Søderberg electrode technology and the potential for higher performance metallurgical silicon for the solar and chemical industry

M.Sc. Valdiney Domingos de Oliveira, MBA, C.Eng[1], Dipl. Eng. Rodrigo Silva de Faria[1], Dipl. Eng. Luciano Biazutti[1] , Dipl. Eng. Gabriel Esteves[1] , Dipl. Eng. Lou Parous[1]
1) Viridis.iQ GmbH, von-emmich-str 4, 78467 Konstanz, Germany

Abstract

Metallurgical Silicon is becoming increasingly a critical raw material and industry wide efforts are being made to develop high performance, customized Silicon materials for the production of lower cost derivatives for the solar and chemical sectors. These industries continue to grow at a rapid pace and increasingly demand higher quality feedstock with a focus on lower costs over the entire value chain. Over the past decades, one initiative that many TCS and MCS producers have used is the addition of selected catalyst to the metallurgical Silicon feedstock as a way to increase downstream performance. In parallel, development in silicon smelting electrode technology has undergone changes in the past years with a trend away from prebaked solid electrodes towards graphite core electrodes with Søderberg paste. More recently, volatility in the supply and price of graphite core composite electrodes has shocked the industry and has furthered the trend of developing 100% Soderberg paste electrodes for metallurgical silicon production. The conflation of the two trends of 100% Søderberg paste electrodes and the demand for higher performance metallurgical silicon with catalyst has resulted in the development of the alternative electrode technology with 100% Søderberg paste which can be used to add specialized and tailored catalyst to increase the reactivity and selectivity of the produced silicon in the TCS and MCS downstream sectors while reducing costs and supply risks. The aim of this article is to explore the possible benefits of capitalizing on the electrode trends with improving performance of metallurgical Silicon in TCS and MCS production processes.

Overview of Søderberg electrodes for Silicon production

Introduction

The Søderberg electrode is considered to be a self-baking electrode because the electrode paste and calcination occurs inside the actual furnace in the vertical tubular casing. The components of the Søderberg electrode for Silicon production are similar with that used for Ferrosilicon production with a principle difference being the material used in the casing. Various casing options are available depending on producer needs and materials characteristics. It´s very import that that the specific engineering aspects are considered during the system design and built into the design by experienced and qualified experts. Lastly, process operational experience is key to successful implementation and capitalization of the economic benefits of the technology. The following figure shows the principle components of the Søderberg electrode column.

The electrode itself is made of a metallic casing with internal radial fins for structural support that are also used for conductivity of the electrical energy to provide the calcination of the electrode. The fins also have the function to increase the mechanical and flexural strength of the electrode column (in the crude paste area and under contact pads region during the self-baking process at high temperatures). As the electrode is consumed in the furnace, additional segments of casting, ribs and electrode paste are added in the upper part of the column much like additional segments are added in other electrode types. This conjunct that is prepared prior to the welding/addition process on top of the electrode column.
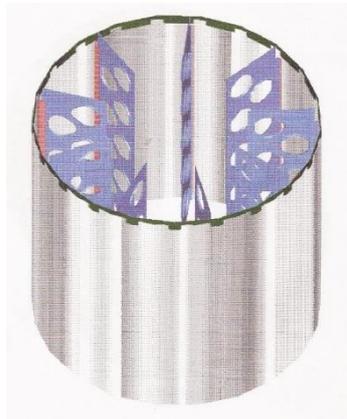
Figure 1: Example of the internal stainless steel ribs

History of using Søderberg electrodes in Silicon

The use of Søderberg electrodes has been well established for the ferroalloy production industries and was developed initially by the precursor company to Elkem, Elektrokjemisk, in the early 1900s. The use of Søderberg electrodes for ferrosilicon and other ferroalloys, as well as for slag cleaning processes has been a revolutionary achievement for those processes and the dissemination of the technology is widespread. Historically, Søderberg electrodes have not been adapted in a similar widespread manner for Silicon production due in part to the operational challenges in using non-Iron based casing materials, unwanted contamination of the Silicon with the casing material, and lastly the equally unwanted contamination of Iron in the Silicon caused from the structural fins of the casing that are normally made from stainless steel.

