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Modelling Solidification of Binary Alloys

Ferran Brosa Planella

UNIVERSITY OF OXFORD

Elkem
A Bluestar Company

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1 Introduction

Solidification is a key part of many industrial processes, and a better understanding of this phenomenon is necessary to improve material production methods. Silicon production is no exception and the casting process has a huge impact on the mechanical and chemical properties of the final product.

Even though silicon is the second most common element in the Earth's crust (only after oxygen), it is rarely found in its pure form. Therefore, a complex process is required to transform quartz (silicon dioxide) into pure silicon, as depicted in Figure 1. Broadly, the raw materials provide silicon dioxide (in form of quartz) and carbon (in form of coal, charcoal and woodchips) so when the mixture is heated up in the furnace a reduction reaction takes place. One of the products of the reaction is silicon in liquid form which flows downwards and is tapped at the bottom of the furnace and, after some refining processes, is left to solidify. Our work focuses on this part of the process.

Our main interest are casting techniques such as iron moulds, water-cooled copper plates and granulation. As opposed to directional solidification, in these techniques the velocity of the solidification front is not controlled, causing an uneven distribution of impurities across the cast.

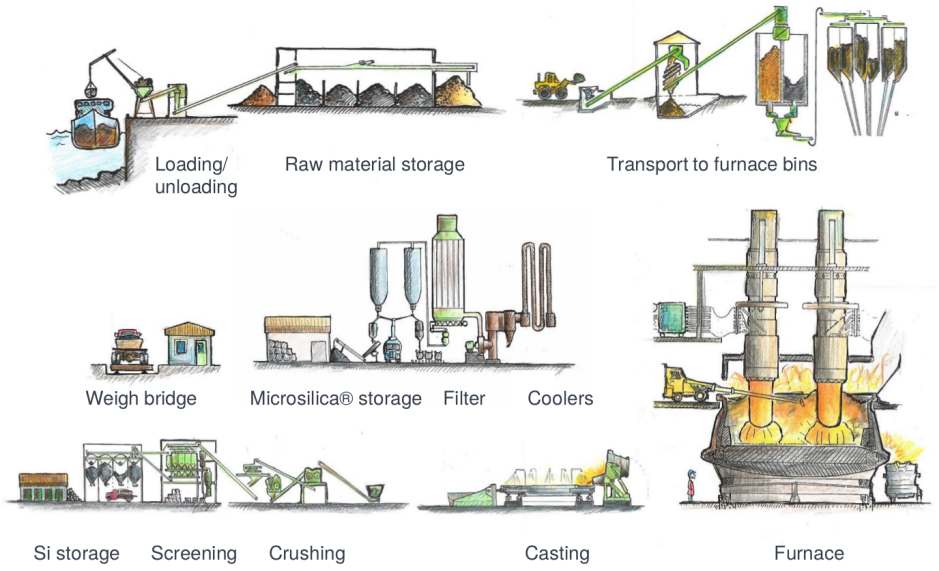

Figure 1 – Sketch of the silicon production process, reproduced from [1].

The goal of the project is to derive, analyse and solve mathematical models which allow us to gain a better understanding of the solidification process for a binary alloy, with a special interest in the metallurgical grade silicon application. These models will provide insight to our industrial partner, Elkem, that can lead to a better understanding and improvement of their casting process

2 Mathematical model

In order to describe the solidification process we pose a Stefan problem including the transport of impurities both in the solid and liquid phase and the constitutional supercooling they cause. Therefore, we refer to this model as the extended Stefan problem. In the model we define two regions: the liquid phase and the solid phase, which are separated by a sharp interface. The position of this interface evolves in time so it is an additional unknown in our equations.

We model temperature and concentration of impurities, respectively in each subdomain, while also keeping track of the time evolution of the interface. We impose conservation of mass and energy in each phase and across the moving interface, and couple the phases under an assumption of constitutional supercooling. The effects of constitutional supercooling are reflected in phase diagrams which become rather complex when more

than two components are considered. Therefore, we assume that all impurities constitute a single phase, resulting in a binary phase problem between the pure material and the impurities. We assume as well that the relation between the impurity concentration and the temperature on both the liquidus and the solidus is linear. We also assume that the solid and liquid are stationary so heat and mass transport are driven only by diffusion.

