

THE MAIN REASONS TO DEVELOP AN IMPROVED CASTING PROCESS FOR SILICON - NEW REQUIREMENTS FOR WORKING ENVIRONMENT, INCREASED POST TAPHOLE YIELD AND PRODUCT QUALITY

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ABSTRACT

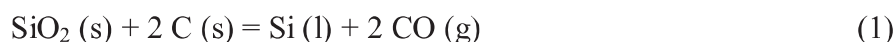
Silicon is produced in an electric arc furnace from raw materials; quartz, coke and coal. Liquid silicon at a temperature above 1450 °C is tapped from the bottom of the furnace into a ladle. After refining, silicon is poured into a mould for solidification. Traditionally this has been a cast iron mould covered in silicon fines or a bed of silicon fines. There are several challenges when pursuing the ideal casting procedure. Silicon deviates from metals like iron and aluminium due to large heat of fusion and the aggressiveness towards other materials. The casting process will affect the product quality and the post taphole yield. Also it may impact the environmental standard and the economy of a silicon plant. The traditional casting procedure does not result in an optimal quality of the final product and it will lead to the generation of fines and dust formation in both the casting and crushing/screening area. New EU standards for the working environment may require new casting technologies.

A full understanding of today's process will enable the evaluation of parameters that needs to be improved in the casting area. This paper discusses an industrial experiment using the traditional casting procedure. Samples have been collected for metallographic and chemical analysis. These are put in connection with the thermal history of the cast. The study shows that there is a significant chemical segregation in the cast. There is also a large variation in the thermal history in the different parts of the casted silicon. This means that the casting process give a variation in the product that may not be favourable. The challenge for a new casting process is to optimize the silicon product consistency and quality with a high yield and to meet the new requirements for the internal working environment.

KEYWORDS: Solidification, metallurgical grade silicon, environment, yield and quality.

1. INTRODUCTION

In the earth's crust silicon is the second most abundant element and is usually found in the form of different silicates. Elemental silicon is produced in a carbothermal reduction between quartz, SiO₂ and carbon. The production takes place in an electric arc furnace. A simplified equation for the production of silicon can be written as [1].



The silicon melt is tapped from the furnace, usually into a ladle, and then poured into a mould for solidification. The quartz and carbon materials used in the production contain impurities and as a consequence the silicon produced will contain other elements than silicon. Metallurgical grade

silicon, MG-Si, is here defined as silicon produced from an electric arc furnace with purity around 99 %. The purity of the material can be enhanced using pure raw materials, keeping a good and stable furnace operation and by refining.

Looking at the production of metallurgical grade silicon as a whole, there has been extensive research activity in the production line from raw material to tapping. Even though much still is unknown this research has improved furnace operation and environmental standards at the silicon plants today. However, the same attention has not been given to post taphole processes such as casting and crushing. A reason for this is that MG-Si is not used as a finished product. - As an alloy element in the aluminium industry MG-Si is remelted. In the production of silicones the quality of the solidified MG-Si is of higher importance. MG-Si is involved in the synthesis of dimethyldichlorosilane, a precursor to silicones. The reaction takes place in a fluidized bed reactor (FBR) where MG-Si powder reacts with methyl chloride in the presence of a catalyst [2]. In this synthesis intermetallic compounds formed during solidification can affect both selectivity and productivity in the reactor. The total production of MG-Si was 1 mill metric tonnes in 2000. The aluminium and the chemical industry consume approximately half of the world wide silicon output each. A smaller, but increasing market share is held by the semi conductor and solar cell marked. The marked share increased from 2 % in 2000 [2] to 10 % in 2010 [3].

