

Oxidation of Liquid Silicon – Reaction Mechanisms and Kinetics

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ABSTRACT

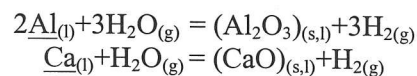
When liquid silicon reacts with water, an oxide layer forms on the surface of the melt. The composition and structure of this oxide layer is determined by the initial composition of the melt, the temperature and the flow conditions at the surface. We have used two different techniques to oxidise molten silicon, with varying content of impurities (Al and Ca). The results show that the initial oxidation product is gaseous SiO. This gas will not necessarily deposit on the surface of the silicon melt, but may be carried away depending on the local flow conditions. Impurities in the melt will result in a slag film on the surface of the melt. This slag consists of a mixture of SiO₂, Al₂O₃ and CaO. Depending on the composition and temperature, this slag mixture may be solid or liquid. As a consequence of this slag formation, more hydrogen is produced, which has a desirable effect as to prevent large-scale steam explosions.

1. INTRODUCTION

One of the operational steps in commercial production of Si and FeSi today, is the water granulation process. The main principle of this process is to break up a continuous flow of melt into appropriate sized drops and quench these to granules in a water tank. However, this mixture of molten metal and water are in steam explosion theory known as the premixing stage, a necessary condition to obtain a large-scale steam explosion¹.

A laboratory study has been initiated to investigate how to decrease the possibility of a steam explosion during granulation of Si and FeSi. It is known from industrial experience that the composition of the melt is a very decisive factor². This has also been verified experimentally³. They released single drops of silicon-rich alloys into a water tank to investigate the effect of impurities. In agreement with industrial experience, they found that small additions (<0.05%) of Al and Ca practically eliminated the possibility of violent melt-water interactions.

We believe that additions of Al and Ca prohibit a steam explosion in two ways. Dissolved Al and Ca will react very easily with water vapour at this temperature (over 1400 °C), i.e. the equilibria



will be displaced to the right. The hydrogen mixes with vapour in the film surrounding the molten drop, making it more stable against pressure disturbances, as hydrogen is a non-condensable gas under these conditions. The other way Al and Ca may prohibit a steam explosion, is the film of slag that forms on the melt-vapour interface, which consists of a mixture of SiO₂, Al₂O₃ and CaO, depending on the initial composition of the melt. This film will in general have properties that differ from those of molten

silicon, some of which may have a protecting effect against fragmentation.

In this work, we have oxidised molten silicon samples in a spray of water. Four different alloy compositions have been studied at two different melt temperatures. The treated samples have then been analysed with an X-ray microprobe, where we can get good images of the oxide film that forms on the metal-vapour interface. Finally, the same alloy compositions have been granulated in water and analysed the same way. We can then compare the results obtained in our experimental apparatus with the granulation experiments described by Nelson³.

2. EXPERIMENTAL

2.1 APPARATUS

Our apparatus allows a rapid heating to a high temperature (1400-1600 °C) and a subsequent rapid cooling. We also need to inject a jet of water when the melt has reached the desired temperature in order to oxidize the melt surface.

A schematic cross-section of the apparatus is shown in figure 1. A graphite susceptor, with the shape of an open cylinder, is located inside a strong, fluctuating magnetic field. Inside the susceptor, we place a small crucible (12 mm high, wall thickness 1.5 mm, radius 12 mm). These crucibles are for the present work made of glassy carbon, but alumina has also been used⁴. Under the base of the graphite susceptor an S-type thermocouple measures the temperature during the experiment. This thermocouple is calibrated to compensate for the temperature drop between the interior of the crucible and the base of the graphite susceptor. These vital parts are all located inside a transparent silica tube. The tube has double walls, which allow water cooling of the walls. The interior of the tube is evacuated prior to the experiment and flushed with inert gas at all time thereafter. During the heating and oxidizing stage, argon gas is used, but after the

sample is oxidized, helium is used to achieve rapid cooling.

When the melt is oxidized, a syringe is inserted from above. Inside the apparatus, the pressure is slightly higher than atmospheric pressure to avoid any oxygen leakage into the apparatus. The syringe is taken down to the top of the crucible and 0.2 ml of water is inserted during a three-seconds period of time.

The thermocouple is connected to a reader (Hewlett-Packard 34970A) to obtain a continuous temperature reading during the experiment.

