^j) \simeq c_i^j + \frac{c_{i+1}^j - c_{i-1}^j}{2\Delta r^j} (r_i^{j+1} - r_i^j).$$

For  $a > 0$  a division by zero could occur in (15) when  $r_i^{j+1} = 0$ . Since  $i \geq 1$  and  $S_1^j \geq M_1 \geq 0$ , the value of  $r_i^{j+1}$  is always positive, so (15) is valid also for  $a > 0$ .

### Discrete boundary condition at a fixed boundary

At a fixed boundary the Neumann boundary condition (4) holds. For a discrete version of this condition we assume that (15) is also valid for  $i = 0$ , and  $i = N$ . Note that virtual concentrations  $c_{-1}^{j+1}$ , and  $c_{N+1}^{j+1}$  occur. These concentrations are eliminated by using the discrete analogue of (4):

$$\frac{c_1^{j+1} - c_{-1}^{j+1}}{2\Delta r^{j+1}} = 0, \quad \frac{c_{N+1}^{j+1} - c_{N-1}^{j+1}}{2\Delta r^{j+1}} = 0. \quad (16)$$

An exception is made for the case  $i = 0$ , and  $a > 0$ , because then equation (15) contains a division by zero. Now equation (4) is replaced by a balance of atoms. For  $a = 2$  the balance is considered for a sphere with radius  $\frac{\Delta r^{j+1}}{2}$ :

$$\frac{c_0^{j+1} - c_0^j}{\Delta t} \cdot \frac{4\pi}{3} \left(\frac{\Delta r^{j+1}}{2}\right)^3 = \mathbb{D} \cdot 4\pi \left(\frac{\Delta r^{j+1}}{2}\right)^2 \cdot \frac{c_1^{j+1} - c_0^{j+1}}{\Delta r^{j+1}}.$$

Using cylinder coordinates a similar expression holds. After simplification for spherical and cylindrical geometry the resulting equations are

$$\frac{c_0^{j+1} - c_0^j}{\Delta t} \cdot \frac{\Delta r^{j+1}}{2(a+1)} = \mathbb{D} \cdot \frac{c_1^{j+1} - c_0^{j+1}}{\Delta r^{j+1}}, \quad a \in \{1, 2\}. \quad (17)$$

### Discrete boundary condition at a moving boundary

In the numerical method we assume that the positions of the boundaries are known at  $t^{j+1} = (j+1)\Delta t$ . Hence, on each boundary  $(S_1, S_2)$  two boundary conditions (6, 8) are necessary. The derivatives used in (8) are discretized with central differences including the virtual concentrations  $c_{-1}^{j+1}$ , and  $c_{N+1}^{j+1}$ . We assume again that (15) holds for  $i = 0$ , and  $i = N$ . Condition (6) is replaced by:

$$(c_{B,0}^{j+1})^m \cdot (c_{C,0}^{j+1})^n = K, \quad (c_{B,N}^{j+1})^m \cdot (c_{C,N}^{j+1})^n = K. \quad (18)$$

Summarising, we note that at the new time-step  $2(N+3)$  unknowns are used, whereas up to now only  $2(N+2)$  equations are specified. This implies that the solution consists of a two-parameter family. To determine a unique solution we assume that all concentrations are a function of  $c_{B,0}^{j+1}$ , and  $c_{B,N}^{j+1}$ . These remaining unknowns are determined by the following coupled nonlinear equations (compare (8)):

$$f_1(c_{B,0}^{j+1}, c_{B,N}^{j+1}) \equiv \mathbb{D}_B (c_{C,part} - c_{C,0}^{j+1})(c_{B,1}^{j+1} - c_{B,-1}^{j+1}) - \mathbb{D}_C (c_{B,part} - c_{B,0}^{j+1})(c_{C,1}^{j+1} - c_{C,-1}^{j+1}) = 0, \quad (19)$$

and

$$f_2(c_{B,0}^{j+1}, c_{B,N}^{j+1}) \equiv \mathbb{D}_B(c_{C,part} - c_{C,N}^{j+1})(c_{B,N+1}^{j+1} - c_{B,N-1}^{j+1}) - \mathbb{D}_C(c_{B,part} - c_{B,N}^{j+1})(c_{C,N+1}^{j+1} - c_{C,N-1}^{j+1}) = 0. \quad (20)$$

So the problem has been reduced to obtaining a root for the vector function  $(f_1, f_2)$ . We approximate this root by the Newton-Raphson method.