The main reasons for a new and improved casting process is to meet new requirements for working environment, increase the post taphole yield and improve the product quality. The quality of the finished product and the post taphole yield will be affected by both the chemical composition out of the furnace, the solidification process and crushing procedure. The main impurity elements in MG-Si are Fe, Al, Ca and Ti and the distribution of the impurity elements will dependent on the solidification process. A common procedure for silicon casting is shown below in figure 1. Several silicon moulds covered in silicon fines/gravel are filled successively. At the silicon plants it is experienced that if the cast is to be removed in one piece it has to be removed from the mould shortly after casting and it is thought to be because silicon changes from a ductile to a brittle material during cooling [4]. The casts are then left to cool in another nearby location before they are moved to the crushing/screening area. Dust generated during these process steps will have an impact on the internal environment of the plant. There are several areas where dust is generated. i.e.: during casting due to poor or a lack of suction in the proximity of the casting area, as seen in figure 1. Dust generation in the handling and transport step from cooling area to crushing facilities.

Dust generation during crushing. The crushing will also generate undesired fines, and the amount will be dependent on both the means of crushing and the mechanical strength of the material. The mechanical properties of a material are affected by the solidification process, which is related to distribution of intermetallic phases and grains size. Thus, the applied technology and procedures for casting and crushing will have an effect on the post taphole yield through the influence on fines generation. This paper discusses an industrial experiment using the traditional casting procedure outlined above. The main focus has been the product quality of the cast and its relation to the cooling rate. The experiments have been used to establish accurate temperature-time models for the solidification process. There is an ongoing study related to the mechanical properties of the material, but this will not be discussed in more detail in this article.

2. MATERIALS AND METHODS

A cast iron mould (2100 x 2100 cm, outer dimensions) was prepared for the experiment: 8 holes were drilled through the cast iron mould walls to fit the thermocouples. To avoid movement of the thermocouples during casting two steel plates were mounted to the bottom of the mould. A Kaowool plate was attached to this and the thermocouples were placed as seen in figure 2. To protect the mould a 15 mm layer of silicon gravel of size 10-15 mm covered the mould. During the

experiment silicon melt was poured from the ladle into the mould, as shown in figure 1. The temperature in the melt/cast was recorded by 6 C- type thermocouples. Two K- type thermocouples recorded the temperature under the layer of silicon gravel and one K-type thermocouple logged the temperature underneath the mould. A DT80 Datataker was used to collect the temperature data in both experiments. After pouring the melt from the ladle into the mould the cast was left to cool to ambient temperature.



Figure 1: Pouring of silicon from the ladle to the mould. The casting process may create smoke and dust from silicon surfaces at temperature above or near the melting point

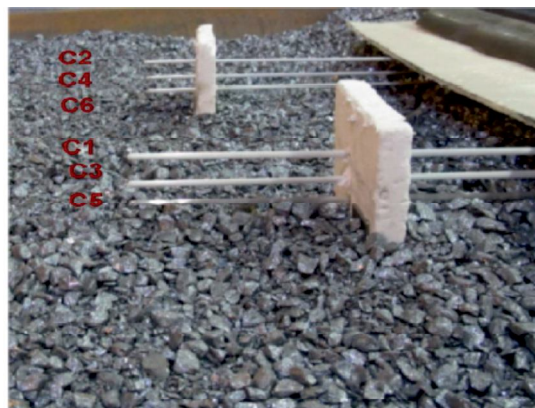


Figure 2: Placement of C-type thermocouples

Vertical sections of the cast, to be used for chemical and metallographic analysis, were extracted in the proximity (sample B and D) and away (sample G) from the thermocouples. These were cut in vertical from the top surface to the bottom of the cast. The chemical composition was determined with a Panalytical – Axios XRF, using the standard program for that specific silicon quality. The instrument had been tested with a reference material.

For the metallographic analysis the samples were mechanically ground and polished down to 1 μm . Investigation of the microstructure was performed by a LV-Fe-SEM (Zeiss Supra 55 VP). An electron probe micro-analyzer, EPMA, (JEOL JXA-8500F) was used to determine the composition of the intermetallic phases observed. Areas for analysis of intermetallic phases were selected 1 cm from the top of the sample, the middle of the sample and 1 cm from the bottom of the sample. To reveal the grain structure the samples were etched in a stirred solution of 20 g/ml NaOH at 70-80 $^{\circ}\text{C}$ for 5 minutes. The heat transport during solidification has also been modelled using the heat transport module of COMSOL Multiphysics 4.3a [5].

