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Monolithic furnace linings for production of ferro-alloys

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Abstract – Elkem developed a monolithic furnace lining that incorporates a gas / metal / temperature 'stopping' layer, after experiencing severe problems with carbon block linings back in the 1980s (Hyldmo & Johansen, 1990). On some furnaces, the monolithic lining lasted shorter than expected and this demanded further improvements. Initial work was done internally within Elkem, but, over the past years, this was extended, together with Professor Merete Tangstad at the Norwegian University of Science and Technology, through the masters degree of Sofie Aursjo (Aursjo, 2016).

Different installation techniques and equipment have been tested, before the rammed materials were heated and baked to different temperatures, at different heating rates. Samples of materials were tested by traditional destructive testing. Other samples were subjected to computed tomography (CT) scanning before they were exposed to molten metal and slag. Further CT-scanning of the samples was conducted after this, to show if and where the rammed monolithic lining was attacked by the metal and slag.

The development work has shown that rammed monolithic linings are robust during the heating and curing process, but that correct installation and ramming of the material is critical. Suitable installation equipment and the correct installation techniques will deliver a monolithic lining with a homogeneous density and particle size distribution. In addition, optimal mechanical strength with minimal crushing of the carbon particles/aggregate will be achieved.

This paper describes the monolithic lining solution and advantages, the development work which has been done, and the correct installation and heating of monolithic linings.

Keywords: furnace lining, high-temperature materials, ramming paste, carbon material, silicon carbide material

INTRODUCTION

Production of ferro-alloys is most commonly carried out in circular submerged arc furnaces with three electrodes. Temperatures in the hottest part of the furnace are normally in the range 1500–2000°C for metal and slag, and we need materials that can withstand these temperatures in the inner part of the furnaces. The submerged arcs, that normally arise from the bottom of the electrodes, have a much higher temperature than this, and linings will fail after some time, if the submerged arcs are in direct contact with them.

Linings are normally divided into two different designs, insulated linings and freeze linings. The purpose of an insulating lining is to reduce energy loss, and, through this, power consumption of the metal production. Temperatures will be higher through an insulated lining, compared to a freeze lining, and the inner lining material needs to be stable against melted metal and slag.

A freeze lining is normally a lining where the inner part is kept at a temperature below the melting temperature of metal and slag. The inner part of the lining will, due to this, get a frozen protective layer of slag, metal, or raw materials, and does not need to be thermodynamically stable against melted metal and slag. Temperatures inside the lining are kept down with the conductive transfer of energy through the lining, where it is actively removed on the outside. Steenkamp (2015) stated that in a freeze lining there will be energy transfer through conductivity also in the frozen layer of slag and metal, while in an insulated lining this transfer will be through melted metal and slag that is in motion, giving rise to convection and higher temperatures in the lining.

A furnace lining normally consists of four different layers of material, as shown in Figures 1 and 2. The outer wall and bottom are made of thick steel plates that are rolled to make the correct furnace diameter. The steel plates keep the lining in place, and prevent air from getting into the furnace, and, in old linings, prevent process gases from leaving. Cracks in the steel layer should be repaired immediately, to avoid oxygen from the air starting to attack carbon materials in the lining. The steel wall will, in the case of a freeze lining, have water cooling, either as water sprayed on the outside, or in closed water channels that are welded to the outside of the steel wall.

An insulated lining has a layer of insulation materials inside the steel plate that protects the steel against temperatures that are too high, while a freeze lining has a material with a high thermal conductivity that contributes to the transfer of energy from the inner lining and into the water-cooled steel plates.

For both insulated and freeze linings, the next layer consists of refractory bricks made of oxides as Al_2O_3, SiO_2, MgO, and Cr_2O_3 (Seltveit, 1992). The oxides often withstand the temperatures in the furnace, but are not necessarily thermodynamically stable against the furnace contents. Freeze linings will often have less refractory bricks than an insulated lining, and bricks with a higher thermal conductivity. Both contribute to a higher energy transfer outward in the lining, and a lower temperature on the inner lining.