The  $p$ -th iterates of the concentrations are denoted by  $c_{B,i}^{j+1}(p)$ ,  $i \in \{0, N\}$ . The continuous Newton-Raphson method runs as follows

$$\begin{pmatrix} c_{B,0}^{j+1}(p+1) \\ c_{B,N}^{j+1}(p+1) \end{pmatrix} = \begin{pmatrix} c_{B,0}^{j+1}(p) \\ c_{B,N}^{j+1}(p) \end{pmatrix} + (J(p))^{-1} \cdot \begin{pmatrix} -f_1(p) \\ -f_2(p) \end{pmatrix}, \quad (21)$$

where  $J$  is the Jacobian. In practice it is impossible to compute  $J$ , so we use a discrete approximation  $\hat{J}$ . The elements of the  $2 \times 2$  matrix  $\hat{J}$  are

$$\hat{J}_{k,i} = [f_k(c_{B,0}^{j+1} + (2-i)\varepsilon, c_{B,N}^{j+1} + (i-1)\varepsilon) - f_k(c_{B,0}^{j+1} - (2-i)\varepsilon, c_{B,N}^{j+1} - (i-1)\varepsilon)]/2\varepsilon, \quad k, i \in \{1, 2\}.$$

The discretization of the Jacobian is determined using a central difference in order to guarantee an accuracy of  $O(\varepsilon^2)$ . From a numerical point of view it is important to note that  $\varepsilon$  has to be sufficiently small, but larger than the accuracy of the numerical scheme to evaluate the concentrations.

To start the Newton-Raphson procedure an initial guess has to be found. To prevent convergence to an undesired root, the initial guess is chosen as close as possible to the root. For time-steps  $j > 1$ , the boundary concentrations from the former time-step are chosen as initial guesses. However, at time step  $j = 1$ , the roots of (see equation (14))

$$\frac{x - c_B^0(r_i)}{c_{B,part} - x} \sqrt{\frac{\mathbb{D}_B}{\mathbb{D}_C}} = \frac{\sqrt{\frac{K}{x^n}} - c_C^0(r_i)}{c_{C,part} - \sqrt{\frac{K}{x^n}}}, \quad i \in \{0, N\} \quad (22)$$

are used. We terminate the iteration when

$$|c_{B,0}^{j+1}(p+1) - c_{B,0}^{j+1}(p)| + |c_{B,N}^{j+1}(p+1) - c_{B,N}^{j+1}(p)| < \varepsilon.$$

The given approach is adapted for the case  $a > 0$  and  $S_1^{j+1} < \Delta r^{j+1}$ . In this case the virtual grid-point near  $S_1$  is released. The derivatives in equation (8) are replaced by one-sided differences, and (15) is no longer used for  $i = 0$ .

### Adaptation of the moving boundaries

We have only used one half of the boundary conditions given in (7) to determine the concentrations. The remaining conditions are used to adapt the positions of the moving boundaries. An explicit time discretization yields

$$\begin{aligned} \frac{S_1^{j+1} - S_1^j}{\Delta t} &= \frac{\mathbb{D}_B}{c_{B,part} - c_{B,0}^j} \frac{c_{B,1}^j - c_{B,-1}^j}{2\Delta r^j}, \\ \frac{S_2^{j+1} - S_2^j}{\Delta t} &= \frac{\mathbb{D}_B}{c_{B,part} - c_{B,N}^j} \frac{c_{B,N+1}^j - c_{B,N-1}^j}{2\Delta r^j}. \end{aligned} \quad (23)$$

