EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling

Solidification of Silicon

Graham Patrick Benham

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1. Introduction

Background

In the casting process of silicon, liquid silicon is poured into a metal mould and allowed to cool and solidify. It is well known that the cooling rates and mould size affect the microstructure. This is true both in the context of pure silicon and silicon alloys. Typically, when cooling rates are too fast the silicon grains are very small, causing dust, or fines, to be lost in the post-casting stage when the silicon is re-crushed. Although the yield is reduced, the small grains allow for a homogeneous distribution of impurities, which is an advantage in the silicon alloy industry.

In contrast, when the silicon is cooled too slowly, the grains which form are much longer and hold impurities in the intervening cracks. These impurities are therefore distributed in a less homogeneous manner and, in fact, when the silicon is re-crushed, a large portion of them drop out from the long crack boundaries and are lost.

New markets demand high yield silicon of a more homogeneous consistency and recent experiments have shown that the casting of silicon in small, thin containers shows promise. Hence there is an emerging interest in the silicon industry of the so-called 'thin casting' technique. There has also been recent interest in casting in a wedge shaped mould in order to investigate a range of cooling rates simultaneously.

To predict the silicon microstructure, we must first derive a mathematical model for the thermal history during solidification.

In practice, casting operators must lay down a layer of crushed silicon fines prior to pouring in order to buffer the cast from temperatures that would otherwise melt it. Operators need to know how much fines to put down to protect the mould.

Silicon manufacturers, such as Elkem, are keen to predict the silicon microstructure. However, this requires a detailed knowledge of the thermal history during solidification.

2. Solidification of Silicon

We have developed simple mathematical models for the solidification of silicon to simulate two sets of experiments conducted by Elkem. The first experiments involve casting in shallow moulds between 3cm and 8cm. The second experiments used wedge-shaped casts with a wedge angle of 45°.

Our models track the temperature in the cooling silicon and take account of convection and radiation at the air-silicon surface, conduction into the mould, and latent heat at the solidification front(s).

We have used a combination of COMSOL simulations and simplified mathematical approximations to gain insight to the solidification problem and to estimate the parameter values based on thermal data taken from Elkem experiments. In addition, we have derived useful predictive tools to estimate key features of the solidification, such as the time it takes for the material to become entirely solid.

We have also made an initial mathematical model to try to predict the depth of penetration of liquid silicon into the fines layer. This could provide a useful tool for operators to know how deep they should lay their fines so as to separate the molten silicon from the mould.

The Stefan number St is a comparison between the heat required to cool the material to the mould temperature and the latent heat. For the solidification of silicon, St=0.74.

Glossary of terms

- Solidification Front: During solidification, liquid silicon is separated from solid silicon by a solidification front. Solidification fronts tend to emerge from edges of the material that are subject to heat transfer (such as the silicon-mould and silicon-air interfaces).
- Solidification Distance: The solidification distance is the distance, measured from the bottom of the cast, at which the solidification fronts meet. This can be observed by a clear discontinuity in grain size and alignment in the microstructure.
- Solidification Time: Time taken for the solidification fronts to meet, and therefore the silicon to become entirely solid.
- Quasi-Steady Approximation: The quasi-steady approximation is a neat mathematical simplification of the solidification problem based on the assumption that the heat diffuses much more quickly than the solidification front moves (i.e. small Stefan number). This approximation makes the mathematics simpler and yields analytical results.
- Triangle Model: In the wedge casting model, if we assume that the solidification fronts move from each wedge wall independent of each other then we can use three separate one-dimensional quasi-steady approximations to track the fronts. This *Triangle* model is so-called because it predicts that the area of liquid silicon will diminish in shrinking self-similar triangles