The inner layer of the lining is usually made from carbon. It can be as pre-baked carbon blocks, or as a rammed carbon paste. Carbon can withstand temperatures above 3000°C and keep mechanical strength at these temperatures. An advantage for some processes is that carbon conducts electricity well. A problem, on the other hand, is that most of the processes use carbon as a reducing agent and that the lining sometimes acts like that. Metal might also take carbon from the lining if it is not saturated with carbon.

Lining problems
Hyldmo & Johansen (1990) described the most common lining problems at that time. These are illustrated in Figure 1. All of these problems are still valid for furnaces with cheaper lining materials and design.

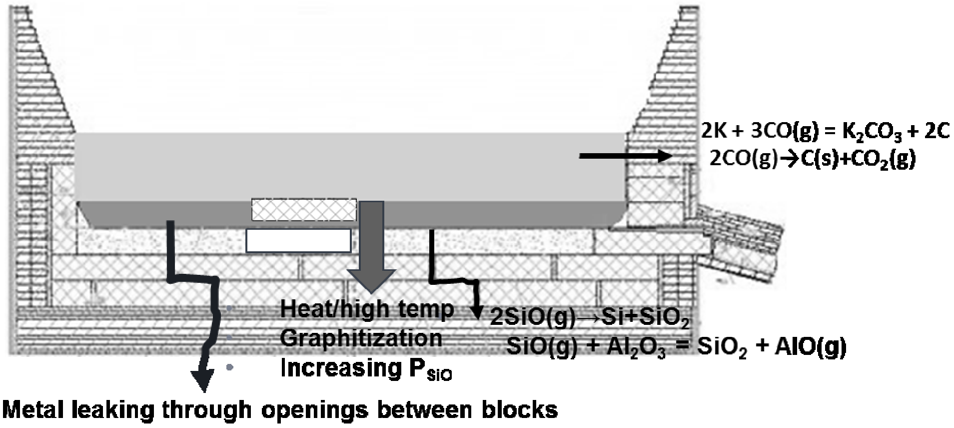

Figure 1: Some of the most common lining problems before Elkem developed their monolithic lining

Problems above the carbon hearth were connected to CO-gas and alkalis. CO-gas penetrates the refractory brick from the hot side, and diffuses against the colder side. When the temperature drops enough, CO-gas decomposes inside the bricks according to the Boudouard reaction.

$$2\,CO(g) = C + CO_2(g) \qquad [1]$$

The carbon deposition would first fill the porosity in the refractory bricks, and afterwards cause swelling and disintegration of the bricks. Alkalis that were reduced to K and Na and that evaporated from the hot zone of the furnace, would react with CO gas in the same area and form alkali carbonates that attacked the refractory bricks, partly dissolving Al_2O_3 and SiO_2.

The bottom lining was often the problem in Si-producing furnaces. A problem was that metal could come through openings between the carbon blocks or into the joints between blocks and ramming paste, finally all the way through the lining. Metal could also start to lift carbon blocks/layers in the lining.

Another problem was graphitization of the carbon in the lining. This increased the thermal conductivity of the carbon material to about 25 W/mK. This gave too-high temperatures in the refractory bricks, and some minerals in these started to melt. Increased temperatures also increased partial pressure of gases such as SiO that came through the carbon lining. The SiO gas would condense in the refractory bricks, and densify these or replace aluminium oxide in the oxide bricks. Bricks could then disappear or shrink in size.

ELKEM'S MONOLITHIC LINING

Figure 2 shows the principle of Elkem's inner monolithic lining made of carbon and silicon carbide cold ramming paste, that can be made in a few weeks and which will always fit to the other lining materials. The steel wall gets cooling from heatsinks and air that is blown between these. Air is blown up under the centre of the furnace and outward to the sidewall, where it goes up and contributes to cooling. The temperature in the steel wall should be kept below 300°C, due to the steel itself.