Due to the explicit nature of this adaptation it is important to choose the time-step not too large relative to the grid-size. In our computations we choose  $\Delta t$  such that  $\Delta t \leq 10(\Delta r^0)^2 / \max\{\mathbb{D}_B, \mathbb{D}_C\}$ . The virtual concentrations  $c_{B,-1}^j, c_{B,N+1}^j$ , are computed from (15). For  $a > 0$  and  $S_1^j < \Delta r^{j+1}$  the central finite difference to approximate  $\frac{\partial c_B}{\partial r}(S_1(t), t)$  is replaced by a one-sided finite difference, as has been mentioned in the previous paragraph. When the distance between a moving boundary and a fixed boundary is small ( $\frac{S_k^{j+1} - M_k}{S_k^0 - M_k} < \varepsilon$ ,  $k \in \{1, 2\}$ ) we fix the boundary ( $S_k^{j+1} = M_k$ ,  $k \in \{1, 2\}$ ), and change the boundary conditions accordingly.

## 5 Numerical experiments

### The accuracy of the computations

In order to determine the accuracy of the calculations, grid-size and time-step dependence tests have been carried out. The results are shown in figures 1 and 2. The following input

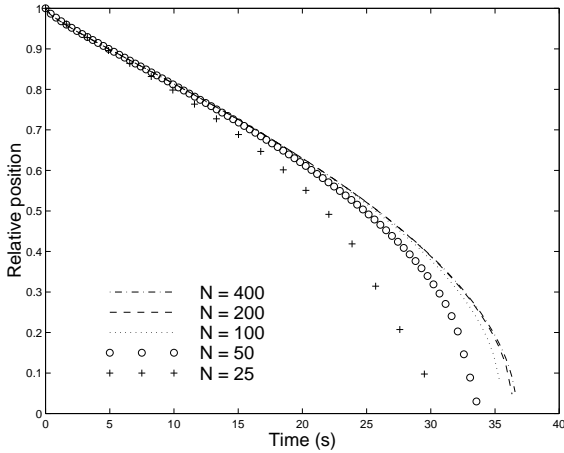


Figure 1: Relative position of the interface  $S_1(t)/S_1(0)$ ; with a virtual point

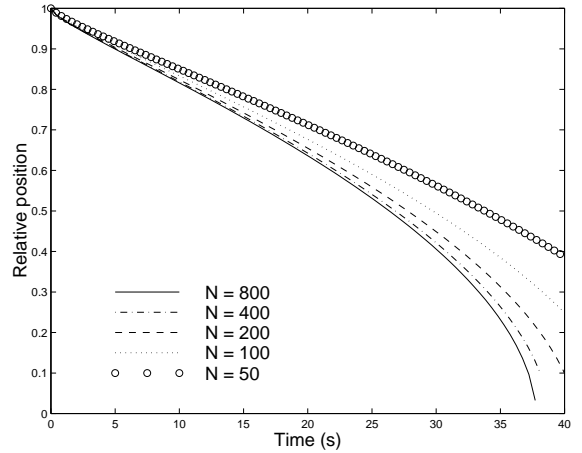


Figure 2: Relative position of the interface  $S_1(t)/S_1(0)$ ; without a virtual point

parameters have been used:  $\mathbb{D}_C = 2 * \mathbb{D}_B = 2 \cdot 10^{-13} \text{ m}^2/\text{s}$ ,  $c_p^0 = 0$ ,  $c_{p,part} = 50$ ,  $p \in \{B, C\}$ ,  $K = 1$ ,  $m = n = 1$ ,  $S_1(0) = 10^{-6} \text{ m}$ ,  $M_2 - S_1(0) = 5 \cdot 10^{-6} \text{ m}$ ,  $S_2(0) = M_2$ , and we assume spherical geometry. The grid-size and time-step were decreased until the differences are negligible for the whole simulation. It can be seen in figures 1 and 2 that the distances between all curves are negligible for small times. For larger times the differences increase. The use of a virtual point at the interface increases the accuracy considerably. The observed rate is  $O(\Delta r^2)$  with a virtual point and  $O(\Delta r)$  without a virtual point.