2. RESULTS

Figure 3 plots the surface temperature after 1250 seconds in a 2D section. The temperature in silicon is shown in the upper region, silicon gravel in the middle and the cast iron mould in the lower region. In figure 4 experimental and modelled values of temperature as a function of time for the solidification experiment are plotted.

Figure 5 give the mean chemical analysis of two vertical samples, sample B1 and B2, cut in the proximity of thermocouples C1, C3 and C5. The height of sample B1 was 10.2 cm while the height of sample two was 11.2. Each vertical sample was divided into five pieces from top of the cast to the bottom. Thermocouples C1 was close to the 0-2.5 cm sample, C2 close to the 2.5-5 cm sample and C5 in the proximity to the 7.5-10 cm sample.

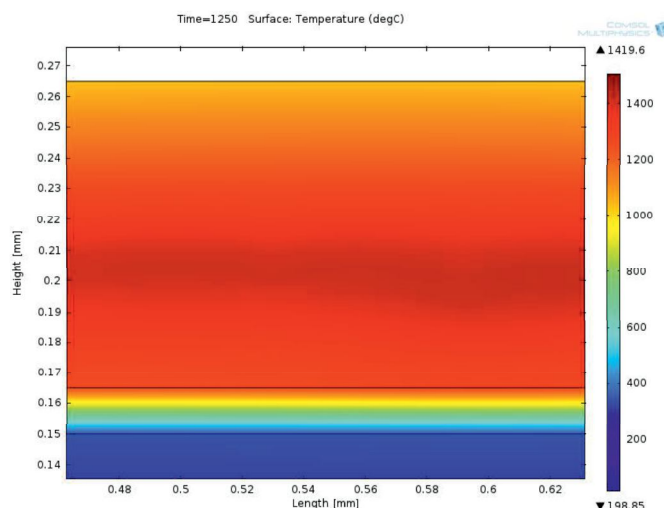


Figure 3: Surface plot after 1250 seconds illustrating the temperature in the cast, gravel and silicon