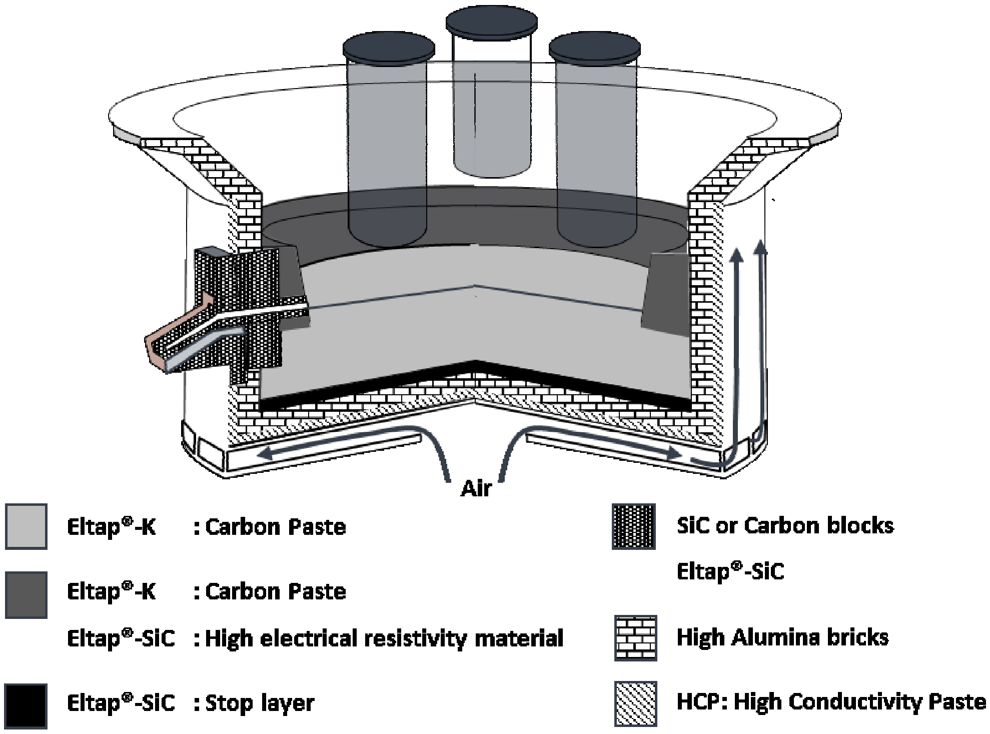

Figure 2: Elkem's monolithic lining

Elkem's lining design has, as the freeze lining, a material with high thermal conductivity inside the steel plates. This material assists energy transfer from the lining into the air-cooled steel plates.

For the next layer, the refractory bricks, Elkem's lining design is close to the freeze lining with fewer layers of bricks in the bottom, and a thinner furnace wall which also contributes to greater energy transfer out of the lining. In FeSi and Si furnaces, Elkem uses refractory bricks and blocks, from the company Borgestad, that are high enough in Al_2O_3 and low in porosity and iron contents. This gives better high-temperature properties, reduces CO-cracking, and increases strength against alkalis. In the tap-hole area, bricks, blocks, and ramming paste have a high content of SiC. This gives strength against oxidation. Bricks made of SiC also have a much higher thermal conductivity compared to oxide bricks (5–6 times), which increases energy transfer, and contributes to better cooling of the tap-hole area.

SiC stop layer

The most important improvements of the lining came with the SiC stop layer in the bottom of the furnace, on top of the refractory bricks. Eltap®-SiC is a ramming paste that makes a direct-bonded SiC material when the temperature is passing 1200–1300°C. The SiC stop layer has a low gas permeability, which makes it difficult for SiO gas to come through and attack the refractory bricks below (Hyldmo & Johansen, 1990).