In case of the use of a virtual grid point, the central discretization reads as follows:

$$\frac{c_{p,1}^j - c_{p,-1}^j}{2\Delta r^j} = \frac{\partial c_p}{\partial r}(S_1(t_j), t_j) + \frac{(\Delta r^j)^2}{6} \frac{\partial^3 c_p}{\partial r^3}(\theta_1, t_j), \quad \theta_1 \in (S_1(t_j) - \Delta r^j, S_1(t_j) + \Delta r^j).$$

Without the use of a virtual grid point we have the following one-sided discretization:

$$\frac{c_{p,1}^j - c_{p,0}^j}{\Delta r^j} = \frac{\partial c_p}{\partial r}(S_1(t_j), t_j) + \frac{\Delta r^j}{2} \frac{\partial^2 c_p}{\partial r^2}(\theta_2, t_j), \quad \theta_2 \in (S_1(t_j), S_1(t_j) + \Delta r^j).$$

In the vicinity of the interface we observe the following inequalities:

$$\frac{\partial c_p}{\partial r} < 0, \quad \frac{\partial^2 c_p}{\partial r^2} > 0, \quad \frac{\partial^3 c_p}{\partial r^3} < 0.$$

Therefore respectively in case of the presence of a virtual grid point and without a virtual grid point, the discretization at the interface overestimates (Figure 1) respectively underestimates (Figure 2) the interface velocity.

### A comparison of the analytical and numerical solution

As has been mentioned before, the initial guess for the interfacial concentrations is based on some analytical considerations. The derivation of this analytical approximation is summarised in Chapter 3. This expression holds for spherical symmetry, but it can be used for planar geometry as well [1]. Unfortunately, this derivation has to be done under the assumption that the interfacial concentration remains constant during the entire dissolution process. At the early stages of the dissolution process, the interfacial concentration does not remain constant (see Figure 3). To compute the interfacial concentration we iterate the analytical solution using the following predictor-corrector method with a sufficiently small time-step:

### Predictor-corrector method

1. Compute  $\hat{c}_{B,sol}(\Delta t)$  from (14),  $j = 1$ ;
2. Substitute  $\hat{c}_{B,sol}(\Delta t)$  in (12) and compute  $S_1(j \cdot \Delta t)$ ;
3. Using  $S_1(j \cdot \Delta t)$ , obtain  $c_{B,sol}((j+1) \cdot \Delta t)$  from (8) and (13),  $j := j + 1$ , go to 2.

The results obtained with the analytic approach are of the same order of magnitude as the results obtained using the finite difference scheme (see Figure 3). The finite difference results in Figure 3 have been obtained using various  $M_2/S_1(0)$ -values. Though there is a

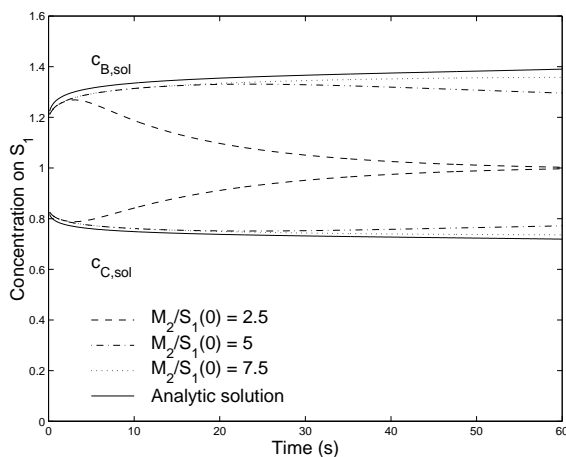


Figure 3: Interface concentrations for various values of  $M_2/S_1(0)$

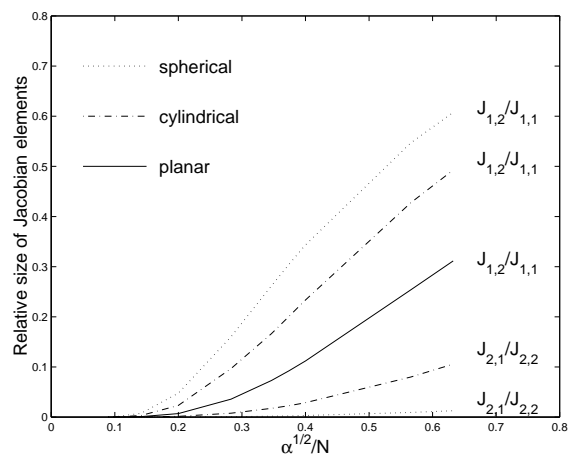


Figure 4: Relative size of the Jacobian elements

small difference between the results from the analytical and numerical scheme already at early stages, it can be seen that for large  $M_2/S_1(0)$ -values the match between the analytical approximation and the numerical solution is good. This is as expected, because the analytical