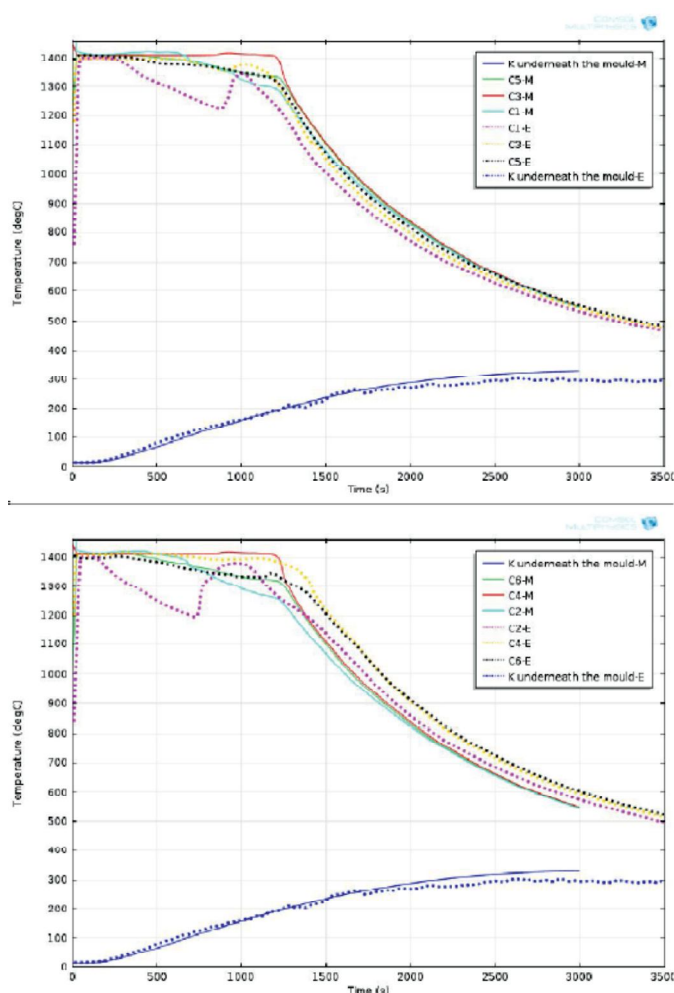


Figure 4: Temperature vs. time curve for thermocouple C1, C3 and C5 (located 23.4 mm, 20.6 and 18.5 mm from mould bottom) and temperature vs. time curve for thermocouple C2, C4 and C6 located 23 mm, 20.4 and 18.3 mm from mould bottom). E is the experimental temperature and M the modeled temperature. See figure 2 for placement of the thermocouples

The micrographs in figure 6 illustrate the microstructure at different locations in sample B in the proximity of thermocouple C1, C2 and C5.

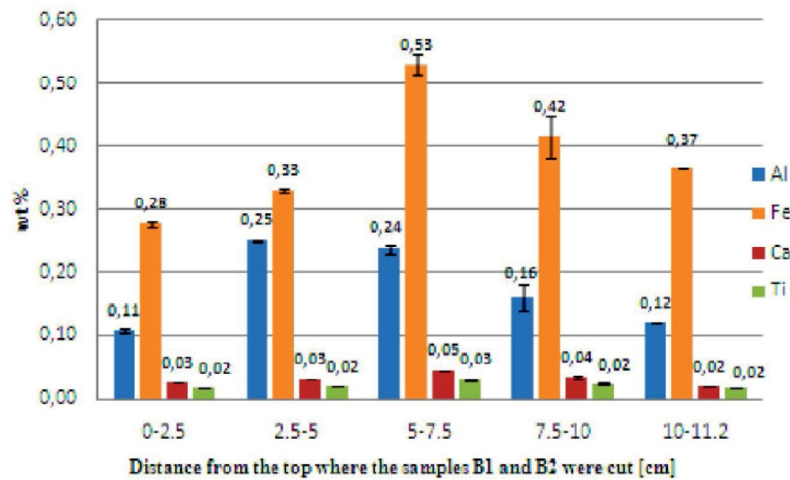


Figure 5: Chemical analysis of samples cut from top to bottom of the cast. The error bars give the standard deviation of mean