The SiC stop layer also protects the refractory bricks against too-high temperatures when the inner carbon lining graphitizes and gets a high thermal conductivity. A reduced temperature also reduces the SiO-gas pressure in the previous paragraph.

The SiC stop layer will, when the inner carbon lining is worn out, stop or slow down metal that wants to penetrate through the bottom of the lining, especially for metal in the system Si to FeSi50. In this way, a break through the bottom lining is avoided, which could easily give a much longer stop of production.

Eltap®-SiC is stronger against alkalis than oxide-bonded SiC bricks; it has a lower gas permeability (Hyldmo & Johansen, 1990); it has a lower thermal conductivity; and it has no weak mortar joints. Eltap®-SiC should, due to this, not be replaced by oxidic-bonded SiC bricks.

The inner layer of the lining is made of Eltap®-K tamping paste that forms a monolithic lining, without joints and openings where gas or metal could leak through, and with good electrical conductivity. Eltap®-K is made with electro-calcined anthracite, where some has been heated up against 3000°C and contains 30–40% graphite which conducts both energy and current well (Holm, 2017). This is important for energy transfer out of the lining during the baking process. The material shows no macro shrinkage, which means that the lining should have no opening that metal can leak through.

The inner side lining is, on some Si and FeSi75 furnaces, made of Eltap®-SiC instead of carbon paste, because SiC has a much higher electrical resistivity. Side arcing on the outside of the electrodes can then be avoided. It was also seen during the repair of a 17-year-old FeSi lining that the SiC side lining was in better condition than the adjacent carbon lining. The carbon lining had probably been oxidized by air/oxygen blown in through the tap-hole.

IMPROVEMENTS OF RAMMING PASTE SOLUTION

New and eco-friendly binder

A new and eco-friendly binder replaced the standard coal tar pitch binder in all cold ramming pastes from Elkem in 2014. For some time, the new binder demanded better storage conditions and had a shorter shelf life. Improvements were done on the binder, and today's products are better than the old when it comes to installation at cold temperatures. Use of materials made from the new eco-binder is not regulated by REACH.

Our most health-friendly paste, Eltap®-SMB, is completely free of polycyclic aromatic hydrocarbons (PAH) and other hazardous substances. Due to this, this paste is used in tapping spouts, runners, and for tap-hole repair. Eltap®-SMB can also be used in furnace linings, but will need a more controlled and slow heat-up compared to our other lining materials, and has, due to this, not been used in larger furnace linings, as PAH have not been an issue during the heat-up of these.

Figure 3: A steel mould, and equipment for ramming of carbon and SiC materials

Laboratory testing

In the Elkem Carbon laboratory, we have a steel box measuring 551 x 308 x 350 mm, for the testing of ramming paste, see Figure 3. Different installation techniques and equipment can be tested for installation, and different heat-up procedures can be tested for temperatures up to 950°C. All of the following tests have been done in this box.

Heating rate

The refractory linings are normally heated and baked with energy coming from resistance heating of coke drums under each electrode. Later in the baking process, there is a contribution from the furnace charge between the electrodes. Ramming paste close to the electrodes will, due to this, have the quickest heat-up, while the lining in the periphery will have the slowest. Due to this, it was tested whether too-quick or too-slow heating of the ramming paste would influence the property of the material. Figure 4 shows the different heating rates that were tested, which varied between 0.4 and 80°C/hour, and Table I shows the measured densities after the heating of the four samples.

