EFFECT OF THERMAL GRADIENTS ON THE RANDOM DIFFUSION OF A LIGHT SOLUTE IN A HEAVIER SOLVENT

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Abstract

Atoms diffuse in a molten metal alloy under the influence of a temperature gradient at high pressure and temperature. They change phase and form synthetic crystals. An equation modelling the diffusion phenomenon is presented, relating the concentration of diffusing atoms to the temperature gradient and the crystal formation rate. Models for the crystal growth are also presented. The governing equation is first interpreted at microscopic level. Analytical and numerical solutions are then investigated. As observed experimentally, the sign and magnitude of the temperature gradient in the alloy affects the potential crystal formation and the rate of crystal growth. The value of the key physical parameters involved is discussed and model improvements are suggested.

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1 Introduction

Crystals of high perfection are required in applications such as X-ray optical systems and synchrotrons of high brilliance like the ESRF (European Synchrotron Radiation Facility). To meet these criteria, crystals are grown using atom transport in an alloy of several metals. The atom/metal mixture is placed in a high pressure device and the crystal growth occurs when a temperature gradient is applied [25, 24, 26]. As a first approximation, at the start of the crystal growth, a uniform atom concentration is assumed throughout the sample. No further atoms are introduced and only the movements of the atoms present initially in the mixture will be considered. Practically, a uniform thermal gradient is applied with the maximum temperature at the top of the solvent volume [5]. Migration of atoms towards the colder end, in the direction opposite to buoyancy forces, is observed. This feeds the crystal growth that occurs at the bottom of the alloy. The objective of the present work is to model the movements of the atoms in the alloy solvent leading to the crystal growth and interpret observations made during experimental work by our industrial partner.

The movement of diffusing atoms is governed by two simultaneous phenomena, thermal diffusion and Fick's diffusion. Thermal diffusion, also known as thermomigration or the Soret/Ludwig-Soret effect, describes the movement of atoms under a temperature gradient. The phenomenon was first discovered by Ludwig in 1856 and further investigated by Soret some twenty years later. This type of diffusion is triggered by a temperature gradient. Depending on the composition of the metal alloy, thermal diffusion will induce movement of the diffusing atoms towards either the cooler or the hotter end of the solvent [35, 33]. The magnitude and direction of the migration depends on a parameter known as the heat of transport.

The second form of diffusion operating is the standard Fick's diffusion. This diffusion is caused by a concentration gradient in the alloy and forces atoms to move from regions with high diffusing atom concentration towards regions where the concentration is lower.

Depending on the concentration and temperature gradients, the two types of diffusion, Soret and Fick, may act in the same or opposite directions. In the experiments on which this work is based, the Soret effect may be important since some observations are difficult to explain if only Fick's diffusion is considered. These include

- Using the same temperature field, the crystal growth rate varies with the alloy composition,

- Crystals, called rogue crystals, are growing on sites other than the pre-emplaced initial crystals.

Although generally small [33], the Soret effect seems to play an important role in the present situation.

In the following report, a simple configuration for crystal growth in an alloy is presented in Section 2 together with the standard diffusion equation and the models used for the crystal growth. The diffusion equation is a macroscopic description of what is happening at a lower level. An interpretation at atomic level is presented in Section 3. An analytical study is then conducted. The governing equation is non-dimensionalised and explicit solutions are calculated for a simplified governing equation in Section 4. Preliminary results are also presented. Finally, the governing equation is solved numerically in Section 5 and the results are discussed.

2 Typical configuration and governing equations

2.1 Configuration

High pressure and temperature are necessary to allow for crystal growth. In the present study, pressure and temperature, denoted respectively P and T, are typically $P = 5 - 6$ GPa and $T \approx 1300^o$C. Figure 1 shows a typical configuration of the experimental setting. A molten metal alloy of height $L = 2\,\mathrm{cm}$ is considered, containing a concentration $c_0 \approx 0.24\mathrm{g}\cdot\mathrm{cm}^{-3}$ of diffusing atoms.

At $z = 0$, small crystals are assumed to be present from the start of the process, the early stages of the growth will not be considered here. Crystal growth may be observed when a temperature difference $\Delta T = 20\mathrm{K}$ is applied, with the minimum temperature at the bottom of the alloy and the maximum temperature at its top. This temperature gradient is key to the process: when the maximum temperature is at the bottom of the alloy, the crystal growth does not occur. This phenomenon will now be modelled using standard diffusion equations.

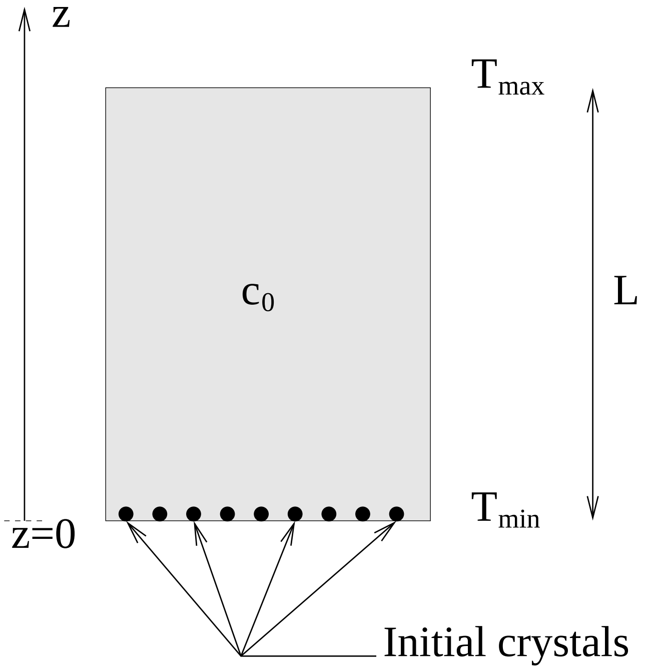

Figure 1: Typical configuration.