A high-frequency generator (Philips PH 1012) powers the solenoid, which consists of four loops of water-cooled tubes of Cu. The tubes have an outside diameter of 6 mm.

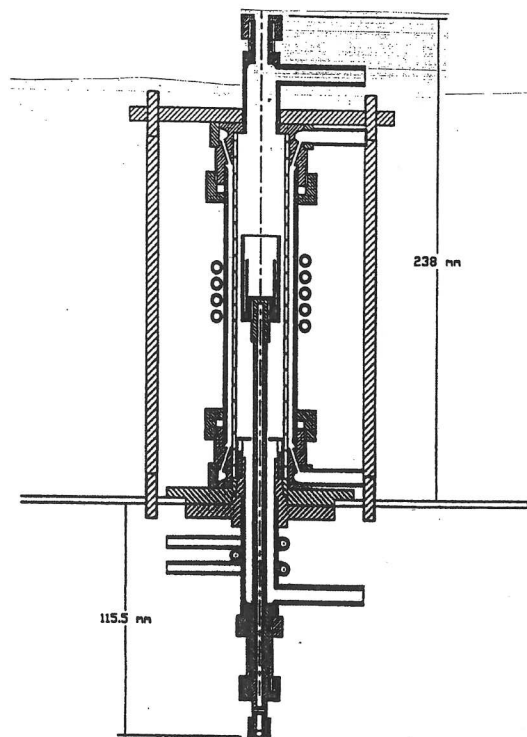


Figure 1 - Schematic cross-section of the apparatus.

2.2 ALLOY COMPOSITIONS

We used four different compositions for our experiments. These were pure Si, Si with 0.4% Al, Si with 0.04% Ca and finally Si with 0.4% Al and 0.04 % Ca. These four compositions were oxidized at two melt temperatures, 1450 and 1550 °C. The concentration of other elements is negligible (totals less than 0.01%) for all practical purposes.

2.3 MICROPROBE

We use a microprobe (JEOL Superprobe JKA-8900M) to analyze the surface of the oxidized silicon samples. The crucibles are filled with a cold mounting epoxy resin (EPO-Fix). This is a two-component resin that penetrates voids in the sample easily. Then, the crucible is cast into another resin, Demotec-20, before we make a cut through the encapsulated crucible. After polishing, the sample is ready for the microprobe. The images given by the microprobe shows concentrations of the important elements, which in this context are Si, O, Al and Ca. Along with the element concentration profiles, a scale giving the concentration (in weight %) for each color is located next to the profiles. Note that different elements have different scales to improve the contrast in the images.

3. RESULTS

3.1 VISUAL OBSERVATIONS

A video camera (8 mm Canon UC-X30) was used to record the experiments. The experimental layout did not allow us to observe the melt surface directly, but any smoke or gaseous products can be seen as they rise inside the apparatus with the inert gas. In general, the behavior of different compositions at different melt temperatures did not seem to change much. Usually, a stream of smoke was observed just before the water jet was sprayed onto the melt surface, due to some evaporation of water from the lower tip of the syringe. Upon water injection, water drops were thrown out of the crucible onto the transparent walls, with some smoke production.

3.2 WEIGHT CHANGES

The crucible is weighed prior and after the experiment to detect weight changes during the experiment. These weight changes originate from reactions inside the hot zone. A number of reactions can take place, some of which increases the weight, while others decrease the weight. Reactions between the water vapor and the crucible tend to decrease the weight, as carbon is lost as CO or CO₂-gas. Also, if a considerable amount of SiO-gas is allowed to escape the hot zone, this gas may condense away from the crucible, thereby reducing the mass of the sample. If SiO-gas condenses on the metal surface or the crucible, this will increase the weight of the sample. In general, small weight increments were detected, of the order 0.01 grams. In two cases, a decrease in weight took place. One of these was negligible, while the other was as big as 0.07 gram, which corresponds to 3% of the total mass (crucible and metal). We can not rule out the possibility of an experimental error in the last case. The water injection is 0.2 ml, which is approximately 0.18 gram oxygen. So comparing with the weight changes, only 10% (at most) of the oxygen can be found on or inside the crucible after the experiment. This is expected, as most of the water is thrown out of the crucible and onto the transparent silica walls.