We impose boundary conditions at the outer boundary, which corresponds to the wall of the mould or the surface of the granule. In particular, we prescribe a no-flux condition for the concentration of impurities (as they cannot flow outside the cast through the boundary), as well as a fixed uniform temperature. A more realistic approach could be taken by using a heat exchange condition (as done in [2]). However, in the limit where the heat exchange coefficient is large, this condition can be approximated by a Dirichlet boundary condition. We assume that initially the entire domain is liquid, with homogeneous temperature and concentration of impurities. A more detailed derivation of the model can be found in [3].

3 Stability analysis

Both the classic and the extended Stefan problems admit self-similar solutions when they are defined in semi-infinite or infinite one-dimensional domains. In these cases, we can calculate closed-form expressions for the solutions and we find that the interface motion is proportional to the square root of time. However, when we look at silicon casts we observe two-dimensional structures (silicon grains) therefore the question of whether these one-dimensional solutions are stable arises.

In order to determine the stability of these solutions, we introduce small perturbations to the temperature and concentration fields, and also to the position of the interface. Substituting into the governing equations and linearising, we can find the equations governing the perturbations. We consider both a semi-infinite domain (finite solid domain and semi-infinite liquid domain) and an infinite domain (both semi-infinite solid and liquid domains). For both geometries we find that, regardless of the parameter choice, there are always unstable perturbations (that is, perturbations that grow unboudedly in time). This means that planar solutions will break down into two-dimensional structures (which are not captured by the model) and therefore not observed in real life. The details of these analysis can be found in [4].

4 Solidification of finite domains

Self-similar solutions, such as the ones studied in the previous section, cannot be found when the solidification domain is finite. Therefore, we need to use asymptotic techniques to find analytical approximation to the solutions. We take the limit of large Lewis number, which means that heat diffuses much faster than impurities do. We also assume small diffusivity of impurities in the solid, small initial temperature and concentration, small constitutional supercooling and almost complete rejection of impurities from the solid phase. All these assumptions are reasonable for the cast of metallurgical grade silicon. We consider two different geometries (planar and spherical) and perform a matched asymptotic expansion to obtain analytical expressions for the solutions for the whole time domain. These two geometries are representative of different types of silicon cast: solidification into iron moulds and water cooled copper plates (for planar geometry), and water granulation (for spherical geometry). The details for the planar geometry can be found in [3] and for the spherical geometry in [5].

Planar geometry

We first perform the asymptotic analysis for the planar geometry. We consider a finite planar domain cooled from the boundary, and assuming symmetry in the problem we only need to consider half of the domain. The asymptotic analysis reveals four different time regimes, and a total of ten different spatio-temporal layers across them. We find that the first two time regimes are physically relevant, while the last two are not physical. We can determine analytical solutions in each layer and by matching the solutions across layers we can describe the behaviour of the solidification process across the entire time domain. In order to validate the asymptotic solutions, we implemented a finite volume scheme in MATLAB to solve the full model numerically.

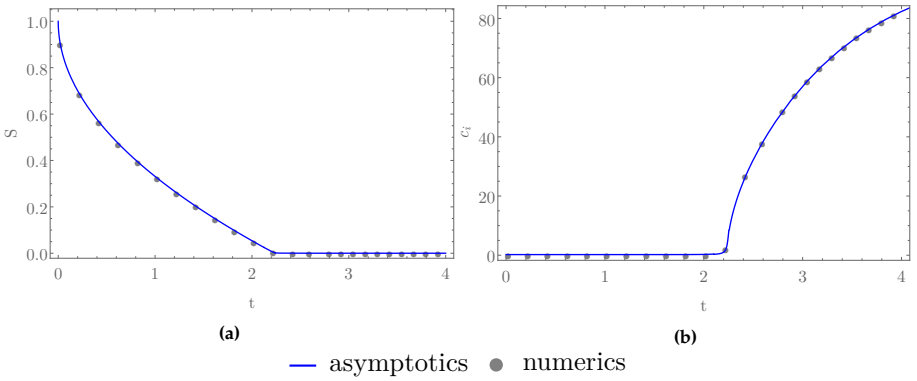

Figure 2 – Comparison of the analytical and numerical solution of (a) the interface position and (b) the concentration of impurities on the liquid side of the interface against time for the planar geometry.