2.2 Governing equations

In this first approach, the study is one-dimensional: the movements of diffusing atoms are only studied in the vertical direction. The diffusing atom concentration is constant in each horizontal layer. At the bottom of the alloy, all crystals are assumed to grow in an identical fashion and they do not affect each others growth. This clearly simplifies the problem but, obviously, this model only provides a first approximation of the crystal growth and diffusing atom movements. The different aspects of diffusion and crystal growth will now be modelled.

2.2.1 Fick's diffusion

Fick's diffusion is a widely studied phenomenon. The governing equation may be written:

$$\frac{\partial c}{\partial t} + \frac{\partial Q}{\partial z} = 0 \ , \tag{2.1}$$

where c is the concentration of diffusing atoms in the alloy, z is the vertical Cartesian coordinate and Q denotes the atom flux defined by:

$$Q = -D\frac{\partial c}{\partial z} \ , \tag{2.2}$$

with D the diffusion coefficient. The flux of diffusing atoms is proportional to the concentration gradient and the minus sign shows that the diffusion occurs from regions with high concentration of diffusing atoms towards regions with lower concentration. The diffusion coefficient varies with the following ambient conditions:

- Pressure.
  The diffusion coefficient in (solid) metals varies significantly with pressure at high temperature [11]. The diffusion coefficient in the alloy may vary if the pressure in not well controlled. This aspect will be neglected in the present study.

- Gravity.
  The effect of gravity on diffusion has been investigated, see for example [17, 18, 19]. If the value of the gravitational acceleration changes significantly, the diffusion coefficient will change, but this effect is negligible for the set up considered here and so gravity may be considered constant.

The diffusion coefficient in the alloy reflects its composition and is a weighted average of the values of each component. This will however only provide an order of magnitude:

- These values are not precise. They are apparently calculated at ambient pressure and would probably be modified at the pressure considered here for crystal growth.

- The mixture is most certainly not perfect and the weighted average used to evaluate D may not be appropriate. Similarly, the eutectic nature of the liquid alloy will modify the outcome as well.

The weighted average calculated with present values will be used in the following. A more precise estimation should be provided by experimental results.

2.2.2 Soret diffusion

Soret diffusion may be described with the same equation as Fick's diffusion (2.1), but the diffusing atom flux Q is [35, 33]:

$$Q = -D \frac{Q^* c}{RT^2} \frac{\partial T}{\partial z} , \tag{2.3}$$

where D is the Fick's diffusion coefficient, R is the ideal gas constant, T denotes the temperature and Q^* represents the heat of transport. The value of the heat of transport is the crux of the problem. The flux of atoms is proportional to the diffusing atom concentration and the temperature gradient. The sign of the heat of transport Q^* determines the direction of movement of diffusing atoms:

- if $Q^* > 0$, the diffusing atoms move towards the cooler end,
- if $Q^* < 0$, the diffusing atoms move towards the hotter end.

The value of Q^* also determines the balance between the Fick's and Soret diffusion. Experimental results show that the Soret effect is dominant in the process. The value of the heat of transport for molten metals is however difficult to evaluate. Here again, the operating conditions complicate matters and make data difficult to find. Values could be found for the solid state [2, 3] but unfortunately, no values could be found for the liquid metals at the pressure used here. The sign of this parameter varies with the diffusing atoms and the metal. The value of the heat of transport will be further discussed in Section 4.

2.2.3 Crystal growth

Two models are considered for the crystal growth, one independent from the surrounding diffusing atom concentration, the other taking this parameter into account.

- Basic model
  A number n of crystals are placed at the bottom of the alloy. They remain spherical at all times, are all exactly similar and their mass increases at a constant rate, $\mathcal{V}$. The expression for the sink term S may be easily calculated by performing a mass balance in a slice of alloy of depth Δz

and surface Σ_0. If the diffusion terms are neglected, the mass balance in this layer may be written:

$$m_{\Delta z}\,(t+\Delta t) - m_{\Delta z}(t) = -n\,\mathcal{V}|_{\Delta z}\,\Delta t\ , \tag{2.4}$$

where $\mathcal{V}|_{\Delta z}$ represents the amount of mass growth between z and $z+\Delta z$. A straightforward analysis on a sphere shows that the surface of crystal available for $z_1 \leq z \leq z_2$ is

$$s = 2\pi r\,(z_2 - z_1)\ ,$$

and $\mathcal{V}|_{\Delta z}$ may be expressed as the ratio of the surface available in the layer of thickness Δz and the total surface of the sphere:

$$\mathcal{V}|_{\Delta z} = \mathcal{V}\frac{2\pi r\Delta z}{4\pi r^2} = \mathcal{V}\frac{\Delta z}{2r}\ . \tag{2.5}$$