3.3 OXIDISED SILICON SURFACES

3.3.1 PURE SILICON

The surface of the specimen is dominated by a white, patchy SiO₂-layer. The typical thickness is 100-120 µm, but at several locations, this thickness drops to a few µm. The oxide layer is very porous, which can easily be seen from microprobe analysis of the specimen. This layer also contains several spherical particles, which are rich on Si, typically around 80-90 wt%. The Si-spheres form a band along the silicon matrix, approximately 50 µm from the matrix.

Another interesting feature is that a layer of SiO₂ is covering most of the crucible wall. This is most likely due to a condensation of

SiO-gas. Particles of Si inside this oxide layer confirm this hypothesis. Compared to the oxide layer on the metal surface, the oxide on the wall is thinner, around 20-40 μm .

On the effect of increased melt temperature prior to oxidation, the most striking difference is the change in color of the oxide layer, from white to brown. Besides from that, the SiO_2 -layer does not appear to be any different from the lower melt temperature. A similar layer is found on the crucible walls, although it appears less porous, with more stable concentrations of Si and O. Clusters of Si-rich particles have formed close to the wall. It is possible that these clusters contain some C, in the form of SiC-particles.

The thickness of the SiO_2 -layer is larger for the sample oxidized at the highest melt temperature. The oxide layer of pure silicon oxidized at 1550 $^{\circ}\text{C}$ reaches a thickness of 300 μm , while a sample oxidized at 1450 $^{\circ}\text{C}$ has a maximum thickness of 130 μm . The density of the oxide layers does not change noticeably when the melt temperature is increased. In figure 2, the composition of the oxide layers is plotted against the distance from the oxide surface. The concentration of SiO_2 is less than 100% for both of the samples, indicating that there is some porosity in the oxide. We also note that the concentration increases well above 100 % some places. This is an effect of small spheres of Si inside the layer of SiO_2 . The microprobe uses SiO_2 as standard, and if the probe detects an area of pure silicon, it will give us values that are too high. Figure 3 shows the element analysis of the surface of silicon oxidized at 1450 $^{\circ}\text{C}$. As we can see from the picture, there exist several spheres of pure silicon in the oxide layer, and these will give us wrong estimates on the concentration of SiO_2 .

Another effect of elevated oxidation temperature is a somewhat rougher interface between the silicon matrix and the oxide layer, this will be explained later.

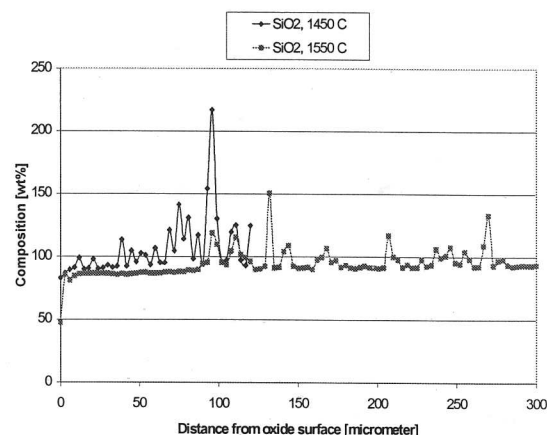


Figure 2 - Oxide layer composition plotted as a function of the distance from the surface.

Figure 3 includes an image of the same alloy composition, granulated in water. The temperature of the melt was at its liquidus temperature, approximately 1412 $^{\circ}\text{C}$, when it was released into the water. Note that the two magnifications differ by a factor of two. The most striking difference between these two images is the absence of the porous layer of SiO_2 on the drop of melt granulated in water (lower image). The surface is clean, with no traces of any oxide. However, there is evidence in the form of collected hydrogen that there has been a chemical reaction between silicon and water. Based on the lack of oxygen-containing compounds on the surface of the granule, we conclude that the oxidation products formed in the reaction between water vapour and silicon have been gaseous, presumably SiO . The gaseous products have been efficiently washed away from the surface of the drop, due to turbulent flow in the gas mixture (water vapour, hydrogen, SiO) around the granule. In these experiments, one can see that small bubbles are regularly released from the gas film surrounding the drop of melt. These bubbles will transport silicon oxide away from the surface of the drop.