In Figure 2 we compare the analytical and numerical solutions for the position of the interface and the concentration of impurities at the interface as functions of time, for a parameter set relevant to solidification of metallurgical grade silicon. We find really good agreement between analytical and numerical solutions, which validates the asymptotic analysis.

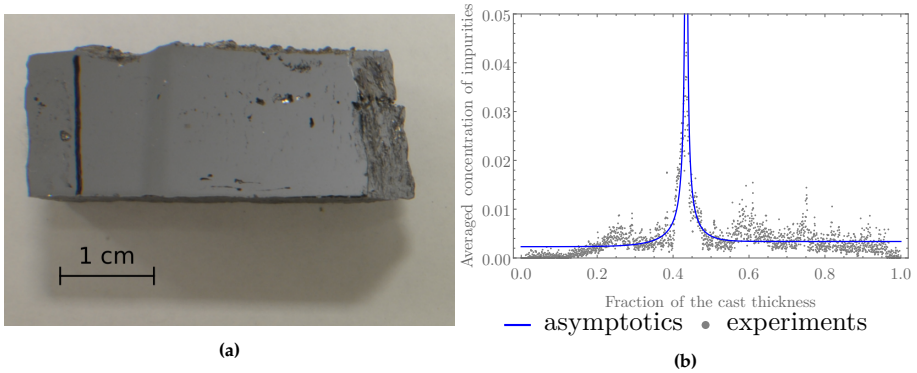

Figure 3 – (a) Image of the sample used for the experimental data (imaged provided by Elkem). The experiment corresponds to a 14mm silicon cast over a water cooled copper plate. The data is taken at a given central section of the cast which has been polished and chemically treated in order to take the measurements. (b) Comparison of the asymptotic solution and experimental data for the concentration in the solid phase. The experimental data has been provided by Elkem. For the asymptotic solution we used parameter values $c_0 = 0.01$, $\mu_r = 17$, $\mu_l = 10$, $\alpha = 0.03$, and $z_0 = 0.43$.

In Figure 3(b), we compare the asymptotic solution and the experimental data, in which we only observe the first two time regimes. The corresponding composite asymptotic solution for the impurity concentration valid in both regimes (at leading order) is

$$c_s(z) \approx \frac{\alpha\mu}{\alpha\mu+1} c_0 \sum_{n=1}^{\infty} n \left(e^{-\mu(n+1)nz} + e^{-\mu n(n-1)z} \right), \tag{1}$$

where $\mu = 2\lambda^2 \mathrm{Le}$, c_0 is the initial concentration of impurities in the melt, α is the segregation coefficient, λ is a dimensionless parameter related to the cooling rate (see [3] for details), and Le is the Lewis number, defined as the ratio between the thermal over impurity diffusivity in the liquid phase. Thus, we find that the concentration profile depends only on three parameters: μ, α, and c_0.

In the experimental data, we observe that the concentration profiles produced by the two solidification fronts are not symmetric, and that they eventually meet at a point z_0 of the cast. To match this with asymptotic solutions, we assume each side of the plot can be modelled by (1) combining $c_s(z - z_0)$ and $c_s(z_0 - z)$, both with the same parameters α and c_0 (as these are given by the material properties). However, we assume the parameter μ

depends on the cooling rate which has different values at the left and the right of the cast due to the different heat transfer mechanisms. However, we know that both fronts meet at the same time, and at $z = z_0$, therefore we have the relation

$$\mu_l = \left(\frac{z_0}{1 - z_0}\right)^2 \mu_r, \tag{2}$$

where subscripts r and l denote the right and left side of the central cross section $z = z_0$. We use reasonable parameter values for our problem to compare the asymptotic solution (1) with the experimental data. Using the parameter values $c_0 = 0.01$, $\mu_r = 17$, $\mu_l = 10$, $\alpha = 0.03$ and $z_0 = 0.43$, we obtain the asymptotic solution shown in Figure 3(b). Given the simplicity of our model, we treat these parameters as effective coefficients that can be determined experimentally for a given physical set-up. The asymptotic solution captures the rapid growth of the concentration near the region where the solidification fronts meet, and the constant concentration outside of this region. The noise in the data is caused by the bubbles and pores of the cast, as impurities tend to aggregate around them. In spite of these complications, the asymptotic solutions show good qualitative agreement with the experimental data.