The cost savings of using Søderberg electrodes in Ferrosilicon production was eventually seen as providing a value contribution to Silicon production and its use in Silicon production was driven by market forces. In Brasil, Silicon producers were highly dependent on imported prebaked electrodes from Europe and were forced to seek cheaper alternatives. Similarly, European Silicon producers were seeking competitive advantages again lower cost competitors in Norway and the United States and eventually developed what is now known as the composite electrodes.

Presently, a few companies have succeeded in fully adapting the use of Søderberg electrodes to the production of Silicon in submerged arc furnaces of various sizes. These companies are mainly in South America and over the past 20 years have perfected the practical use of this technology in both the engineering of the electrode column as well as the operational nuances required for this electrode variant. To this day, it is believed that at least three Silicon production facilities in Brasil still use the technology in the production of Silicon. The following table shows the History of the development and consolidation of Søderberg electrode technology for Silicon production in Brazil.

Company	Country	Year	Active Power (MW)	Electrode Diameter(mm)
CBCC	Brazil	1997	12.8	1060
CBCC	Brazil	1998-2001	15.0	1060
CBCC	Brazil	2001-present	20-24	1300
Italmagnesio	Brazil	2001	17.5	1143
Italmagnesio	Brazil	2002	17.5	1143
Italmagnesio	Brazil	2003	17.5	1143
Rima	Brazil	2002-2003	20,21	1143
Rima	Brazil	2004-2011	20,21	1205
Rima	Brazil	2012	26 - 27	1320

Figure 2: History of Søderberg electrode technology in Brazil.

Self-baking process description

The Søderberg electrode is a system of three components: electrode paste, metal casing and stainless fins, along with rivets for the connection of the fins to the casting and

possibly additional components such as measurement probes of various materials. As the purpose of the electrode is to conduct a high electrical current, the electrical conductivity is an important component in the electrode. As the temperature increases, conductivity in the metal casting is reduced, but is increased in the carbon paste. With a proper of metal to carbon ratio, the metallic casing and the calcinated electrode paste acquire the same conductivity at a specific temperature. With increasing temperature, the conductivity of the paste increases as the metallic casing and ribs melt resulting in a baked carbon electrode suitable for conducting current on its own. The following figure is shows an overview of the self-baking process in the tubular casing.
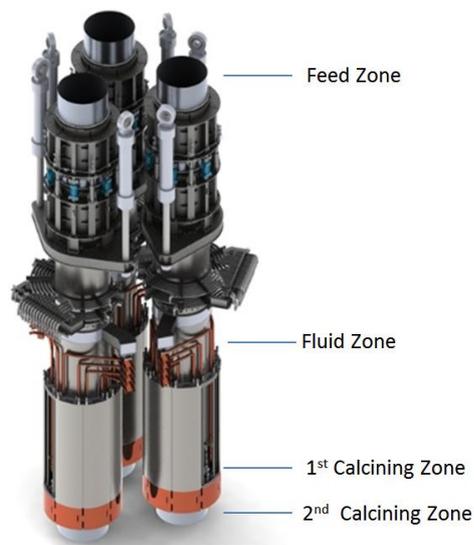
Figure 3: Viridis.iQ Alternative Søderberg electrode column (source Virdis.iQ)

- Feed Zone: column top, where new segments of liners are welded and where the solid Electrode paste is fed.
- Fluid Zone: Where the temperature increases and the paste receives certain amount of heat causing the paste to flow and fill the entire interior of the shirt.
- 1st Calcinating Zone: where the electrode paste transitions from a liquid to conductor with high mechanical strength. Pyrolysis removes the volatiles thru the pores of the electrode depositing crystals and increasing strength Contact Shoes
- 2nd Calcinating Zone: the electrode graphitizes and forms the electrode itself performing its basic function, which is to allow the formation of the arc and the consequent generation of heat to the reduction process.