Since the mass of diffusing atoms in the layer may be written as the product of the concentration of atoms and the volume of the layer, equation (2.4) may be rewritten:

$$\frac{\partial c}{\partial t}\Sigma_0\Delta z\Delta t = -n\mathcal{V}\frac{\Delta z}{2r}\Delta t \quad\Longleftrightarrow\quad \frac{\partial c}{\partial t} = -n_S\frac{\mathcal{V}}{2r}\ , \tag{2.6}$$

where $n_S = n/\Sigma_0$ denotes the number of crystals per surface unit. The sink term S may then be defined as

$$\mathcal{S} = -n_S\frac{\mathcal{V}}{2r}\ . \tag{2.7}$$

The equation governing the radius, r, of the crystal may then be written:

$$\frac{dr}{dt} = \frac{\mathcal{V}}{4\pi\rho r^2}\ . \tag{2.8}$$

- Advanced model
  The crystal mass growth rate depends on the concentration of atoms available around the crystal. The parameter $\mathcal{V}$ is not constant over the entire sphere surface and may be written as

$$\mathcal{V} = \mathcal{V}_0\frac{c}{c_0} = \mathcal{V}_1 c\ , \tag{2.9}$$

where $\mathcal{V}_0$ is constant. The sink term becomes

$$\mathcal{S} = -n_S \frac{\mathcal{V}_0}{2r} \frac{c}{c_0} = -\frac{n_S \mathcal{V}_1 c}{2r} , \tag{2.10}$$

and the constant $\mathcal{V}_1$ is chosen to fit an initial condition. The radial growth rate is only affected through the value of $\mathcal{V}$: since the value is not constant in space, the global value should be estimated using the integral:

$$\mathcal{V} = \int_0^{2r} \mathcal{V}|_{dz} \, dz , \tag{2.11}$$

where $\mathcal{V}|_{dz}$ is the local value of $\mathcal{V}$ per distance unit.

2.2.4 Complete equation

The equation governing diffusing atom migration and the crystal growth area may be summarised as:

$$\frac{\partial c}{\partial t} - \frac{\partial}{\partial z}\left(D\frac{\partial c}{\partial z} + \frac{DQ^* c}{RT^2}\frac{\partial T}{\partial z} \right) = 0 , \tag{2.12}$$

and at the bottom of the alloy, depending on the model considered for crystal growth, this equation becomes:

$$\frac{\partial c}{\partial t} - \frac{\partial}{\partial z}\left(D\frac{\partial c}{\partial z} + \frac{DQ^* c}{RT^2}\frac{\partial T}{\partial z} \right) = -n_S \frac{\mathcal{V}}{2r} , \tag{2.13}$$

$$\frac{\partial c}{\partial t} - \frac{\partial}{\partial z}\left(D\frac{\partial c}{\partial z} + \frac{DQ^* c}{RT^2}\frac{\partial T}{\partial z} \right) = -n_S \frac{\mathcal{V}_1 c}{2r} . \tag{2.14}$$

The flux of diffusing atoms in the mixture is defined as:

$$Q = -D\left(\frac{\partial c}{\partial z} + \frac{Q^* c}{RT^2}\frac{\partial T}{\partial z} \right) . \tag{2.15}$$

The governing equation is coupled with the initial condition

$$c(t=0, z) = c_0 ,$$

and two zero-flux boundary conditions at the top and bottom of the alloy:

$$\left[-D\left(\frac{\partial c}{\partial z} + \frac{Q^* c}{RT^2}\frac{\partial T}{\partial z} \right) \right]_{z=0} = \left[-D\left(\frac{\partial c}{\partial z} + \frac{Q^* c}{RT^2}\frac{\partial T}{\partial z} \right) \right]_{z=L} = 0 .$$

The flux will now be interpreted at microscopic level and then the governing equations (2.12-2.14) will be solved numerically and analytically.

3 Diffusion and thermomigration at atomic level

The two terms of the diffusion equation derived in Section 2 will now be studied at atomic level. A traditional model for Fick's law is detailed in Section 3.1 and the Soret effect is presented in Section 3.2.

3.1 Fick's law

Fick's diffusion of atoms in the metal alloy may be interpreted using Brownian motion. The diffusing atom movement is governed by the Langevin equation [32]:

$$m\frac{d\mathbf{u}}{dt} = -\zeta\mathbf{u} + \mathbf{F} \ ,$$

where m is the mass of the atom, $\mathbf{u}$ is its velocity, ζ is the the drag coefficient slowing the particle down and $\mathbf{F}$ is the Brownian force, oscillating rapidly because of the collisions and interactions between the diffusing and the alloy atoms. The solution of this equation is averaged for a high number of particles and this leads to the Fick diffusion law as described in the previous section [32]. In practice, particles are equally likely to go in any direction because of the oscillating Brownian force. Consequently a region with a high concentration of diffusing atoms next to a region with a lower concentration will lose more atoms to the neighbouring region than it can gain from it and the concentration of diffusing atoms becomes uniform in the entire alloy.