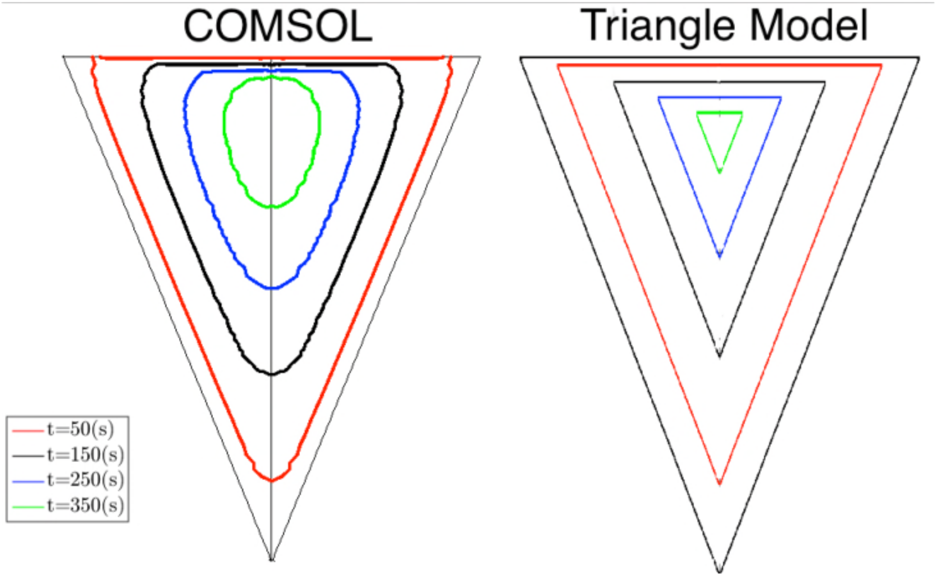
Mathematical model

Thin casting

We have applied our models to address the solidification of 100% pure silicon due to cooling from both the metal mould and the surrounding air. The metal mould is water-cooled at its external surface. We investigated the relative importance of different cooling mechanisms, namely conduction, convection and radiation. We have assumed that the liquid silicon is stationary.

Since the casts we are interested in are wide and shallow, away from the walls we expect little dependence in the direction along the width of the cast. Thus, the problem can be thought of effectively in one dimension, along the depth of the cast.

We have assumed that the thermal properties of silicon, such as the density, specific heat capacity and thermal conductivity are all taken to be constant in each of the liquid and solid silicon phases



Wedge casting

Unlike thin casting, wedge moulds are made from graphite and are not water-cooled. Given the geometry, our model in this case is necessarily two-dimensional.

Having identified the key parameters for both thin casting and wedge casting, we use thermal data taken from the experiments to estimate the parameter values. The fitted models are versatile, since these parameter values apply to thin casting in moulds of all depths, and wedge casting in wedges of any angle.

Fines Penetration

We have created a preliminary mathematical model to predict the penetration depth of liquid silicon into a bed of fines. We approximate the porous layer of fines by a series of narrow channels. Our key assumption is that the liquid silicon flows into the channels due to the overlying weight of fluid. As it penetrates, it also begins to solidify from the channel edges. We can predict the moment at which the channel closes up so that no more liquid silicon can enter.

Comments

- We have used COMSOL to solve our model and simulate the solidification of silicon in thin casting and wedge casting.

- Our quasi-steady approximation provides good approximation and easy predicting tools for the thin casting problem, such as solidification time and distance.

- The *Triangle* model, which is an extension of the quasi-steady approximation to the wedge problem, provides good approximation and easy predicting tools for the wedge casting problem.

The quasi-steady approximation provides easy-to-use predictions for the solidification time and distance.

3. Specific Results

Quasi-Steady Approximation: Solidification Time/Distance vs. Depth

If we increase the cast depth, the solidification distance, as a fraction of the total depth, does not appear to change. However, the solidification time varies almost linearly.

The quasi-steady approximation provides analytical results for the solidification time and distance in the thin casting model. The results of the quasi-steady approximation agree very well with those produced by the full-scale COMSOL simulation.

We want to be able to apply this model to the solidification problem in moulds of different depths. Interestingly, as we vary the depth, the solidification distance, as a fraction of the total depth, does not change very much. The solidification time varies almost linearly.

Triangle Model: Solidification Time/Distance vs. Wedge Angle

The *Triangle* model also provides analytical results for the solidification time and distance in the thin casting model. The results of the quasi-steady approximation agree very well with those produced by the full-scale COMSOL simulation. In fact, as we decrease the wedge angle, the solidification time predicted by the *Triangle* model converges to furnace and are cut open after being cooled, to analyse the remaining material. Photographs are shown in Figure 3. The solid is stationary in these experiments, and we assume that the internal pressure gradients are not large enough to move any of the liquids.