Søderberg Column Equipment

The main equipment used in the Södeberg electrode column can be divided into two main areas: the upper column and the lower column as well as the power system, as explained below.

1) Upper column – The slipping device, mainly the upper and lower slipping rings, the pressure control system, the regulating cylinder for the column, etc.
2) Lower column – The pressure rings, water cooled jackets, electrode tube, contact clamps/pads, etc),
3) Power system – includes the cooling pipes, insulation system and air heating and insuflating system

There are various considerations that should be noted in the electrode equipment design, of which a few are outlined below.

- It is important and essential that the coking of the electrode paste take place entirely and must occurs before the temperature level of shirt reaches 630 °C.
- Sufficient heating systems and fans are well designed to provide proper temperature profiles for the contact shoes.
- The interface between the electrode column equipment and the electrode itself (casing) must to be kept under pressure to avoid dust accumulation.
- The contact pads should be designed in the high conductivity material and provide a design to cover the expansion of the paste and melting of the electrode casing material in between the electrode and internal contact pad facings.
- Pressure rings should be designed considering one segment per contact pad and the system should be able to operate at lower pressure ranges with high accuracy..
- The cooling circuit on the contact pads should allow the operator to regulate the flow and temperature of the water in order to help the control of self-baking curve during start and ramp ups.
- The paste feeding system should allow the feeding process to be handled in a smooth way in order to avoid damage during this process
- Thermal control of the electrode column should be installed properly in the right positions on electrode.
- Pressure control of the regulating cylinder, as well as load cells to control the electrode column weight will help the electrode management during the production process
- The electrical insulation chain of the electrode column should be technically designed to mitigate operational risks
- The electrode casing and fins conjunct should be designed to ensure the heat and electricity transference from the contact plates to the electrode, as well as the formation of the electrode to support the paste in the solid and liquid transition state.
- The internal ribs of the electrode must be designed for the optimal heat and electrical transference and the conjunct of the ribs and the casting material must be carefully designed for the mechanical demands of the entire electrode.

Cost Benefits of Alternative Søderberg Electrodes

The implementation of the Søderberg electrode various substantial cost benefits to Silicon production.

Table 1: Qualitative benefits of Alternative Søderberg Electrodes

Benefit	Description
Operational Costs	The Søderberg electrode operational cost is lower that prebaked and composite electrodes[13].
Improved Process Control and Product Quality	Higher operational process controls are needed which benefit the overall production process and require additional operator training and in depth process knowledge, resulting in higher product quality.
MTTR	Slightly lower MTTR (mean time to repair) during breakages (soft + hard breakages vs only hard breakages for prebaked electrodes).
Catalyst Addition	Addition of specialized catalyst for downstream applications is possible with the substitution of the internal ribs with catalyst containing materials.

The authors have published previously a simulation of the cost advantages of Alternative Søderberg Electrodes considering the following basecase scenario. The results of the simulation are shown following.

- 24 MW SAF
- 1271 mm electrode dia (types)
- 50in PB 4TPO m-f, 52Al10SS Alt, 50450 C
- Low ash coal + charcoal
- 84 kg/t, 2.55 kg SiO_2/t
- 10.75 MWh/t
- Viridis.iQ process design assumptions

Capital Equipment Cost Benefits

In terms of capital equipment costs, due to the fact that the composite electrode requires a higher level of control and an additional slipping system, the capital expenditures expected for the Alternative Søderberg electrodes column is slightly higher than the other standard technologies. The Søderberg electrodes could be operated with similar equipment (with a simple observation that the design of the electrode column either for prebaked or Søderberg electrodes must permit operating the slipping clamps and lower electrode column parts at lower pressures with good accuracy). One important point of this initial equipment comparison is the flexibility that the operator will have if the electrode installation is planned to operate with Søderberg electrodes or Prebaked electrode. In both cases, the flexibility will allow the plant to convert between the two technologies without significant problems so long as there is a well-developed transition plan involving the operational staff. The slight difference between the Søderberg electrodes and Prebaked electrodes from the capital costs standpoint is