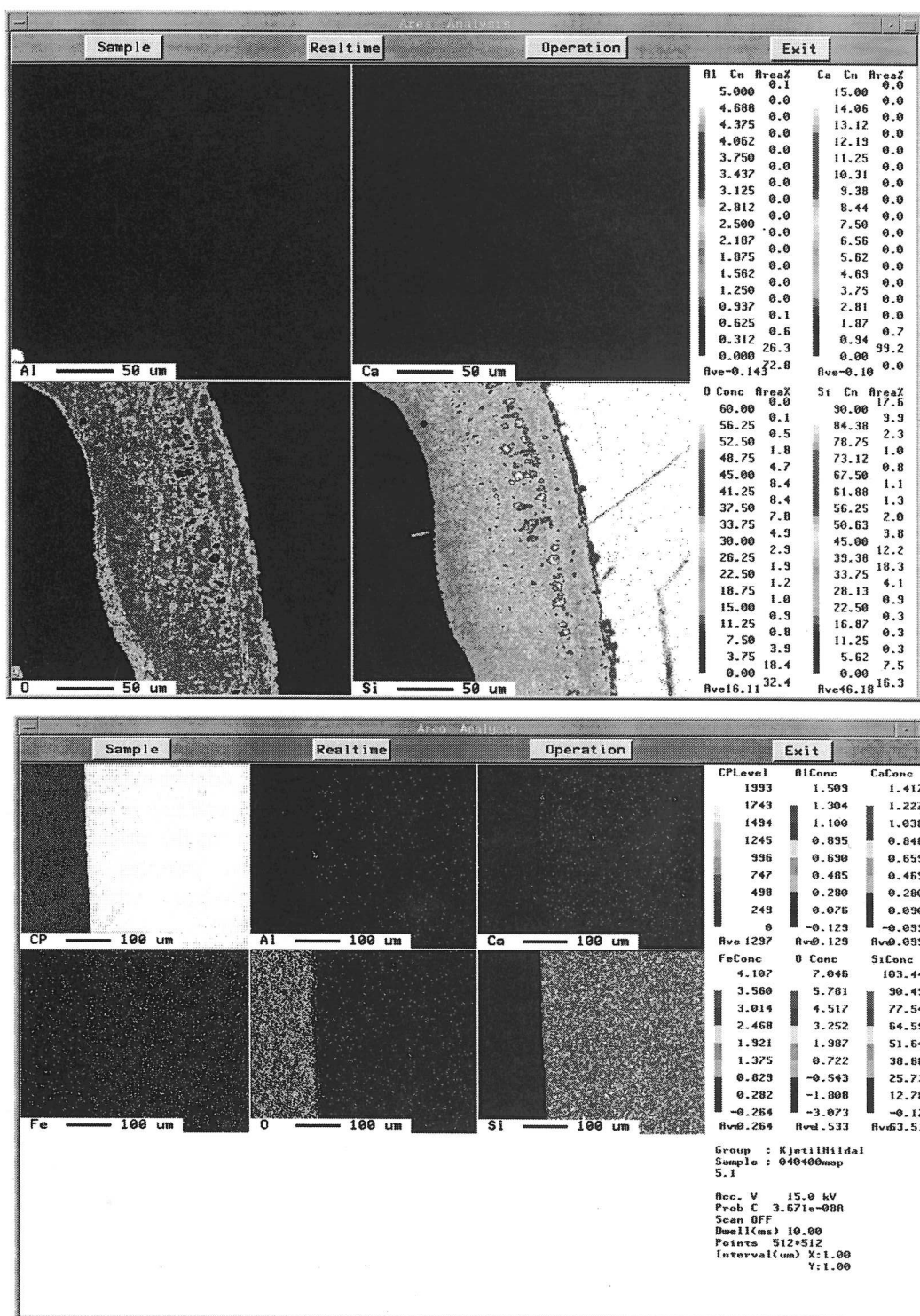


Figure 3 – Microprobe images of the surface of non-alloyed, oxidized silicon. The upper picture is taken from a sample oxidized with water at a melt temperature of 1450 °C, using the method described earlier in this paper. The lower image is taken from a sample at liquidus temperature (~1412 °C), granulated in water using the method described by Nelson³⁾.

3.3.2 SILICON WITH 0.5 % Al

The specimen containing Al appear similar to the ones without. A white, patchy oxide layer is covering the entire metal surface and most of the interior of the crucible. At the lower melt temperature, the thickness of the oxide is typically 35-55 μm . A layer of mixed oxides of Al_2O_3 and SiO_2 is deposited as a thin film along the interface between the matrix of silicon and a porous layer containing only SiO_2 . This interface appears to be denser than in the specimen not containing Al, as already described.