approximation is based on the dissolution of a spherical particle in an infinite medium. The differences at early stages are due to the rather large variation of the Dirichlet conditions with time. At later stages, the Dirichlet conditions vary less with time and the difference between the results stops increasing. An advantage of the analytical approximation is that it costs a negligible amount of CPU-time. However, in reality the effects of soft-impingement (a bounded domain) are relevant. Then the analytical approximation is not reliable.

### An analysis of the discretized Jacobian

In Section 4 the Newton-Raphson procedure to obtain the Dirichlet conditions has been outlined. In this method the Jacobian plays an important role. The Jacobian consists of the derivatives of both boundary functions  $f_i, i \in \{1, 2\}$  with respect to  $c_{B,sol}$  at both boundaries. Therefore during each zero point iteration we determine  $f_1, f_2$  at  $(c_{B,sol}(S_1), c_{B,sol}(S_2))$ ,  $(c_{B,sol}(S_1) \pm \varepsilon, c_{B,sol}(S_2))$ , and  $(c_{B,sol}(S_1), c_{B,sol}(S_2) \pm \varepsilon)$ , which means that in every iteration the discretized equations have to be solved 5 times. It is obvious that for the case that the diffusion fields between the boundaries  $S_1$  and  $S_2$  do not interact, the off-diagonal coefficients of the Jacobian are negligible and could be set zero. In this case it is sufficient to evaluate  $f_1, f_2$  at  $(c_{B,sol}(S_1), c_{B,sol}(S_2))$ ,  $(c_{B,sol}(S_1) + \varepsilon, c_{B,sol}(S_2) + \varepsilon)$ , and  $(c_{B,sol}(S_1) - \varepsilon, c_{B,sol}(S_2) - \varepsilon)$ , so the discretized equations need only be solved 3 times, which speeds up the calculation. For each time-step, about 4 Newton-Raphson iterations had to be applied to get the desired accuracy.

The off-diagonal Jacobian terms have been analysed relative to the diagonal Jacobian terms (i.e.  $J_{1,2}/J_{1,1}$  and  $J_{2,1}/J_{2,2}$ ). It appeared that these values remained approximately constant during an entire simulation, also when the diffusion fields of both phases started to impinge. In Figure 4 the off-diagonal Jacobian terms have been displayed as a function of the dimensionless time-step defined by:  $\alpha = N^2 * \min(\mathbb{D}_B, \mathbb{D}_C) * \Delta t / (S_2(0) - S_1(0))^2$ . It can be seen that the influence of the cross-terms in the Jacobian increases with increasing time-step. This may be explained using the theory of penetration. It can be proved that for a planar medium the penetration depth as a function of time is given by  $L(t) = \sqrt{\pi * \max(\mathbb{D}_B, \mathbb{D}_C) * t}$ . The penetration depth corresponds to the minimal distance from one of the moving boundaries to the position where the concentration has been unchanged. For the ternary case, the interfacial concentrations change during each time-step  $\Delta t$ . If  $L(\Delta t) \lesssim S_2(0) - S_1(0)$  then the changes of the interfacial concentrations do not influence each other, i.e. the off-diagonal terms of the Jacobian are negligible.

For the planar geometry, we have by symmetry  $J_{1,2}/J_{1,1} = J_{2,1}/J_{2,2}$ . In the cylindrical and spherical cases we have the inequality  $J_{1,2}/J_{1,1} > J_{2,1}/J_{2,2}$ . This inequality becomes stronger for the spherical case. The inequality will be explained for the spherical geometry. As the area of  $S_2$  is larger than the area of  $S_1$  and the area increases from  $S_1$  to  $S_2$ , the influence on the boundary condition at  $S_1$  by the boundary condition at  $S_2$  will be larger than the influence on the boundary condition at  $S_2$  by the boundary condition at  $S_1$ . Therefore we have the inequality  $J_{1,2}/J_{1,1} > J_{2,1}/J_{2,2}$ . A similar explanation may be given for the case of cylindrical geometry.