related to the level of automation and the need for machinery to prepare the casing and fins.
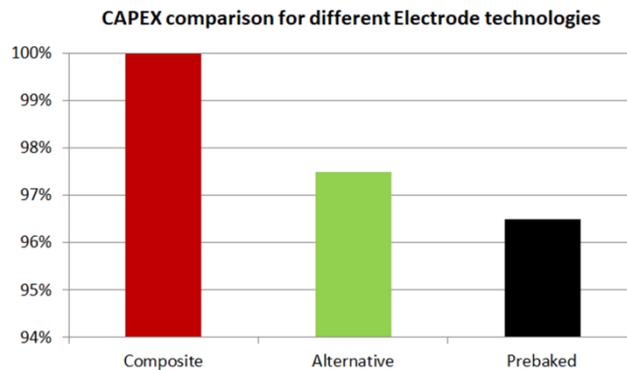
Figure 5: Electrode technologies comparison (normalized) (source Viridis.iQ)

Operational Cost Benefits

Considering the mentioned basecase scenario, under the same operational circumstances in terms of Silicon yield and Overall Equipment Effectiveness (OEE), the authors estimate the expected Operational Costs for the Søderberg electrodes versus prebaked and composite electrodes. The scenario was used as a reference and inputs from the Viridis.iQ data base, such as budgetary offers from the main prebaked, graphite and Søderberg paste suppliers, as well as quotations for Aluminum, Steel (both used in the casings for Extruded and Søderberg electrodes. The labor cost for the casing preparation, based on Viridis.iQ estimates was calculated. The results are shown in the following graph in a normalized basis.
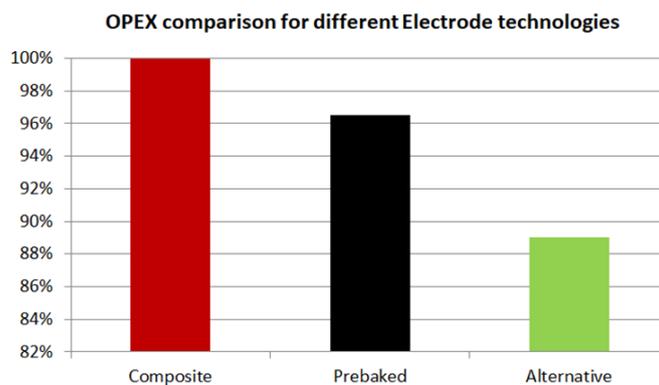
Figure 6 Electrode technologies comparison (normalized) (source Viridis.iQ)

Catalyst usage in MCS and TCS processes

Overview of catalysts usage

The effects principally copper based catalyst in the industrial TCS and MCS process is well documented, although specific industrial usage feed rates and copper concentrations in the reaction mass are relatively unpublished for proprietary reasons. In all cases, catalyst is externally added to the mgSi feed as are promoters - not to be confused with the promoter impact of various impurities that are already in mgSi such as Al, Fe, etc. The following is only meant to be a primer on the subject and not a comprehensive review.

In MCS, the use of copper[1] catalyst ($CuCl$, CuO, Cu_2O, Cu,) along with zinc and tin promoters is well established. Phosphorus can also be used as a promoter. The addition of Phosphorus to the mgSi is a working example of adding a catalyst / promoter to MCS[2]. Without use of copper + Zn + Sn, the MCS process reaction does not work at all and thus the common use of various nuances forms of Cu, Zn and Sn, along with absolute amounts and ratios of Cu/Zn, Zn/Sn, Sn/Cu are kept as closely guarded secrets among main MCS producers. Lastly, each producer has developed optimal process parameters and methods to operate their facility that best fits their overall plant design and knowledge base, not to mention their established mgSi quality and composition. This includes the actual form of copper used ($CuCl$, CuO, Cu_2O or Cu).

In TCS, there are two main process routes that are industrially used.