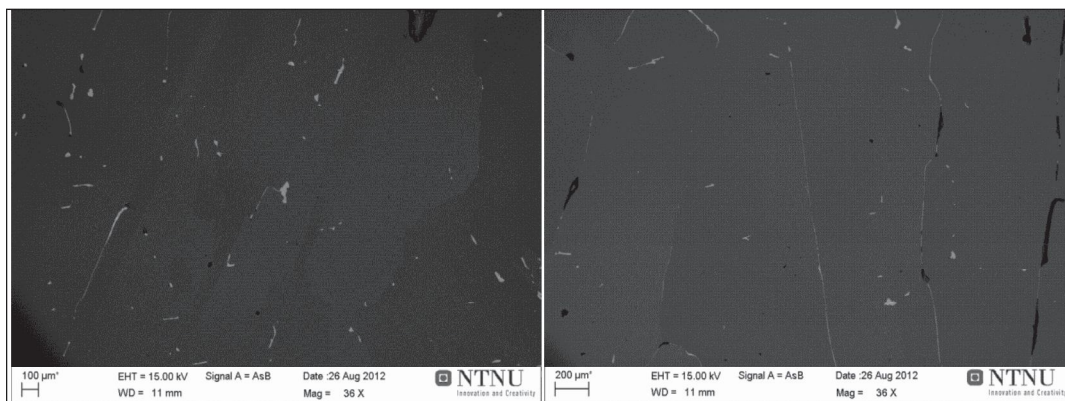


Figure 6: Micrographs of sample B, 0.9 cm and 4.1 cm from top. Magnification 36X

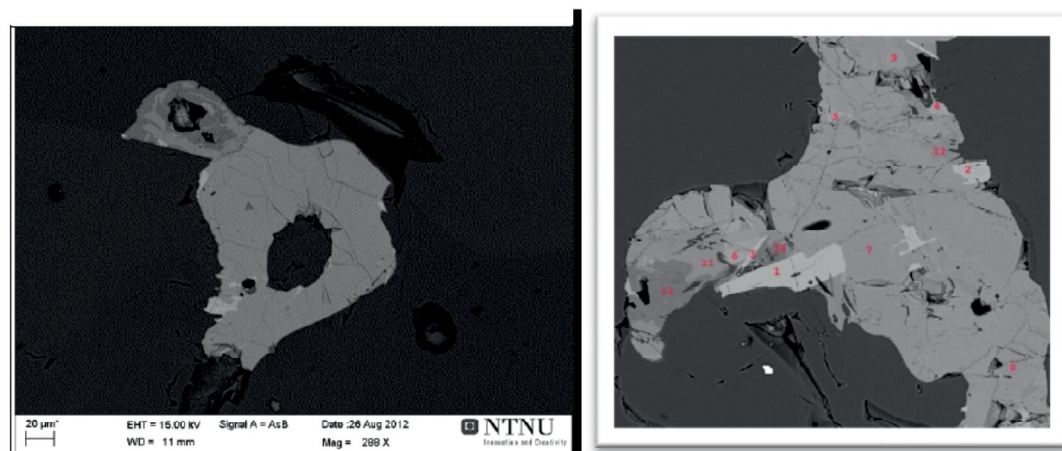


Figure 7: Micrographs 2.6 cm and 10 cm from top. Magnification 182 X and 300X respectively

3. DISCUSSION

A 2D COMSOL model simulating the solidification was built. The latent heat released during solidification is accounted for in the expression for the heat capacity and it is released in the temperature interval between 1412°C and 1402°C. The initial temperature is set to be 1427°C. Values from the review article Mills [6] are used for the thermal conductivity and heat capacity. These are properties that changes with temperature and this is expressed as a function in the model. The same article lists the emissivity for solid and liquid pure silicon as a function of wavelength at the melting point. However the surface of pure solid silicon is highly reflective compared to the MG-Si surface which often is covered with an oxide layer. It is therefore assumed that the emissivity of solid MG-Si will be higher. The emissivity is set to 0.75 which is the same value as used for FeSi in the work by Tveit [7]. As an approximation the emissivity is kept constant for the solid temperature range even though this also is a property that changes with temperature. In the experimental curves the temperature increase for element C1 and C2 after 12-14 minutes. During this time period it was observed that liquid silicon erupted from the surface of the cast. This is due to the volume expansion during solidification which pushes the remaining melt upwards.

The experimental data from the casting are compared to the COSMOL model in figure 4. The experimental temperature curves and the model are quite consistent for the middle and the lower thermocouples. For the top thermocouples, C1 and C2 the temperature in the model does not decrease as rapidly as the experimental values. There might be several reasons for this -The model does not account for the filling of the mould. In the model time zero is set to be when the mould is already filled. This means that a uniform temperature in the melt is assumed at t_0 . There is a temperature difference between the melt and mould/gravel layer of more than 1400 °C so in the real case the solidification will have started from the bottom of the cast before the mould is filled which means there will be temperature gradients in the melt/cast.

The picture in figure 1 was taken during the experiment and a large amount of dust is seen in the picture. The COMSOL model calculated the top surface to solidify during the first 15 seconds. Observations from several castings confirm the dusting is strongly reduced or stops in a range of 15 seconds after the mould has been filled, which is consistent with the solidification of the surface. This means that a good suction is important during the filling the mould and straight after [8] in order to collect the dust.