For the planar geometry, the penetration depth may be written as

$$L(\Delta t) = \sqrt{\pi * \max(\mathbb{D}_B, \mathbb{D}_C) * \Delta t} = \sqrt{\frac{\pi * \max(\mathbb{D}_B, \mathbb{D}_C) * \alpha}{\min(\mathbb{D}_B, \mathbb{D}_C)}} * \frac{S_2(0) - S_1(0)}{N}$$

From this it follows that:

$$\frac{\sqrt{\alpha}}{N} = \sqrt{\frac{\min(\mathbb{D}_B, \mathbb{D}_C)}{\pi * \max(\mathbb{D}_B, \mathbb{D}_C)}} * \frac{L(\Delta t)}{S_2(0) - S_1(0)}$$

is an important dimensionless number. From Figure 4 it can be seen that if  $\sqrt{\alpha}/N < 0.1$  the off-diagonal terms of the Jacobian are negligible for all geometries. In most of our simulations  $\alpha$  is taken in the range [10,100]. So when  $N$  is larger than 100 the off-diagonal terms of the Jacobian contribute very little. This is a weak condition, because  $N$  should also be larger than 100 for accuracy.

### Application to the movement of two boundaries in a ternary alloy

Some calculations for a ternary alloy have been carried out with two simultaneously moving boundaries. Figure 5 shows some results for the boundary position as a function of time. The input parameters for these curves are  $\mathbb{D}_C = 2 * \mathbb{D}_B = 2 \cdot 10^{-13} \text{ m}^2/\text{s}$ ,  $c_p^0 = 0$ ,  $c_{p,part} = 50$ ,  $p \in \{B, C\}$ ,  $K = 1$ ,  $m = n = 1$ ,  $S_1(0) = 7.5 \cdot 10^{-7} \text{ m}$ ,  $M_2 = 5 \cdot 10^{-6} \text{ m}$ ,  $M_2 - S_2(0) = 2 \cdot 10^{-8} \text{ m}$ ,  $N = 500$ ,  $\Delta t = 100 * \Delta r^2 / \max(\mathbb{D}_B, \mathbb{D}_C)$ .

It can be seen in Figure 5 that the dissolution time is largest for a spherical segregation layer ( $S_2$ ). For both cylindrical and spherical geometries the surface of the segregation layer increases during the dissolution process. For the particle ( $S_1$ ) it takes most time to dissolve for the planar geometry, as the surface of the particle decreases during dissolution for both

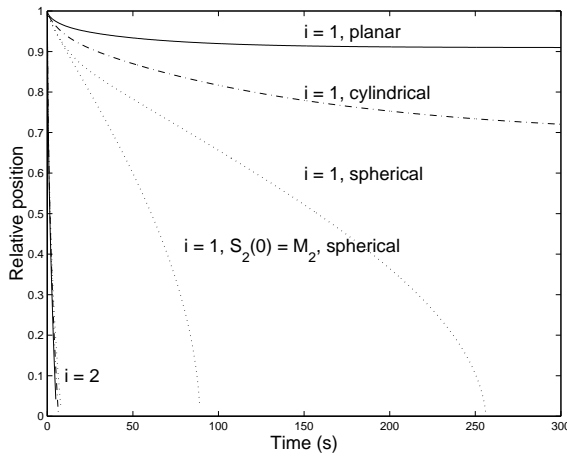


Figure 5: Relative position of the interfaces  $(S_i(t) - M_i) / ((S_i(0) - M_i))$