3.2 Soret diffusion

Interpreting the Soret effect at atomic level is a rather difficult task. The thermodiffusion effects are mainly controlled by six aspects of the diffusing atoms and the surrounding alloy [1]:

- Mass of the particles,
- Diameter of the particles,
- Moment of inertia of the particles,
- Interaction between the particles and the solvent,

- Ionic structure of the particles,
- Interaction between particles.

The first three aspects are directly related to the physical properties of the particles, the last three are chemical properties. These effects are rarely additive, making the effective behaviour of diffusing atoms difficult to work out.

The heat of transport in solids may be interpreted using the movement of electrons due to the temperature gradient. They lose energy and momentum to the diffusing atoms and this affects the Brownian movement of diffusing atoms. In metals, energy is mainly transported by electrons and the sign of the heat of transport should be similar to the sign of electron movements. However, this is far from always the case since the movement of electrons may be screened by other properties of the alloy atoms [27].

The process is more complex in liquids due to interactions likely to affect the diffusing atom movements and the sign of the heat of transport is difficult to predict [1].

4 Analytical solutions

In this section, analytical aspects will be investigated. First, the governing equations (2.12-2.14) introduced in Section 2 are non-dimensionalised and the resulting non-dimensional constants are analysed. A steady state solution is approximated for the relevant boundary conditions.

4.1 Non-dimensional equation

The governing equation in dimensional form is:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[D\left(\frac{\partial c}{\partial z} + \frac{Q^* c}{RT^2}\frac{\partial T}{\partial z}\right)\right] - n_S\frac{\mathcal{V}}{2r}\frac{c}{c_0} \ . \tag{4.1}$$

The variables can be non-dimensionalised in the following manner:

$$c = c_0\bar{c} \ , \quad t = \tau\bar{t} \ , \quad z = L\bar{z} \ , \quad r = r_0\bar{r} \ , \quad T = T_0 + \Delta T\bar{T} \ , \tag{4.2}$$

where c_0 is the initial uniform concentration, τ denotes the time scale, L is the thickness of the alloy considered, r_0 is the initial radius of the crystals and T_0

and ΔT represent the temperature at $z = 0$ and the typical temperature difference in the alloy respectively. After dropping the bars, the non-dimensional equation may be written

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[A\frac{\partial c}{\partial z} + \frac{Bc}{(1+[\Delta T/T_0]T)^2}\frac{\partial T}{\partial z}\right] - C\frac{c}{r} \ , \tag{4.3}$$

where the three non-dimensional numbers A, B and C are defined by

$$A = \frac{\tau D}{L^2} \ , \quad B = \frac{\tau D Q^* \Delta T}{R T_0^2 L^2} \ , \quad C = \frac{n_S \mathcal{V} \tau}{2 c_0 r_0} \ . \tag{4.4}$$

The boundary conditions in non-dimensional form become

$$A\frac{\partial c}{\partial z} + \frac{Bc}{(1+\Delta T T/T_0)^2}\frac{\partial T}{\partial z}\bigg|_{z=0,\ z=1} = 0 \ , \tag{4.5}$$

and the initial condition is

$$c(t=0, z) = 1 \ .$$

The non-dimensional numbers A and B describe the relative importance of the classical diffusion and the Soret effect. Experimental results show that the Soret effect plays a key role so the two parameters A and B should at least have the same order of magnitude. This provides a first estimate for the value of the heat of transfer:

$$\frac{A}{B} \approx 1 \Longrightarrow Q^* \approx \frac{R T_0^2}{\Delta T} \approx 10^3 \mathrm{kJ} \cdot \mathrm{mol}^{-1} \ .$$

This value is considerably higher than the values observed in the solid state. The temperature gradient could explain this rather high value: it may be more localised at the bottom of the alloy where crystal growth occurs.

Crystal growth is going to be the dominant phenomenon in the process and the time scale is chosen accordingly:

$$\tau = \frac{2 c_0 r_0}{n_S \mathcal{V}} \ ,$$

and the governing equation becomes:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[A\frac{\partial c}{\partial z} + \frac{Bc}{(1+[\Delta T/T_0]T)^2}\frac{\partial T}{\partial z}\right] - \frac{c}{r} \ . \tag{4.6}$$

An approximate analytical solution will now be calculated for this non-dimensional equation.

4.2 Steady state solution with no crystal growth

A steady state solution of Equation (4.6) is now considered. This solution describes what happens after a long time, when the phenomenon modelled in the equation has reached equilibrium and no crystals are growing. The governing equation is simplified using the following assumptions:

- The temperature gradient is constant across the alloy, $\partial T/\partial z = 1$.
- The temperature difference ΔT is small compared to the minimum temperature T_0, so $|\Delta T/T_0|\ T \ll 1$.