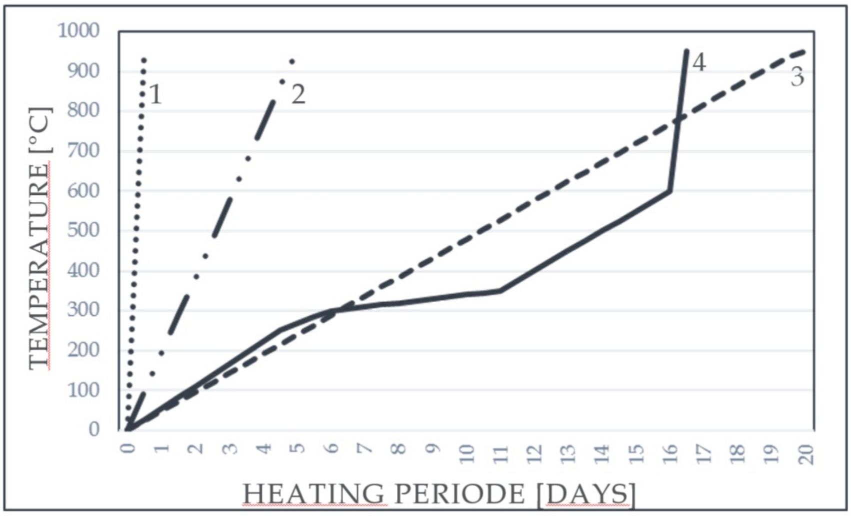

Figure 4: How four different samples of carbon ramming paste were heated to 950°C

Sample 4 was heated according to a furnace start-up where the heating was stopped because of technical problems. The densities correspond well with porosity in the four samples, which is 2% higher for Sample 3 than for Sample 2. Differences between the samples are small, and this shows that Eltap®-K is robust for different heating rates.

Table I: Density of carbon ramming paste for different heating rates to 950°C

Heating curve in Fig.4	1	2	3	4
Heating rate °C/hour	80	8	2	0.4–40
Density kg/m3	1464	1490	1455	1461

Installation of ramming paste

An important part of Sofie Aursjo's masters degree work, Wear of Carbon Refractory Materials in Silicon Furnaces (Aursjo, 2016), was the preparation of samples. Samples were core drilled out of the big sample; see Figure 5. After this, the same sample was CT-scanned, then exposed to molten metal and slag before a new CT scanning was done on the exact same area. We got a lot of information about the ramming layers and techniques from the first CT-scanning. Figure 6 shows two CT-scans from the same sample. The left CT-scan is between two ramming layers, while the right figure is from the top of a ramming layer where the coarse anthracite grains are crushed.

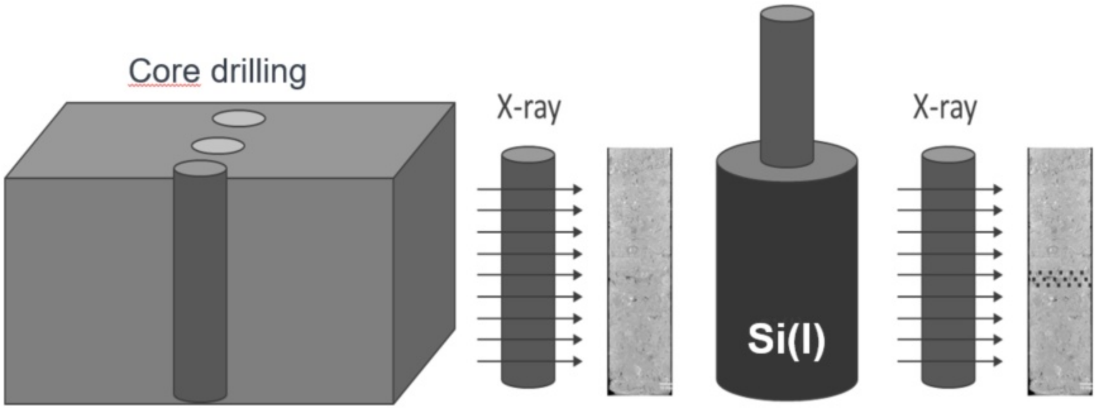

Figure 5: Schematic summary of how Aursjo (2016) sampled, measured, and tested carbon ramming paste against molten Si-metal and slag