The oxide extends up the crucible walls, but here only very small amounts of Al are present. Instead, the concentration of Si is very high, and microprobe results indicate that some SiC is deposited along the walls, together with pure Si. Away from the wall/oxide interface, the oxygen concentration increases and we find the usual, porous SiO_2 -layer. Traces of Al can be found along the interface between pure Si and the oxide layer.

The effect of increased melt temperature seems to be an increase in the thickness of the oxide layer. Basically, the thickness of the area containing Al is the same, but there is more SiO_2 present further out, in the usual porous configuration. The oxide layer is rather patchy, with a maximum thickness of approximately 150 μm . Some Si-particles can be found inside the oxide layer. This was also found, but to a somewhat higher extent, in the pure specimen. There seems to be no appreciable differences in the oxide on the crucible walls for the two different melt temperatures involved.

For the granulated samples, a very thin film ($\sim 5\text{-}10\ \mu\text{m}$) of slag was found on the surface of the solidified drop. The composition of this slag was typically 60% SiO_2 and 40% Al_2O_3 , with no detectable porosity. Similar as for the pure silicon drops granulated in water, no porous SiO_2 was found on the outside of the slag. The slag was found only on a very limited part of the drop surface. Ap-

proximately 80 % of the surface contained no oxide at all. Again, we believe the reason for the lack of SiO_2 relates to the oxidation mechanism. Gaseous SiO , which forms initially, is carried away from the surface due to the flow field around the drop. This may also influence on the oxidation of Al, as the results clearly indicate much thinner, and mostly absent films of Al_2O_3 on the granulated samples. For the samples oxidized with the apparatus described earlier, the oxide film contains a thicker mixture of $\text{Al}_2\text{O}_3/\text{SiO}_2$ as well as the porous layer of SiO_2 outside this mixture.

3.3.3 SILICON WITH 0.04 % Ca

Earlier results have shown that even very small additions of Ca to the molten silicon have a strong influence on the composition of the oxide that forms upon water injection. This was also found to be the case this time. However, the melt apparently had a higher concentration of Al than we aimed for. This was seen from microprobe pictures, where a thin film of Al_2O_3 and CaO cover the surface, together with the expected SiO_2 . This indicates that some contamination of the samples had occurred, and this is most likely to have happened during the preparation of the rods, which these samples are taken from. A chemical analysis, which shows 0.06 % Al, confirms this.

The low-temperature melt has a patchy, white oxide on the surface of the metal and on the crucible walls. The layer is distributed as a square-wave, with a high degree of regularity. The thickness is about 80 μm , but there are areas between the "squares" with no detectable oxide at all. The length of these squares is between 150 and 400 μm . Separation distances are of the order 100 μm .

The oxide layer has certain characteristics. Close to the silicon-matrix, this layer consists of a mixture of SiO_2 , Al_2O_3 and CaO. The thickness of this oxide film is of the order of 5 μm . This is seen from figure 4, where the composition of the oxide is shown

as function of the distance from the outer surface for the two different melt temperatures. We see that the most striking difference is the concentration of SiO_2 in the outer oxide layer. For the high temperature melt, the concentration of SiO_2 is stable around 85 %, but for the low temperature melt, the concentration is only 30 % for a major part of the oxide layer before it increases as we move inwards against the silicon matrix. Concentrations of Al_2O_3 are not shown in figure 4, as they are low, of the order of 2% in the slag mixture at the interface towards the silicon matrix, and zero further out.

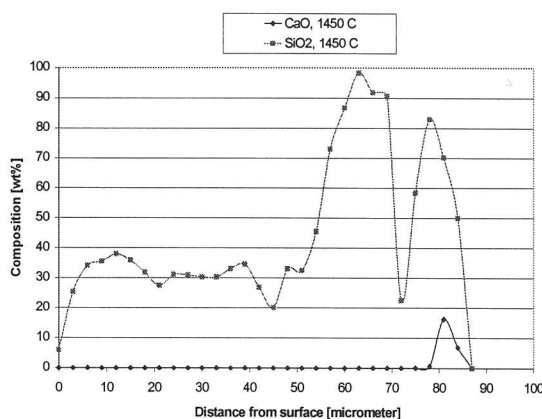


Figure 4a – Oxide layer composition plotted as function of the distance from the surface. (Increasing distance means approaching the silicon matrix.) Melt oxidized at 1450 °C.