The governing equation (4.6) may then be written:

$$\frac{\partial}{\partial z}\left[A\frac{\partial c}{\partial z} + Bc\right] = 0. \tag{4.7}$$

Equation (4.7) has the family of solutions

$$c = k_1 e^{-Bz/A} + k_2\ , \tag{4.8}$$

where k_1 and k_2 are two constants. The boundary conditions (4.5) impose $k_2 = 0$. Mass conservation in the system

$$\int_{z=0}^{z=1} c dz = 1$$

leads to

$$k_1 = \frac{B}{A}\frac{1}{\left(1 - e^{-B/A}\right)}\ .$$

The concentration of diffusing atoms in the alloy at equilibrium is then:

$$c = \frac{B}{A}\frac{e^{-Bz/A}}{\left(1 - e^{-B/A}\right)}. \tag{4.9}$$

The solution depends upon the position z and the ratio B/A:

$$\frac{B}{A} = \frac{Q^{*}\Delta T}{RT_0^2}\ .$$

Since ΔT is positive, the sign of B is the same as that of Q^{*}. This sign determines the direction in which the diffusing atoms migrate:

- If the heat of transfer Q^* is positive, the Soret effect pushes diffusing atoms towards the cooler end of the alloy, at the bottom of the sample:

$$c(0) = \frac{B}{A} \frac{1}{\left(1 - e^{-B/A}\right)} \ .$$

- If the heat of transfer is negative, diffusing atoms move towards the hotter end of the sample at the top.

$$c(0) = \frac{B}{A} \frac{e^{-B/A}}{\left(1 - e^{-B/A}\right)} \ . \tag{4.10}$$

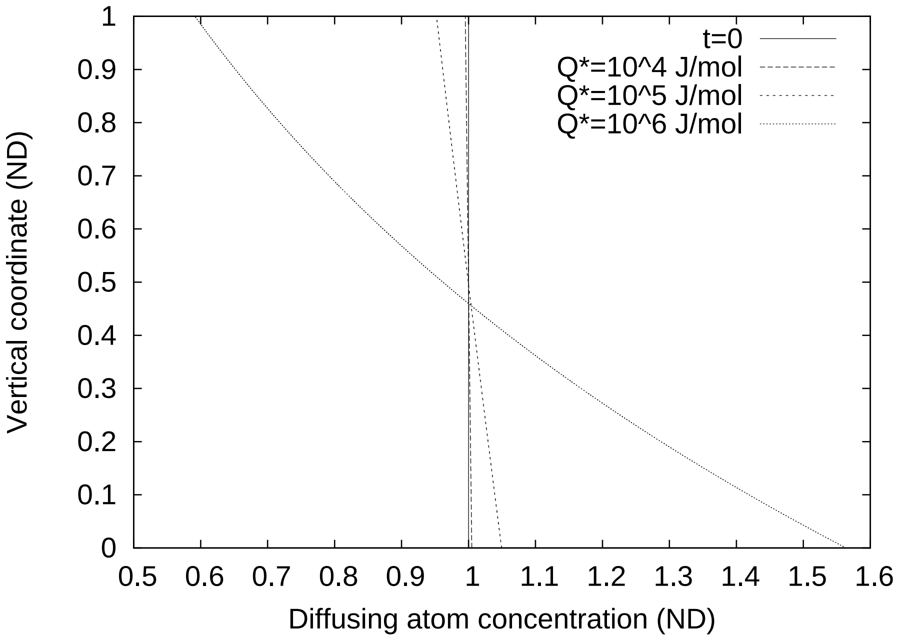

Figure 2: Typical configuration.

Figure 2 shows the steady state equilibrium concentration for various values of the ratio B/A, this means for different values of the heat of transfer, Q^*. In all cases, the non-dimensional temperature gradient is 1 and Q^* is positive. The initial constant atom concentration corresponds to the vertical curve. When the heat of transfer is much smaller than $Q^* = 10^6 \mathrm{kJ{\cdot}mol}^{-1}$, the Soret diffusion only has a small effect. When the value of the heat of transport gets closer to $Q^* = 10^6\text{kJ}\cdot\text{mol}^{-1}$, the effects of thermomigration become more obvious as could be expected from the analysis on non-dimensional coefficients. In all cases, as could be expected, the concentration of diffusing atoms is much higher at the cooler end of the alloy, $z = 0$.

A time dependent solution of the governing equation (4.6) can be calculated explicitly and this is performed in Appendix A. However, these analytical results may not include the sink term easily and numerical solutions will now be investigated.

5 Numerical solutions

5.1 Numerical scheme

Explicit solutions may not be calculated for the complete system. When crystals are growing, little progress may be done analytically. The governing equation will be solved numerically using a standard finite difference method. The concentration c is calculated on equally spaced points numbered from 0 to n_z, including the boundaries, separated by the space step Δz. Similarly, the simulation time t_s is divided in n_t time steps of size $\Delta t = t_s/n_t$. The concentration at $z = i\Delta z$ and at time $t = k\Delta t$ is denoted by c_i^k.

To be consistent with the study performed in the previous section, a non-dimensional form of the equation is used. When a sink term is introduced, the governing equation may then be written:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(A\frac{\partial c}{\partial z} + Bc\frac{\partial T}{\partial z}\right) - S \ , \tag{5.1}$$

where S is the non-dimensional sink term. The equation is solved under the following conditions:

- A constant temperature gradient is applied with the maximum temperature at the top:

$$\frac{\partial T}{\partial z} = 1 \ , \tag{5.2}$$

- The boundary condition (4.5) is applied at the top and bottom of the alloy:

  $$\left(A\frac{\partial c}{\partial z} + \frac{Bc}{(1+[\Delta T/T_0]T)^2} \right)\Bigg|_{z=0,\ z=1} = 0 \ .$$

  This formulation is consistent with the mass conservation assumption used in the previous section.