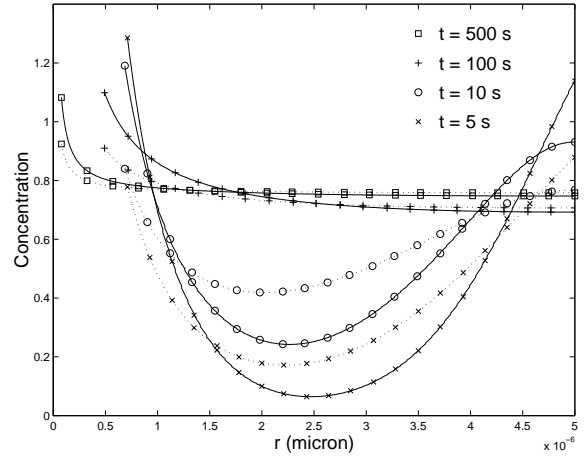


Figure 6: The concentrations for a spherical geometry ( $-c_B, \dots, c_C$ )

cylindrical and spherical geometry. For a comparison the curve of  $S_1$ , without the presence of  $S_2$ , versus time has been displayed for a spherical geometry. It appears that the dissolution of a particle is considerably delayed by the presence of a segregation layer. It can be observed as well that at the early stages there is no influence on the dissolution kinetics of  $S_1$  from the boundary  $S_2$ .

To illustrate the behaviour of the concentration profile, the concentration profiles of both chemical elements at different times have been presented in Figure 6 for the spherical geometry. As is to be expected, at the early stages the profiles are very steep. The interfacial

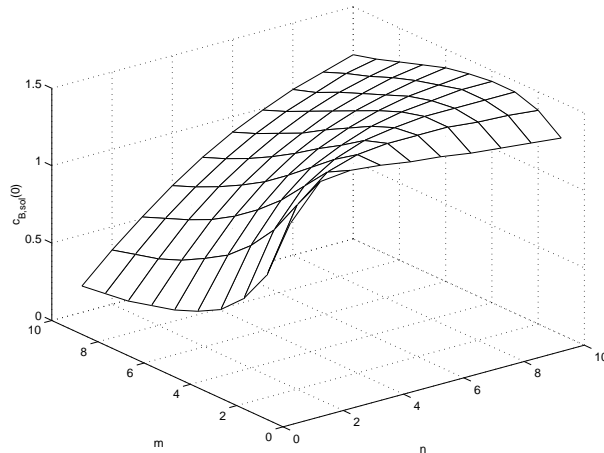


Figure 7: The concentration  $\hat{c}_{B,sol}$  at  $t = 0$

concentrations at  $S_1$  converge during dissolution as a result of soft-impingement. For the concentration profile at  $t = 5$  seconds, Dirichlet conditions are in effect at both boundaries: both  $S_1$  and  $S_2$  are moving. For  $t = 10$  seconds it can be seen that the boundary condition at  $S_2$  has changed into a Neumann condition: no mass transfer is allowed over the boundary. Later, when  $S_1 = M_1$  (dissolution of the particle) a Neumann condition is applied at  $S_1$  too. Finally the profile becomes homogeneous.

#### The influence of the stoichiometry on the boundary conditions at $S_1$

Figure 7 shows the boundary condition at  $S_1$  for the element  $B$  as a function of the particle stoichiometry, i.e.  $B_n C_m$ . As input parameters we used  $\mathbb{D}_C = 2 * \mathbb{D}_B = 2 \cdot 10^{-13} \text{ m}^2/\text{s}$ ,  $c_p^0 = 0, c_{p,part} = 50, p \in \{B, C\}, K = 1$ . The results in the figure are obtained from Equation (14) for various choices of  $n$  and  $m$ . From the figure it is clear that the stoichiometry of the phase contributes significantly to the constitution of the boundary conditions.

#### The influence of the diffusion coefficients of both elements

To illustrate once more the applicability of the model, some calculations have been carried out for the case of a stoichiometric spherical second phase  $Mg_2Si$  and  $Mg_2X$  in a ternary aluminium alloy. The diffusion coefficients  $\mathbb{D}_{Si}$  and  $\mathbb{D}_{Mg}$ , taken from Fujikawa [4] and Yamane [6] for a temperature of 793 K, are  $2.15 \cdot 10^{-13} \text{ m}^2/\text{s}$  and  $3.24 \cdot 10^{-13} \text{ m}^2/\text{s}$  respectively. Furthermore, the initial particle radius, the cell radius, and initial matrix concentrations have been taken respectively as  $10^{-6} \text{ m}, 8 \cdot 10^{-6} \text{ m}, 0, 0$ . For  $K$  the value of 0.35 has been used. As the calculation concerns an  $Mg_2X$  particle, we have  $c_{Mg,part} = 66.7\%$ .