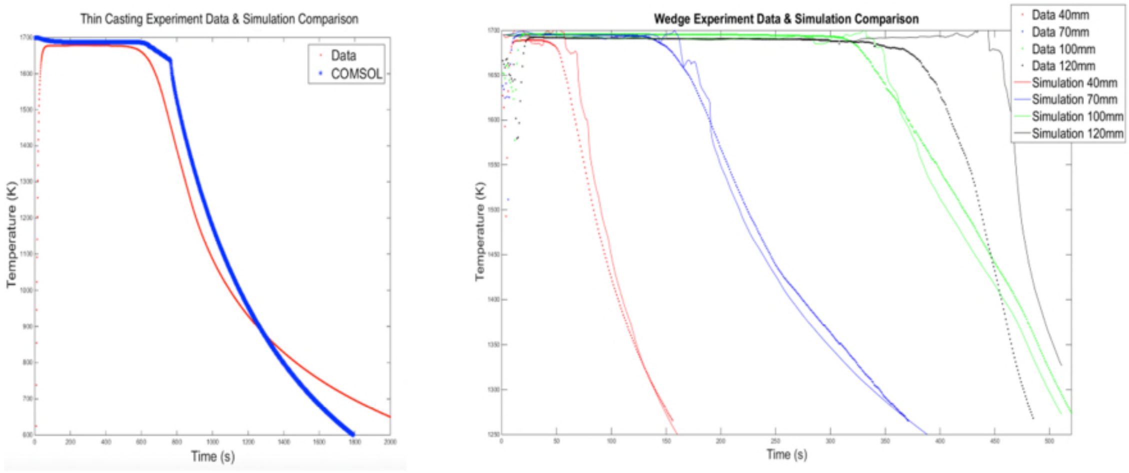


Figure 2: A COMSOL simulation was used to generate a thermal history of a point in the domain corresponding to thermocouple measurement from the appropriate casting experiment. Here we used all available parameters to fit the COMSOL-generated curve to the data (by eye). The graph on the left compares the fitted COMSOL temperature plot to a thermocouple measurement from the midpoint of an 8cm cast. The graph on the right uses four temperature measurements from the wedge experiment located at 4cm, 7cm, 10cm and 12cm from the bottom of the wedge (total depth approximately 15cm).

Data Fitting & Parameter Estimation

We have estimated the important parameters by fitting the simulated temperature profiles to the experimental data:

Parameter	Estimated Value	Units
Contact heat transfer coefficient Si-Copper Mould	100-600	W/Km^2
Contact heat transfer coefficient Si-Graphite Mould	700-1000	W/Km^2
Convective heat transfer coefficient (stagnant air)	5-20	W/Km^2
Convective heat transfer coefficient (water-driven cooling)	1000-5000	W/Km^2
Emissivity of Si	0.3-0.5	~
Emissivity of Cu	0.05-0.1	~

Fines Penetration

We predict silicon penetrates 2.8cm into the layer; 2cm is observed in experiments.

We have a mathematical model for the approximate penetration depth of the liquid silicon into the fines layer. It needs to be validated by experimental data, but it could eventually provide a predictive tool. A key preliminary result is that the model predicts an approximate depth of penetration of the silicon into the fines layer which is in reasonable agreement with experiments.

Extensions to our models

The key things to consider are:

- Revise grain growth literature and create a model for the silicon grain size based on cooling rates. We can then compare the results of this model to the microstructure in the cast samples.
- Model the distribution of impurities and their effect on the thermal history and microstructure of the silicon.
- During experiments, silicon is observed to expand by about 10% as it solidifies, causing cracking and expulsion of worm-like jets of liquid silicon. The mechanical stresses involved during the solidification should be included in the model.
- Investigate whether non-constant thermal properties affect the solution. For example, we expect conductivity, emissivity and heat transfer coefficients to change slightly with temperature.

4. Discussion, Conclusions and Recommendation

Thin Casting

We have created and fitted a COMSOL model to the thermal data, thereby estimating the heat transfer coefficients. With a validated model, it was possible to predict the time taken for the material to completely solidify and the place where the solidification fronts met.

One extremely useful aspect to this problem is the quasi-steady approximation, which is equivalent to the case of small Stefan number. In this limit, we find analytical results for the solidification time and distance which agree well with the full-scale numerical solutions on COMSOL.

Wedge Casting

For the wedge casting problem, we created a COMSOL model and used the thermal data to estimate the heat transfer coefficients, thus obtaining a predictive numerical solution. The simplified *Triangle* model provides analytical results for the solidification time and distances which agree very well with the full-scale COMSOL simulation. The approximation becomes more valid as we decrease the wedge angle.

During the wedge casting experiments, thermal data was also taken from the graphite blocks. We have compared the COMSOL-generated temperature plots (with fitted parameter values) to the thermal data and they do not quite match up. Further work could involve calibration of the to COMSOL model to the graphite temperature measurements.

Fines Penetration

We also considered an initial model for the penetration of liquid silicon into the pre-laid layer of fines which acts as a buffer between the melt and the mould. We were able to find a numerical solution to this initial model which, upon calibration and further analysis, could potentially provide a predictive tool for estimating the necessary depth of fines in order to separate the liquid silicon from the mould.

5. Potential Impact

Elkem are interested in conducting future thin casting and wedge casting experiments. The COMSOL models will provide a useful tool for comparison with future temperature experiments. Furthermore, we have created some easy-to-use Matlab functions which take the analytical results of the quasi-steady approximation and the *Triangle* model to predict the solidification time and distance in both types of experiment. This can act as a useful predictive tool for those conducting the experiments.

Kjetil Hildal, Senior Research Engineer at Elkem, said:

> *Graham collaborated with Elkem personnel on developing a mathematical model for solidification of silicon. The model predicts thermal development in a wedge-shaped mold as a function of cooling time, by considering a 2-D transient heat transfer problem, with phase change, radiation from the free surface, conduction to the solid mold and convection in the liquid silicon. Furthermore, the model has successfully been applied to predict temperature vs. time during solidification of silicon for similar wedge-shaped geometries. Graham's work has given us insight into the silicon solidification process and, particularly, his work on fines penetration has enabled us to interpret the results of our experiments.*