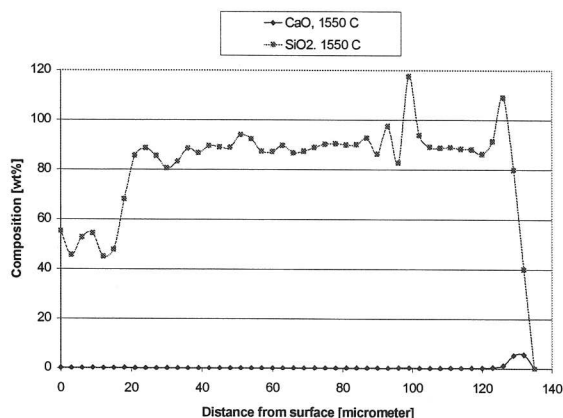


Figure 4b – Same as for 4a, but the sample was oxidized at 1550 °C.

Some oxide has been deposited on the crucible walls. No signs of either Al or Ca can

be found, but high concentrations of Si and O. It appears that some melt has climbed up along the wall, giving pure Si along the graphite wall, with an outer layer of SiO_2 . However, further up on the wall, only SiO_2 can be found, indicating that a condensation of SiO -gas has taken place. From the microprobe pictures available, no spheres of silicon can be detected.

When we compared these results to microprobe investigations of similar alloys granulated in water, we found that there were differences of the same kind as for the other compositions. In general, the surface of the granules did not contain any oxides. On a very limited (~10 %) part of the surface, we found a thin film of slag. The thickness of this slag film was of the order 1 μm . This made it difficult to obtain good quantitative analysis of the oxide. However, the oxide was very low on CaO, an upper estimate is 5 %. Traces (max 3 %) of Al_2O_3 were also found in this slag film, together with SiO_2 . Apparently, the lack of SiO_2 -formation on the surface of the drop affects the formation of CaO.

3.3.4 SILICON WITH 0.4 % Al AND 0.04 % Ca

The effect of alloying the melt with both Al and Ca is the formation of a firm layer of mixed oxides between the metal matrix and the outer layer of porous silica. This is seen from the concentration profiles of the oxide layer in figure 5 and the micrographs showing the results of elemental mapping in figure 6. As observed for the previous samples, the silica layer, which varies in thickness, is most porous for the samples at the lowest temperature. Layers of pure silica are also in this case deposited on the crucible walls, but there are no silicon spots seen in any of these layers, indicating that the deposited SiO has been fully oxidized.

The mixed oxide layer, which covers the entire surface of the metal, has the appearance of a mineralized substance consisting of small grains that differs in composition, but the shape of the interface towards the

metal matrix reveals that this layer must have been in a molten state when formed. According to the chemical analysis given in figure 5a, the mixed oxide layer consists in average of 15 % CaO, 35 % Al_2O_3 and 50 % SiO_2 , and this gives a liquidus temperature of about 1500 °C. It is therefore not unrealistic, even with an initial metal temperature of 1450 °C, that a liquid slag has been formed at the interface in this case. The irregularity of the slag/metal interface and the presence of silicon droplets in the slag phase as seen from figure 6 is typical for a situation where reactants, due to chemical reactions between two liquids, are transferred across the interface at high rates. The interfacial tension may then drop to zero, interfacial turbulence and instabilities are created which may lead to spontaneous emulsification (Turkdogan⁵) as pictured in figure 6. Similar tendencies was also noticed for the Ca-alloyed sample that unintentionally contained 0.06 % Al.

The lower image of figure 6 show the elemental mappings of the oxide layer on a granulated alloy with the same composition as the oxidized sample shown in the upper set of images. The most striking difference between the two, is also in this case the absence of the porous silica layer of the granulated sample, but the mixed oxide layer remains and has the same appearance and chemical composition as the corresponding layer for the oxidized sample.

We also note that the interfaces between the silicon matrix and the oxide mixture layer appear different on the two images shown in figure 6. The granulated drop has a rather smooth, well-defined interface. On the other hand, the water-sprayed sample has a non-uniform interface between matrix and oxide mixture. One explanation for this may be the interfacial turbulence, as described earlier.