- Initially, the atom concentration is uniform in the alloy:

  $$c(0,z) = 1 \ . \tag{5.3}$$

The use of the standard finite volume method leads to the following difference equations:

$$c_0^{k+1}\left[1 + \frac{2A\Delta t}{\Delta z^2} - \frac{\Gamma_{1/2}\Delta t}{\Delta z}\right] - c_1^{k+1}\left[\frac{\Gamma_{1/2}\Delta t}{\Delta z} + \frac{2A\Delta t}{\Delta z^2}\right] = c_0^k - S_0\Delta t \ , \tag{5.4}$$

$$c_{i-1}^{k+1}\left[\frac{\Gamma_{i-1/2}\Delta t}{2\Delta z} - \frac{A\Delta t}{\Delta z^2}\right] + c_i^{k+1}\left[1 + \frac{2A\Delta t}{\Delta z^2} + \frac{\left(\Gamma_{i-1/2} - \Gamma_{i+1/2}\right)\Delta t}{2\Delta z}\right] - c_{i+1}^{k+1}\left[\frac{\Gamma_{i+1/2}\Delta t}{2\Delta z} + \frac{A\Delta t}{\Delta z^2}\right] = c_i^k - S_i\Delta t \ , \tag{5.5}$$

$$c_{n_z-1}^{k+1}\left[\frac{\Gamma_{n_z-1/2}\Delta t}{\Delta z} - \frac{2A\Delta t}{\Delta z^2}\right] + c_{n_z}^{k+1}\left[1 + \frac{2A\Delta t}{\Delta z^2} + \frac{\Gamma_{n_z-1/2}\Delta t}{\Delta z}\right] = c_{n_z}^k - S_i\Delta t \tag{5.6}$$

and the term $\Gamma_{i+1/2}$ is defined as

$$\Gamma_{i+1/2} = \frac{B}{\left[1 + \Delta T/T_0(i+1/2)/n_z\right]^2} \ .$$

The sink term is now expressed for the two models considered:

- Basic model:

$$S_i = \frac{1}{r_i} \quad \text{if} \quad z \le 2r \quad \text{and} \quad S_i = 0 \quad \text{otherwise.} \tag{5.7}$$

The equation governing the radius, r, of the crystal may be written using non-dimensional parameters

$$\frac{dr}{dt} = \frac{\tau}{r_0^3} \frac{\mathcal{V}}{4\pi\rho r^2} \; , \tag{5.8}$$

and the discretised form is:

$$r^{k+1} = r^k + \Delta t \frac{\tau}{r_0^3} \frac{\mathcal{V}}{4\pi\rho (r^k)^2} . \tag{5.9}$$

- Advanced model:
  The discretised form is:

$$S_i = \frac{n_S \mathcal{V}_1 c_i^k}{2r^k} \quad \text{if} \quad z \leq 2r \quad \text{and} \quad S_i = 0 \quad \text{otherwise}, \tag{5.10}$$

  and the radius growth rate is only affected through the value of $\mathcal{V}$: since the value is not constant in space, the global value should be estimated using the integral:

$$\mathcal{V} = \int_0^{2r} \mathcal{V}|_{dz} \, dz \; . \tag{5.11}$$

The discretisation is now complete. The $n_z + 1$ discretised equations form a tri-diagonal system, that may be solved easily, using an LU factorisation algorithm for example. The numerical scheme is now complete, results will now be presented.

5.2 Numerical results

The solutions of the governing equation will be presented for three different configurations. Crystal growth is considered for the two models detailed above, first when the crystal mass increases at a constant rate, then when the growth rate varies with the atom concentration. The simulations are carried out with the values detailed in Table 1.

The value of the heat of transport is chosen to fit experimental observations: when the temperature gradient is positive, diffusing atoms should move towards the cooler end, when the temperature gradient is negative the atoms move towards the hotter end. The value retained here is $Q^* = 10^7 \text{J}\cdot\text{mol}^{-1}$. To

Symbol	Description	Value	Unit
A	Non-dimensional number		
B	Non-dimensional number		
C	Non-dimensional number		
c	Concentration of diffusing atoms		kg·m^{-3}
c_0	Diffusing atoms initial concentration	240	kg·m^{-3}
D	Diffusivity of diffusing atoms in alloy	$4 \cdot 10^{-9}$	m^2·s^{-1}
g	Gravity	9.8	m·s^{-2}
L	Length scale	0.02	m
n_S	Number of crystals/surface unit	10000	m^{-2}
Q^*	Heat of transport in alloy		J·mol^{-1}
R	Ideal gas constant	8.314	J·K^{-1}·mol^{-1}
r	Crystal radius		m
r_0	Initial crystal radius	10^{-4}	m
T_0	Minimum temperature	1573	K
t	Time		
z	Vertical Cartesian coordinate		
$\mathcal{V}$	Initial crystal growth rate	$2 \cdot 10^{-9}$	kg·s^{-1}
Δt	Non-dimensional time step		
ΔT	Typical temperature gap	20	K
Δz	Non-dimensional space		
τ	Time scale	2400	s