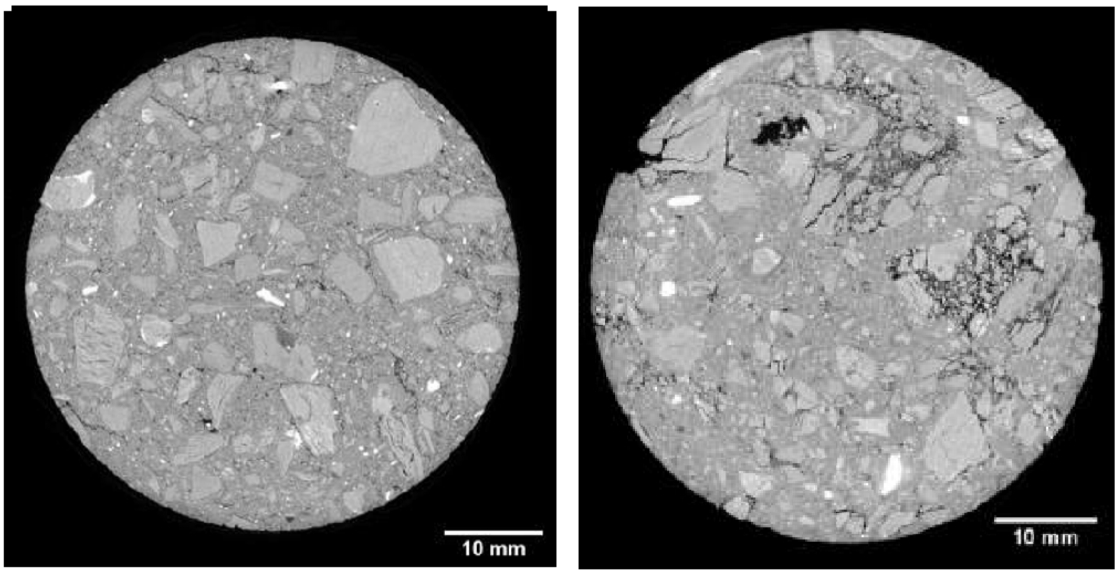

Figure 6: Two CT-scans from the same sample. The left CT scan is between two ramming layers, while the right scan is from the top of a ramming layer. Pictures taken from (Aursjo, 2016).

The crushed grains were found in samples rammed with a star head. The same crushing was not seen in samples made with a flat head, or a rubber head, and the learning was not to use a star head.

Figure 7 shows vertical CT-scans of two different samples of tamping paste, also from (Aursjo, 2016). The left sample was rammed with thin layers and with the ramming machine shown in Figure 3 with a flat head. The left picture in Figure 7 shows a quite homogeneous sample, and computed densities show small variation. The right sample in Figure 7 was made from an old ramming paste with too-thick ramming layers (60 mm) for this old paste. Ramming was done with an Atlas Copco Ram 20 with a star head which crushed grains in the top of each ramming layer. It is also seen that this ramming has given segregation with too many coarse particles in the bottom of each ramming layer, and that calculated densities show huge variation. These findings have led to new installation procedures and equipment.

Testing of lining material against metal and slag

The final purpose of the work of Aursjo (2016) was to see how the internal morphology of different samples affected different wear mechanisms of the lining. All samples were exposed to a metallurgical-grade silicon (average 99.4% Si). Some of the samples were also exposed to a slag containing SiO_2 (65%), Al_2O_3 (15%), and CaO (20%). Some samples where heated to 1500°C and held there, while other samples where cycled in the temperature range 1450–1600°C, or 1350–1600°C (below and above the melting temperature of silicon). Experiments were done in a resistance-heated furnace, or in an induction-heated furnace. All experiments showed little or no lining wear, but in samples exposed to metal and slag, and cycled between 1350–1600°C in the induction-heated furnace, silicon metal penetrated the samples through existing cracks, and lining materiel was partly converted from carbon to silicon carbide; see Figure 8. This silicon carbide is, by itself, an excellent lining product.