Hydrochlorination	$Si + 2H_2 + 3SiCl_4 \rightarrow 4HSiCl_3$ and	(1)
Direct Chlorination	$Si + 3HCl \rightarrow HSiCl_3 + H_2$	(2)
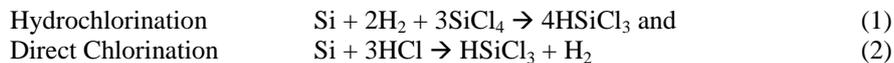
While both routes can proceed on its own without a catalyst, there are benefits from using catalysts. There are no known industrial applications of TCS Direct Chlorination (TCS-DC) production using catalyst but TCS Hydrochlorination (TCS-HC) is known to use catalyst in industrial applications. Unlike the MCS process, the TCS-HC reaction can be run successfully without use of external catalyst but results in lower TCS yield, which is the main reason the catalyst is used in practice as the catalyst can increase yields in practice. Impurities present in the mgSi feed, such as Al and Fe, always provide in-situ catalysis for the TCS-HC reaction; however the use of an external catalyst, principally copper based, helps drive the TCS-HC reaction closer to equilibrium and higher TCS yield[3].

Copper is the preferred externally added catalyst can be added in the form of copper oxide, metallic copper or copper chloride. Cu_3Si (Eta phase) is believed to be the catalytically active form of copper in the TCS-HC reaction, as is the case for the MCS process. In MCS studies meant to identify the form of copper in MCS beds, the Eta phase is generally seen as the catalytically active form of copper[4]. The eta phase is generally assumed to be formed based on the following reaction:

For TCS	$3Cu\ (g) + Si\ (s) \rightarrow Cu_3Si\ (s)$	(1)
For MCS	$12CuCl\ (g) + 7Si\ (s) \rightarrow 4Cu_3Si\ (s) + 3SiCl_4\ (g)$	(2)
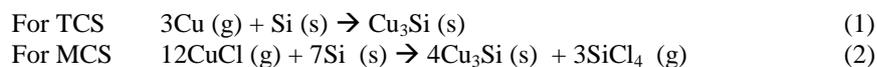
If CuCl is not the external catalyst used, then other forms of Cu (i.e. CuO / Cu_2O or Cu) must be converted to CuCl first.

Catalyst concentration and activity

Industrial catalyst concentration feed rates into the reaction mass are not published due to proprietary reasons. However, lab concentration rates are disclosed from patents and other studies on the subject[5,6]. For MCS, the lab rate catalyst concentration rates are approx. 3% - 5% by weight of the reaction mass while for TCS-HC the rates are 1%-5% by weight of the reaction mass. As most lab scale reactors run with higher copper catalyst than industrial plants, the authors will assume a mid-range for the copper catalyst concentration in subsequent discussion of 3%.

The external copper catalyst used in the MCS process (along with Zn and Sn promoters) and TCS-HC are mainly surface reactions. In MCS, Copper diffuses into the surface of the silicon particle and creates an alloy which releases Silicon and creates a diffusion front that moves deeper into the particle until the kinetics are exhausted[7]. In theory, the number of surface reaction sites would lead to a higher reaction rate in both processes. It can be surmises that the mgSi had a dopant concentration of the catalyst embedded in the particles, on the surface and throughout, the reaction rate also would accelerate.

Addition of Copper to mgSi

Some mgSi smelters have experimented with doping of mgSi with Copper in an effort to increase the reaction rates for TCS-HC and MCS customers. The high segregation rates of Copper in Silicon along with the traditional slow cooling of mgSi ingots upon casting results in ample opportunity for the added dopant to segregate to the heterogeneous grain boundaries of the mgSi cast ingot resulting in, once crushed and ground to a powder, a wide variability in concentration level of the catalyst from particle to particle. This heterogeneity can cause uneven results in the TCS and MCS reactors and has been the rationale for adding catalyst externally to the ground mgSi powder at the TCS-HC and MCS reactor site. Lastly, externally added CuCl must be converted to Cu_3Si (Eta phase) before the intended catalysis effect takes place. It is likely that if mgSi is doped with Copper in the liquid state, on cooling, the Copper would form Cu_3Si and therefore be readily available in the active form without the need for an external catalyst addition[1]. Cu_3Si (eta phase) has been reported to be an important copper source in the MCS direct process in the catalysis of the reaction.