In Figure 8 the interfacial position for the case of dissolution of a spherical  $Mg_2X$  particle in aluminium is given. Various choices for the diffusion coefficient  $\mathbb{D}_X$  are used. The special choice  $\mathbb{D}_X = \mathbb{D}_{Mg}$  corresponds to the dissolution of an  $Mg$  particle, so this is a binary alloy. Note that initially the interfacial velocity decreases. At the final stages of dissolution, the interfacial area has become so small, that the interfacial velocity has to be large to satisfy the Stefan condition. It can be seen from Figure 8 that the addition of a second element can influence the dissolution kinetics strongly.

Figure 9 represents the interfacial concentration at  $S_1$  of both alloying elements as a function



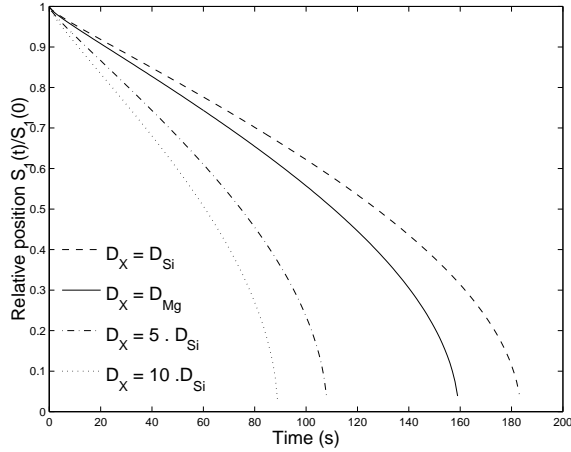


Figure 8: Relative position of the interface

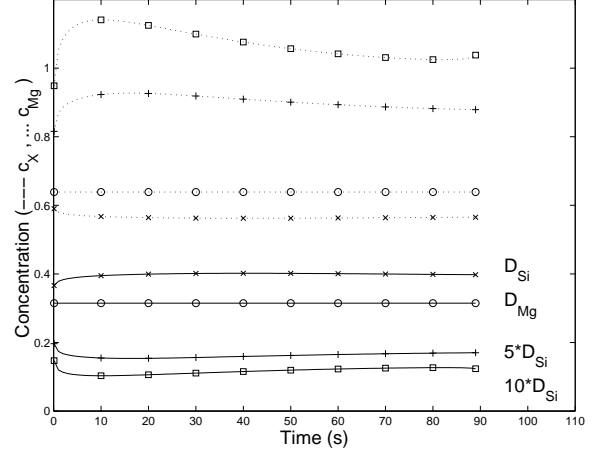


Figure 9: Concentration at the interface

of time. From Figure 9 it is clear that at the initial stages the atoms of the slower element accumulate near the interface. On the other hand, the atoms of the faster element diffuse deeper into the matrix. This causes the diverging behaviour of the interfacial concentrations at early stages.

A more detailed analysis in which the stoichiometry, cell size and diffusion coefficient have been varied can be found in [15].

## 6 Conclusions

A mathematical model is given to describe the dissolution of stoichiometric multi-component particles in ternary alloys. Some results concerning existence and uniqueness are given. However, a number of open questions remain.

An analytical approximate solution is given, valid when the dissolution takes place in an unbounded domain. The results are cheap to calculate and they are reasonably accurate. This analytical approximation can also be used for short simulation times in a bounded domain, or as starting solution for the Newton-Raphson process used in the numerical method.

The numerical method described is second order accurate when virtual points are used to discretize the boundary conditions at the interface.

A criterion is given to estimate when the off-diagonal terms of the Jacobian are negligible. Then the computational work can be decreased considerably.

The numerical solutions lead to valuable insight for metallurgical applications.

## Acknowledgement

The authors thank Prof.dr.ir. P. Wesseling for carefully reading the manuscript and giving advice to improve it.

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