Table 1: Nomencalture

start with, the crystal growth is not concentration dependent. With the values given in Table 1, the time scale is 40 minutes and the radius scale 10^{-4}m. Figure 3 shows the evolution of the crystal diameter during one day for a positive and negative temperature gradient. With the value retained for the heat of transport, the temperature gradient plays the key role observed experimentally. The two growth rates are similar until $t = 6$, this corresponds to 4 hours. The two curves then differ drastically: when the temperature gradient is negative, the crystal growth stops suddenly, when the temperature gradient is positive, the growth continues at a rather steady rate. This may be explained when considering the diffusing atom concentrations shown in Figure 4. When the temperature gradient is negative, there are no more diffusing atoms at the bottom of the alloy, and therefore the crystal growth is stopped. When the temperature gradient is positive, the concentration of diffusing atoms is very high at the bottom of the alloy and there is no shortage of raw material to fuel the crystal growth.

The results are very similar when crystal growth is concentration dependent. Figure 5 compares the growth rates for concentration and non-concentration dependent growth models for a positive temperature gradient. As could be expected, the radius grows faster when the growth rate model is concentration dependent. This is consistent with the evolution of the concentrations: diffusing atoms are piling up at the bottom of the alloy and this accelerates the crystal growth.

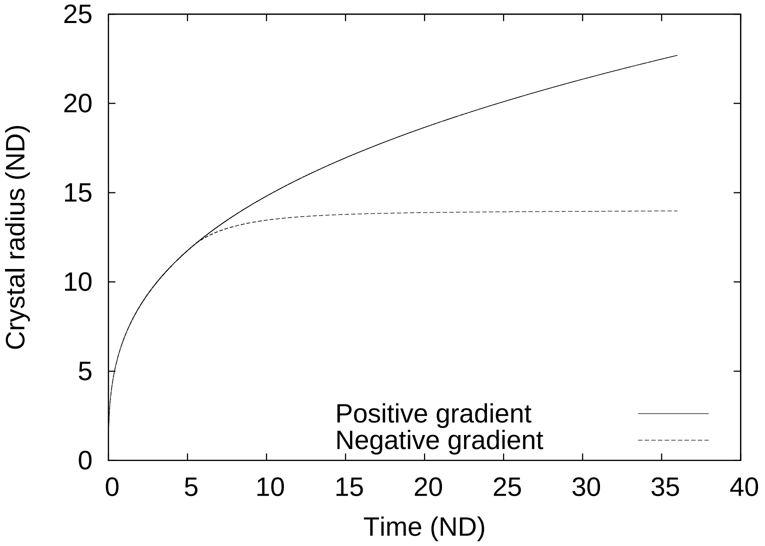

Figure 3: Crystal radius evolution with different temperature gradients.

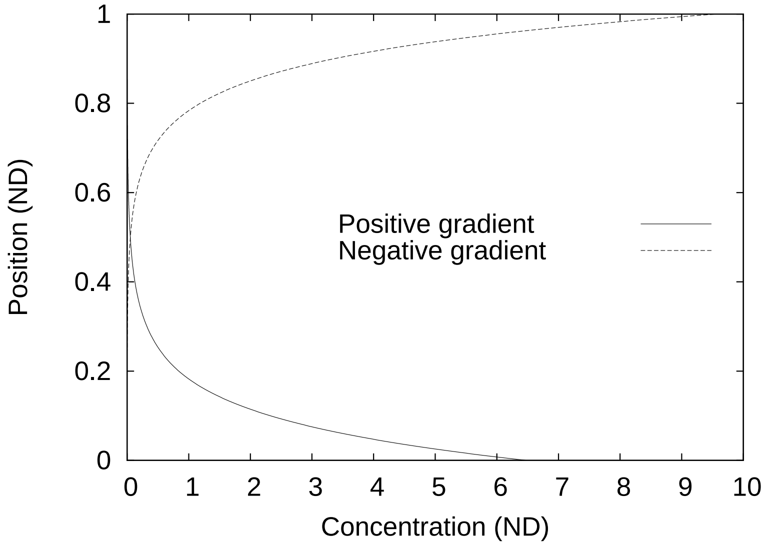

Figure 4: Diffusing atom concentrations after one day.

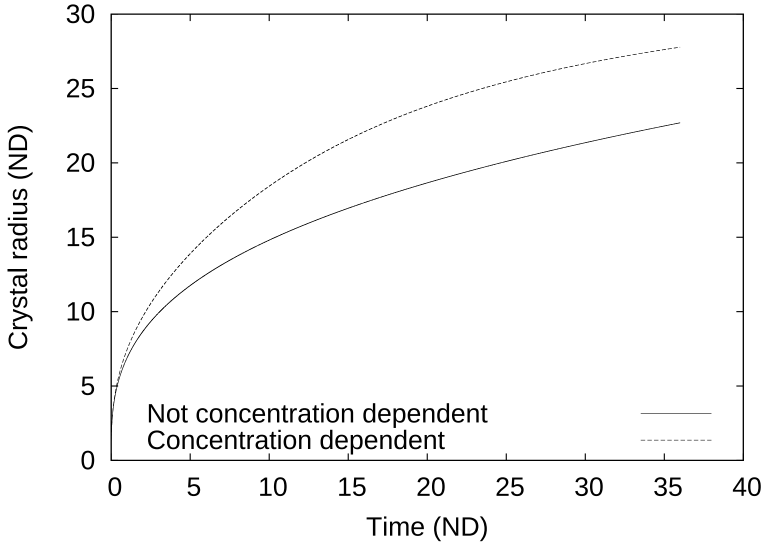

Figure 5: Crystal radius evolution with different growth models.