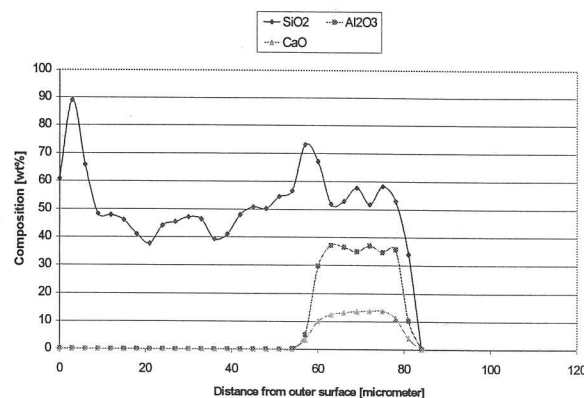


Figure 5a - Oxide layer composition plotted as a function of the distance from the surface. Melt oxidized at 1450 °C.

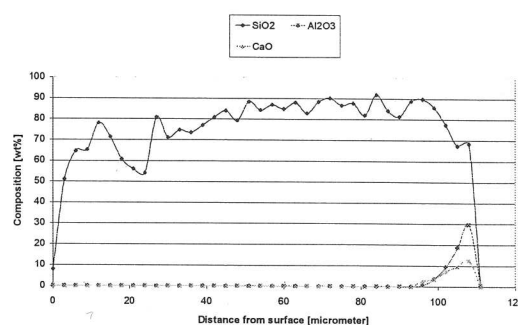


Figure 5b - Oxide layer composition plotted as a function of the distance from the surface. Melt oxidized at 1550 °C.

From figure 5, we clearly see the difference in the density of the porous silica layer between samples oxidized at different temperatures. There is no change in composition of the mixed oxide layer. It appears that the thickness of the mixed oxide layer is larger in figure 5a, but this is an effect of where we choose to analyze, as thickness variations exist on all of the samples. In overall, no change in thickness of the mixed layer could be detected.

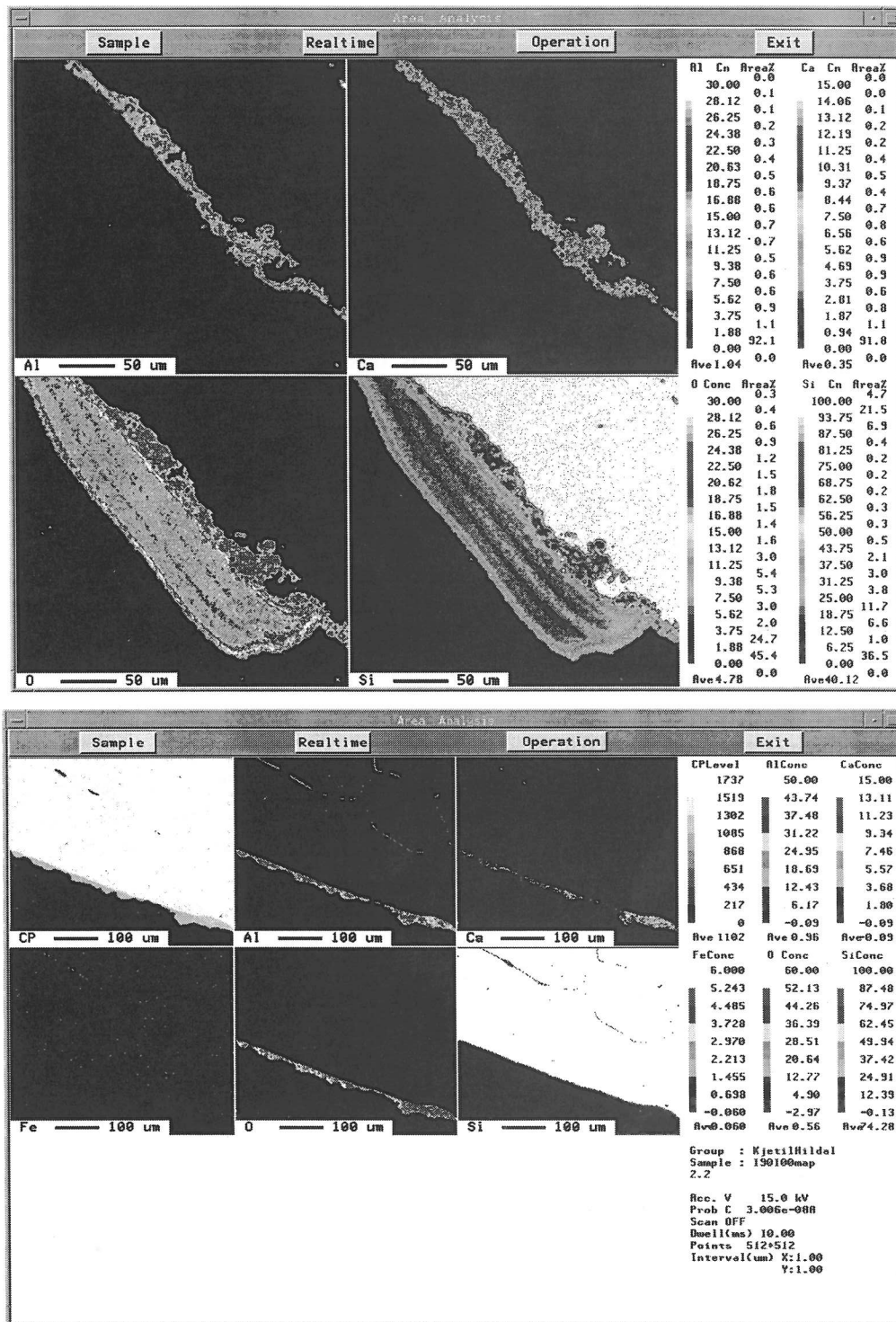
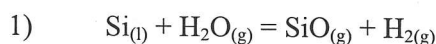