Spherical geometry

We also perform a similar analysis for a sphericallly symmetric geometry cooled from the outside. In this case, the large Lewis number (Le) limit is not enough and we need to take the small Stefan number (St) limit (i.e. time scale of the motion of the interface is much smaller than heat diffusion time scale). We can take the two limits independently as long as $\mathrm{Le}^{-\frac{2}{3}} \ll \mathrm{St} \ll 1$. The analysis distinguishes three regimes with eight layers overall for the Lewis number analysis, and, within the first regime, three subregimes for the small Stefan number analysis. As before, we solve each layer separately and then match the solutions. We use a finite volume scheme in MATLAB to validate the asymptotic solutions.

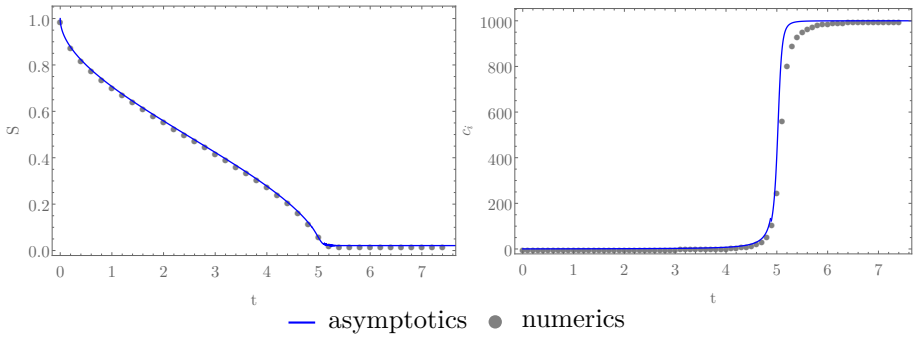

Figure 4 – Comparison of the analytical and numerical solution of (a) the interface position and (b) the concentration of impurities on the liquid side of the interface against time for the spherical geometry.

In Figure 4 we compare the analytical and numerical solutions for the spherical problems, showing the position of the interface and the concentration of impurities at the interface as functions of time. The parameter set chosen here is still relevant for silicon, but we chose Le and St to make sure that $\mathrm{Le}^{-\frac{2}{3}} \ll \mathrm{St} \ll 1$ holds. We observe good agreement, although not as good as for the planar geometry, especially for the concentration of impurities.

From the asymptotic analysis, we have that the concentration profile in the particle as a function of the radius, r, is described by

$$c_s(r) = \frac{a}{1 + br^3}, \quad \text{where} \quad a = \alpha m_l \ \text{ and } \ b = \frac{3m_l\rho}{c_0 k \mathrm{StLe}}, \tag{3}$$

therefore there are two dimensionless numbers that control the shape of the concentration profiles. The parameter a dictates what is the concentration at the centre of the granule and it is determined by α and m_l, which depend on the material. The shape of the profile is governed by b, which contains St and thus b can be changed by varying the cooling conditions.

We find that the values $a \approx 0.03$ and $b \approx 8$ give reasonable agreements between the