5.3 Discussion

The evolution of the radius reflects the behaviour observed experimentally: the growth rate is strongly affected by the temperature gradient and the crystals do not grow after some time when the temperature gradient is the wrong way round. However, several aspects of the model remain unsatisfactory.

- Heat of transport
  The value of the heat of transport required to simulate adequate crystal growth is extremely high, three to four orders of magnitude larger than heat of transport values measured in solids [3]. Several factors could explain these differences:

  - The alloy used in the present work is liquid, so it is at a much higher temperature and subject to a very much higher pressure, which could make atom movements much more difficult.
  - The alloy is an eutectic state and this might also make atom movements more difficult.

  This high value may also be affected by the thermal model used in the present work as will now be detailed.

- Temperature
  A constant temperature gradient was applied to the alloy throughout the study. However, the crystal formation is endothermic, which means that a much higher temperature gradient could be expected close to the crystal. A thorough study of the temperature should therefore be performed and this new configuration could reduce the value of the heat of transport.

- Concentration
  The concentration profiles shown in Figure 4 are not realistic. The diffusing atom concentration in the alloy may not take the complete range of values observed in the results, this is limited by a saturation concentration. This was not considered here and clearly, this would affect the crystal growth. The movements of diffusing atoms would be limited and the growth rate would be reduced.

6 Conclusion and future work

An equation modelling the diffusion of diffusing atoms in a molten metal alloy was presented. The model is based on the standard Fick's diffusion process and the temperature dependent Soret thermodiffusion. These two phenomena are coupled with crystal growth models. The preliminary results are consistent with experimental observations. However, there are limitations to the present approach and the model could be developed in quite a few directions

- The equation presented does not account for saturation. This value increases with temperature: when saturation concentration is reached throughout the sample, this may create a diffusing atom flux with an order of magnitude similar to the flux simulated with the Soret effect. This element should be included to allow for a more realistic model.
- The value of the heat transport required in the present study is very high. This could be explained by the extreme experimental conditions. Such values might however not be possible and this problem may be solved for more realistic experimental conditions and when saturation is included in the model.
- A number of constants are undetermined due to the extreme operating conditions. Quantitative experimental results would be necessary to simulate the evolution more accurately.
- A more systematic temperature study inside the alloy should be performed. This would not affect the qualitative results but the speed of the crystal growth would be affected. This could also reduce the high value of the heat of transport necessary to reproduce qualitative experimental results.
- Two basic models describing the growth rate were presented. In the first case, the crystals gain mass at a constant rate, in the second, the gain is proportional to the surrounding diffusing atom concentration. These are empirical assumptions and a more advanced model would certainly be beneficial.
- This preliminary model was developed for a one dimensional geometry. Obviously, a two or three dimensional model would provide much more valuable (and potentially more accurate) results.

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A Time dependent solution of equation 4.6

A slightly simplified version of equation (4.6) with no sink term may be fully solved analytically. Once more, if the temperature gradient is constant throughout the alloy and if the temperature difference between the top and the bottom of the alloy is small, the governing equation may be written

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[A\frac{\partial c}{\partial z} + Bc\right] \ . \tag{A.1}$$

The solution may be calculated as $c(t, z) = Y(t)Z(z)$. A straightforward analysis shows that the concentration c may be written as

$$c(t, z) = \sum_{n=0}^{\infty} a_n Y_n(t) Z_n(z) \ ,$$

where

$$\begin{aligned} Y_n(t) &= \exp\left[-\left(An^2\pi^2 + \frac{B^2}{4A}\right)t\right] \ , \\ Z_n(z) &= \exp\left(-\frac{Bz}{2A}\right)\left[\cos(n\pi z) - \frac{B}{2n\pi A}\sin(n\pi z)\right] \ , \end{aligned}$$

and the coefficients a_n are defined using the concentration $c_0(z)$ at $t = 0$:

$$\begin{aligned} a_n &= 2\int_0^1 c_0(z)\exp\left(\frac{Bz}{2A}\right)\cos(n\pi z)dz \\ &= 2\int_0^1 \frac{-Bc_0(z)}{2n\pi A}\exp\left(\frac{Bz}{2A}\right)\sin(n\pi z)dz \ . \end{aligned}$$

If the initial concentration is constant throughout the alloy, $c_0(z) = 1$, this leads to

$$a_n = \frac{B}{A}\left[\frac{\exp\left(B/2A\right)\cos(n\pi) - 1}{B^2/(4A^2) + (n\pi)^2}\right]. \tag{A.2}$$

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