According to Steenkamp (2013), the lining wear mechanisms are corrosion, erosion, spalling, and densification in the ferromanganese production. These mechanisms are also valid for most ferro-alloy production.

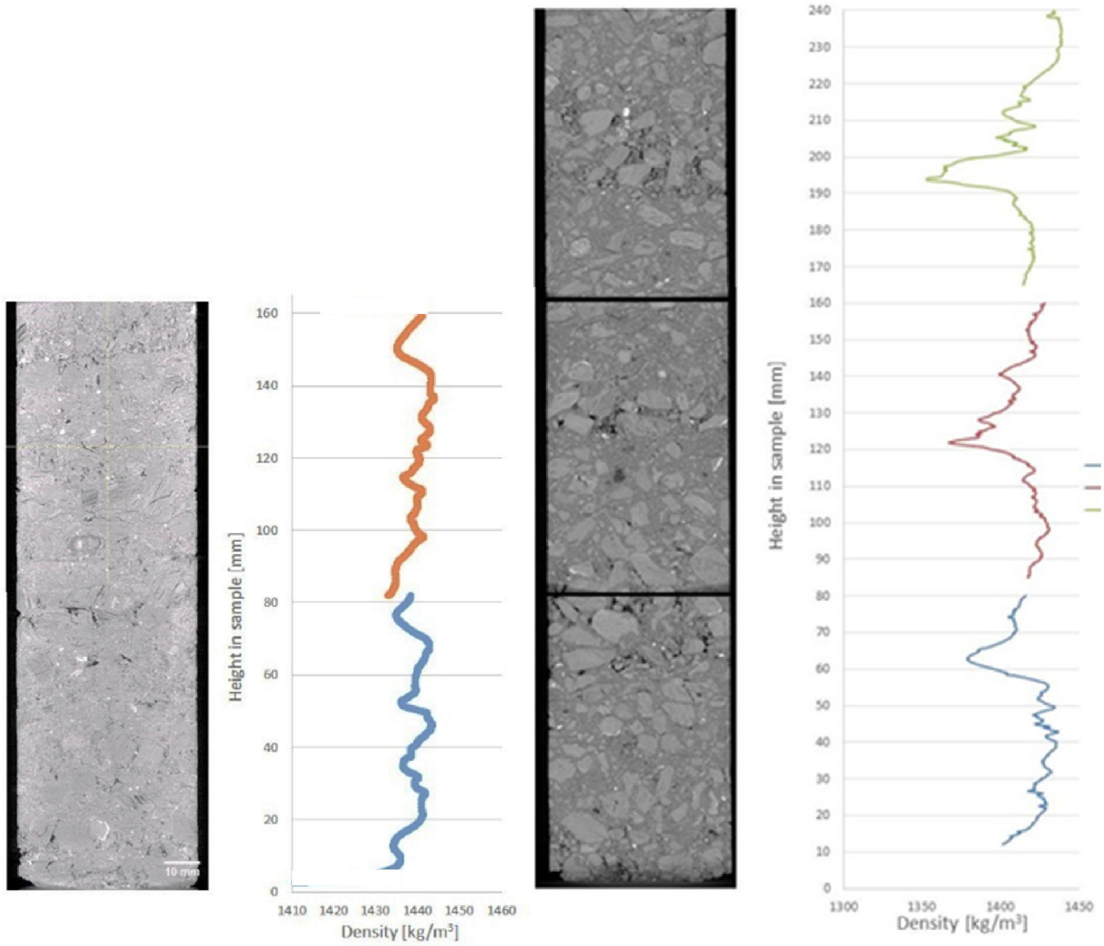

Figure 7: CT scans of a well rammed sample and a sample with too-large variation

Corrosion in our system would be dissolving of lining material from slag/metal. Solubility of carbon in silicon is negligible, and, if silicon reacts with carbon, a solid SiC layer will be formed. This layer would need to be removed before silicon can attack new carbon.