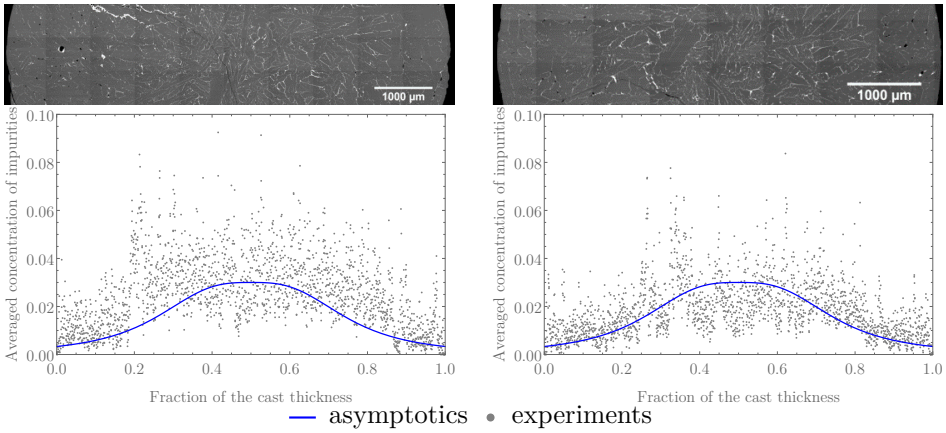

Figure 5 – Comparison of asymptotic solutions and experimental data for the concentration of impurities in a silicon granule for two distinct samples. Both experimental data and images of the samples have been provided by Elkem. The analytical solution corresponds to (3) with parameter values $a = 0.03$ and $b = 8$. Notice that $r = 0$ in the model corresponds to the centre of the horizontal axis in both plots.

experimental data and the asymptotic results as shown in Figure 5; no additional parameter fitting was employed. Despite the noise in the measurements, we observe an increasing trend in the concentration from the boundaries to the interior, and then a region of roughly constant concentration at the centre of the domain, in agreement with the behaviour predicted by (3).

5 Discussion

We have studied different aspects of the extended Stefan problem to model solidification of binary alloys, with particular interest on metallurgical grade silicon. We first derived the general model [3], from which we derived all the subsequent models could be used as a basis to implement numerical algorithms to study the problem, as the model is derived from basic physical principles. In addition, the model can be used as starting point to derive other models that include more physical phenomena.

The stability analysis presented in [4] proves from a mathematical point of view that stable planar solidification fronts are not possible unless the cooling of the system is controlled and the velocity of the solidification front kept below a certain threshold, like in directional solidification or the Czochralski process. Even though this was known from experimental evidence, the mathematical analysis provides theoretical background and highlights the role of the moving boundary as the trigger of the instability, which can potentially lead to the development of new casting techniques.

The asymptotic solutions derived in [3] provide insight into the solidification of thin layers of silicon which, due to their aspect ratio, can be modelled as one-dimensional processes. The solutions show the leading phenomena at each stage of the process and the impact of each parameter over the dynamics. This is important, as the high temperatures prevent Elkem from obtaining this information experimentally. The model allows us to understand which parameters play a role in the impurity distribution over the solid silicon, namely, the concentration of impurities in the initial melt, the segregation coefficient, and a parameter μ related to the cooling rate. The initial concentration acts only as a scaling of the concentration profile and, as it can be easily measured, we suggest to fix its value using the experimental measurements of the liquid used in the cast. The other two parameters should be fit to experimental data. We observe that both parameters play a role on the scaling of the concentration profile, but μ has an impact on the thickness of the layer where the impurities build up as well. Therefore, our model suggests that varying the cooling rate can be used as a way to control the thickness of those layers. Because these layers appear to be correlated to the equiaxed layers, where the grains are smaller, one could use our model for an empirical approximation to the columnar to equiaxed transition.

In a similar way, we have obtained asymptotic solutions to the solidification of a binary alloy in a sphere in [5]. The analysis gives results which are significantly different to those in a planar geometry, highlighting thus the importance of the geometry in the solidification

process. These results can be used to describe the water granulation process as we found reasonable agreement between the analytical solution for the concentration of impurities in the cast and experimental data on silicon granules. The main difference between planar and spherical geometry is that in the latter the rejection of impurities from the solid phase causes an increase of the concentration of impurities at the interface, making the supercooling effects appear earlier than in the planar domain. Even though we analysed two very simple geometries, it provides insight about the qualitative differences one might observe between thin casts and geometries in which all dimensions have approximately the same size.

Kjetil Hildal, Senior Research Engineer at Elkem, stated: *"The modelling work performed by Ferran Brosa Planella on 'Modelling the solidification of binary alloys' has been important to Elkem's fundamental research in solidification of silicon. By combining lab-scale experiments with mathematical modelling, Ferran have contributed to the overall understanding of parameter sensitivity with respect to microstructure development during solidification of silicon. Elkem is using this added insight for the long-term development of alternatives to the current casting methodology. In these alternatives, the control of critical parameters relevant for the solidification process will be improved significantly. The involvement in InfoMM gives Elkem valuable access to competence in mathematical modelling, and the importance of academic-industrial partnerships are crucial for Elkem in order to remain a leading global producer of ferro silicon alloys".*

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