Chemical analysis of samples cut in various distances from the top surface revealed that there is a segregation of the main impurity elements in the cast, as shown in figure 5. The amount of Al, Fe, Ca and Ti is at a minimum in the top sample, which is from 0-2.5 cm from the top. The maximum content of these elements is found in the sample from 5-7.5 cm from the top, but the sample cut 7.5 to 10 cm is also quite high. This can be explained by the solidification pattern. Solidification will start both from the top and the bottom of the cast and two solidification fronts evolve. Most impurity elements will have lower solubility in solid silicon then in liquid silicon[9]. As the solidification proceeds the melt is enriched in impurity elements. Solid silicon has a lower density then liquid silicon. In the case of solidification from the top surface this leads to low density silicon floating to the top, while higher density liquid enriched in impurity elements will sink. Solidification from the bottom will not give the same macrosegregation as expected with solidification from the top. Here if grains start to float they will meet the liquid melt with a higher temperature and therefore melt back. From the COMSOL model, melt in the area below thermocouple C3 will solidify last, see figure 3. This corresponds to a height lower than 20.6 mm in the surface plot.

Since the melt gradually increase in impurity elements there will be an accumulation of them in the area solidifying last. Both the temperature curves and the chemical analysis states that the two fronts met in the area from 5-7.5 cm. In this area there is also a porous layer that is observed

throughout the cast. Since gases like hydrogen and oxygen have a low solubility in solid silicon the gas will move with the solidifying front and the porosity is mainly seen in the area where the fronts meet. In the study of a 75 % FeSi alloy it was concluded that the porosity came from dissolved hydrogen in the melt [7]. In another publication the porosity is explained by gases bubbles trapped during refining [10]. In an experiment performed by the authors silicon was casted on a copper plate. No refining was done prior to the casting, but porosity was still present in the cast. This indicated that the pores can come from other processes than the refining.

A sample cut from top to bottom was etched to reveal the grain structure. In the lower part of the cast small grains growing in all directions were observed. The initial temperature of the mould was only 15 °C and this “shock cooling” will allow many grains to surpass the nucleation barrier. When the rate of heat removal slows down the grains that grow parallel and opposite to the heat flow outgrows the other grains, and longer vertical grains are observed. In the top part of the sample where the cooling rate also was higher compared to the interior area of the cast, the grains are also smaller.

In figure 6 and 7 a selection of micrographs of the sample is shown. Several samples were imaged with a 36x magnification from the top to the bottom of the cast. A backscatter detector was used to image the micrographs. This gives a contrast based on mean atomic number. The higher the mean atomic number the darker the phase will appear in the micrograph. This revealed, as seen in figure 6, an inhomogeneous distribution of the intermetallic phases dependent on the location in the cast. That is- dependent on the cooling rate during casting. At the start of solidification no clear grain boundaries are seen. The intermetallic phases appear as inclusions. The solidification proceeds to rapid for the impurity elements to segregate to the grain boundary. When the cooling rate decreases the intermetallic phases start to accumulate in the grain boundaries. Earlier work with a 92 wt % silicon alloy showed the same trend inside the cast, but when the cooling rate was reduced 5 times, fewer, but larger intermetallic phases were observed [11]. It must however be mentioned that how the intermetallic phases appear also depend on the way the sample is cut. It is not known if the inclusions are connected in some way below the surface that is imaged.