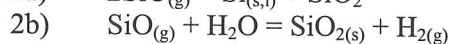
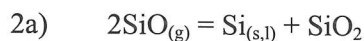
Figure 6 – Microprobe images of the surface of alloyed (0.4% Al, 0.04% Ca), oxidized silicon samples. The upper image is taken from a sample oxidized with water at a melt temperature of 1450 °C, using the method described earlier in this paper. The lower image is taken from a sample at liquidus temperature (~1412 °C), granulated in water using the method described by Nelson ³⁾.

4. CONCLUSION

Liquid silicon, either pure or with small additions of Al or Ca has been oxidized with water under two different experimental conditions. One method is to heat a small sample of silicon in an inert atmosphere, using an induction-heated furnace. The other method simulates a granulation process, as drops of silicon is melted and released into a water tank. It is found that there are substantial differences between the observed oxide layer on drops that have solidified in water (granulated), and samples that have been oxidized with a small pulse of water. Apart from deviations in layer thickness, the most striking difference is the absence of the porous silica layer on the drops and fragments that have solidified in water. One possible explanation may be that there is an initial stage of oxidation, also for the alloyed samples, where the silicon is oxidized by a vapor phase reaction involving SiO. Due to turbulence in the vapor film, this oxidation product of SiO-gas is effectively washed away in the case of granulation, but remains on the surface of the oxidized samples, where it may either condense to Si+SiO₂ or react with oxygen to form SiO₂. Thus, what we suggest is that the oxidation of silicon takes place in two consecutive steps. The first is described by the overall reaction



which is endothermic and takes place at the surface of the melt. The second step is believed to take place at a small distance away from the surface, and offers two alternative reaction schemes, which are both strongly exothermic.



Our results suggest that both these alternative reactions are active in the oxidation experiments. Reaction 2a dominates close to the metal surface where the gas is depleted

in H₂O, and the sum of reaction 1 and 2b causes the silica deposit to grow from the bottom. Further out where the H₂O-pressure is higher reaction 2b is favoured. The result of this is clearly seen on microprobe images, where the porous layer of SiO₂ close to the silicon matrix includes small spheres of silicon. When Ca and Al are present, the oxidation of these, which is very exothermic, has to take place on the interface. If a liquid slag forms, this blocks the evaporation of SiO.

Increased melt temperatures seem to have an effect on the interfacial turbulence. The interface between the silicon matrix and the oxide layer appears more irregular for alloyed melts oxidised at 1550 °C. This is related to the overall faster chemical reactions at elevated temperatures. A high mass transfer rate will lower interfacial tension and induce turbulence.

5. REFERENCES

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