Erosion comes from the flow of metal/slag/solid material or gas abrading the lining material. This mechanism can explain why some SiC was found in the slag in the experiments done in the induction-heated furnace. Corrosion transforms lining material to SiC, while flow coming from the induction heating transports this SiC away from the surface of the carbon lining material.

Both the carbon ramming paste and the transformed SiC have low thermal expansion. This, together with relatively slow temperature changes, should not result in spalling of the lining. Silicon that had penetrated the lining can, on the other hand, expand every time it is brought below solidification temperature, and increase the cracks and openings they have penetrated. Repeated solidification of metal took place three times in these experiments, which did not give any spalling.

Densification of the lining was found in areas where carbon materials had transformed into SiC, as shown in the right picture in Figure 8. This transformation came from SiO gas that had diffused into the carbon material and reacted according to:

$$SiO(g) + 2C = SiC + CO(g) \qquad [2]$$

Maximum density of the carbon particles used in the Eltap®-K carbon lining material is measured to 1.70 (Holm, 2017). The maximum density, after the reaction above, will then be 2.84 g/cm^3, which is below the density of solid SiC, namely 3.21. This densification will then not harm the lining.

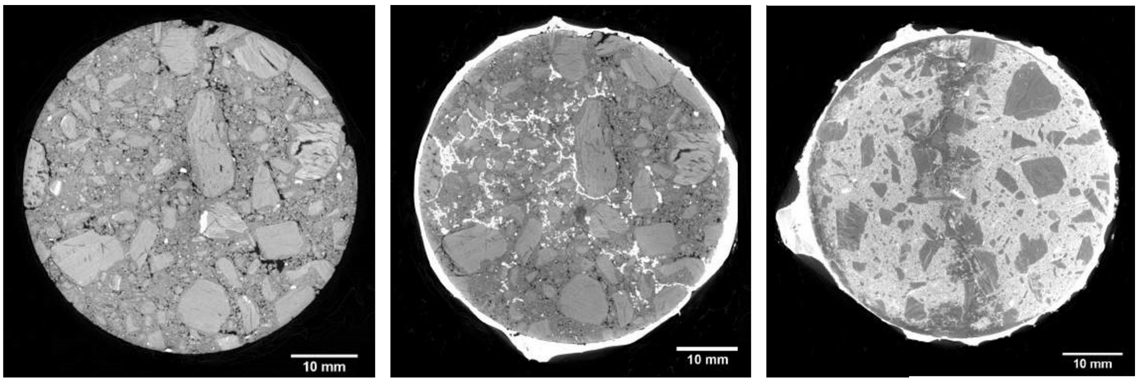

Figure 8: The left picture shows a cross section of a sample with lot of cracks and porosity, after baking of lining material. The picture in the middle shows the same cross section after exposure to molten silicon and slag. The right picture shows a cross section from the same sample where the binder and fines matrix has started to transform into silicon carbide. This cross section had few cracks from the beginning, and was taken from an area where the partial pressure of SiO gas had been larger during the experiment.

CONCLUSIONS

- Eltap®-K is robust against different heating rates during the baking.
- Installation and ramming is especially critical for the K-paste, and this demands correct ramming equipment. A rubber head is preferred on ramming tools.
- The thickness of each ramming layer should be decided from the type of ramming equipment, ramming paste, storage time and conditions, temperature of material, and surroundings.
- Installation of ramming paste demands supervision, and calculation of the correct amount of ramming paste in each layer, as well as quality control to ensure enough ramming, but not too much either.

- Correct installation together with Eltap®-SiC gives the best lining for Si, FeSi, and SiMn.

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Lars obtained a PhD in the recrystallization of SiC, from the Norwegian University of Science and Technology in 2002. He has been employed in Elkem since 1997 in positions as process metallurgist, production manager, development manager, and raw material manager. He has worked on four Elkem sites: Meraker, Bremanger, Iceland, and now Elkem Carbon in Kristiansand, Norway.