A selection of areas containing intermetallic phases was analyzed by the EPMA. For sample B, 156 point analyses were performed, and for sample G, 67 points were analyzed. One such area is shown in figure 7. This showed that the areas analyzed consisted of a few distinct intermetallic phases, mainly $\text{Al}_6\text{CaFe}_4\text{Si}_8$, $(\text{Al})\text{FeSi}_{2.4}$ (high temperature β -Leboite), Al_3FeSi_2 , FeSi_2Ti and $\text{Al}_8\text{Fe}_5\text{Si}_7$. Qualitatively the quaternary calcium phase seem to dominate, with the $(\text{Al})\text{FeSi}_{2.4}$ second. The bulk analysis in the ladle prior to casting was: Ca = 0.06 wt %, Al = 0.26 wt %, Fe = 0.42 wt % and Ti = 0.03 wt %. A system close to this analyzes is described in [12]. Here it is stated that $\text{Al}_6\text{CaFe}_4\text{Si}_8$ is the only calcium containing phase that will solidify in this compositional range. Of the 227 points analyzed another Ca phase, Al_2CaSi_2 , was observed only once. Al_2CaSi_2 had a size of only $60\mu\text{m}^2$ in the 2D surface inspected while the other Ca phase usually had a surface area several hundred times larger. Other studies have also reported the above intermetallic phases to be found in metallurgical grade silicon [10, 13, 14]. Even though only a few distinct phases are observed in the cast, the amount of each varies from the area inspected. Mapping of three areas showed that all intermetallic phases observed contained both iron and aluminium to a varying extent which is consistent with the point analysis. For the cooling rate used in most industrial castings the given system does not reach equilibrium. The amount of a given intermetallic phase will depend on the chemical composition, but also on the cooling rate. The FeSi phase can be seen as an example of this. From the phase diagram the high temperature $\text{FeSi}_{2.4}$, β -Leboite, should transform to FeSi_2 (α -Leboite), at 955 °C [7]. FeSi_2 is the thermodynamically stable phase at room temperature. With the cooling used in the experiment this transformation between α and β does not occur and the meta stable $\text{FeSi}_{2.4}$ is found instead. In all the areas inspected it is seen that the intermetallic phases contain cracks that usually don't extent into the silicon matrix. The cracks are assumed to be a result

of stresses related to the expansion of silicon and the contraction of the intermetallic phases during solidification. The cracks are assumed to reduce the mechanical strength of the intermetallic phases. The mechanical strength of the material will be tested in an ongoing study. When crushing the silicon to a fine powder around of 20-300 μm [2], as used in the dimethyldichlorosilane production, it is assumed that some particles are pure silicon, some contain silicon and intermetallic phases and some particles will contain only intermetallic phases. As described in the introduction parameters like reactivity and selectivity of the FBR for dimethyldichlorosilane synthesis will be affected by the intermetallic phases. The microstructure described above can contribute to variations in these parameters.

4. CONCLUDING REMARKS

The COMSOL model is able to simulate the solidification and it is consistent with observations in grain structure and distribution of phases. The intermetallic phases were distributed inhomogeneously in the cast varying from small and large scale inclusions to finely divided phases in the silicon grain boundaries. Qualitatively the $\text{Al}_6\text{CaFe}_4\text{Si}_8$ phases appeared to dominate, followed by the $(\text{Al})\text{FeSi}_{2,4}$, but the ratio between the phases depended on the area inspected. The grain size also varied from the bottom, middle and top of the cast. If consistency is a measure of quality and not only bulk properties, the traditional casting procedure is not able to deliver a high quality product. If only the bulk chemical analysis is important, the method can deliver a quality according to today's specifications from the aluminium and chemical costumer. Both from the model and experimental observations it was seen that dust was generated during filling of the mould until the surface solidified. This means that a good suction in the first period of the casting would improve the internal environment in the casting area. The results presented above will be utilized to improve the HES and the technical standard of the casting process for MG-Si.

5. ACKNOWLEDGMENT

The authors would like to thank the Research Council of Norway and Elkem Silicon Materials for their financial support. A special thanks to those involved during the experiments and with the post treatment of samples at Elkem Silicon Materials, SINTEF Building and Infrastructure, SINTEF Materials and Chemistry and the Department of Material Science and Engineering at NTNU.

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