Bulk casting of mgSi generally takes place in large ingot moulds at the smelter site which undergo forced convection cooling before being crushed and ground into a powder for TCS-HC and MCS customers. A few TCS-HC and almost all MCS producers have their own grinding plant which allows them to size the mgSi to correct specifications before adding to their process. Heterogeneous impurity concentrations in cast ingots have been reported by Møll, et al due to the slow cooling of standard Silicon casting processes. Slow ingot cooling is well known to impart wide ranging grain sizes

---

[1] The authors plan further work on this subject

in the ingot which is where most of the mgSi impurities are concentrated in the center of the ingot[8]. Upon crushing and grinding, the Silicon is more friable at the grain boundaries and therefore smaller grains tend to break more easily, resulting in most of the impurities being concentrated in the lower size fractions.

W. Kurz, et al showed the temperature vs time data in different positions for a Silicon ingot with 10 cm thickness. Fast temperature degradation is seen initially at the surface and then slower for deeper sections of the ingot as the heat transfers through thicker cooler sections.
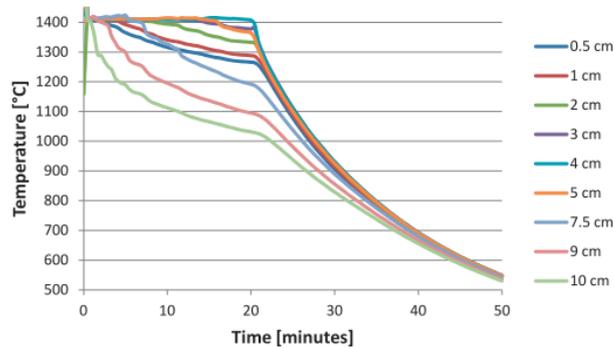
Figure 7: Temperature vs time in different position – 10 cm cast. Source: [12]

Adding Copper to Silicon via ladle addition would lead to high segregation in cast ingots due to the slow cooling characteristics of ingot casting. Based on operational experience, ingot cooling rates are on the order of 17 °C/min and literature reference of Copper diffusivity[12] in Silicon is known. Based on slow cooling rates and high diffusivity, it can be concluded that the normal casting methods in the Silicon industry would lead to Copper being agglomerated at the lattice defect sites with lower activation energy and later will move towards grain boundaries. The final result is a copper distribution with high segregation in the silicon solid. Thus slow cooling and Copper addition in the ladle would lead to highly segregated material and this correlates to known results of adding Copper to Silicon for us in Polysilicon and MCS production.

The authors propose that adding Copper in the Søderberg electrode column via fin substitution would result in the Copper being present as intermetallic bonds in the Silicon versus the grain boundaries and would not lead to this segregation upon cooling. Additional work is needed to validate this theory.

Previous work by the authors tested extremely rapid cooling techniques, namely gas atomization of Silicon with dopant levels of Copper as a possible improvement in performance of metallurgical Silicon. Gas atomization has a cooling rate of approximately 10^4 °C/sec versus a much slower 17 °C/min as in traditional casting. As expected, the Copper dopant, as well as other metallic impurities in the Silicon collected in the grain boundaries of the atomized Silicon and protruded through the surface of the particles. Future work on this subject will include evaluating the phases of Copper present in the grain boundaries as well as a determination of the grain size of atomized Silicon, both subjects could affect the performance of catalyst doped Silicon in the

TCS-HC and MCS process. Atomized Silicon with catalyst dopant is uniquely different that cast Silicon in two main aspects:

- The physical dispersion of the liquid Silicon creates natural barriers that prevent the catalyst from segregating beyond the liquid surface of the particle. As the particles sizes can be manipulated with gas pressure, temperature and speed, the already small sizes of the particles upon cooling means the catalyst is homogeneous throughout all particles.
- The fast cooling rate of the gas atomization process is such that even within the particle the segregation rate of the catalyst is much slower that the solidification of the particle. Precise studies of the cooling rate of gas atomized Silicon versus the
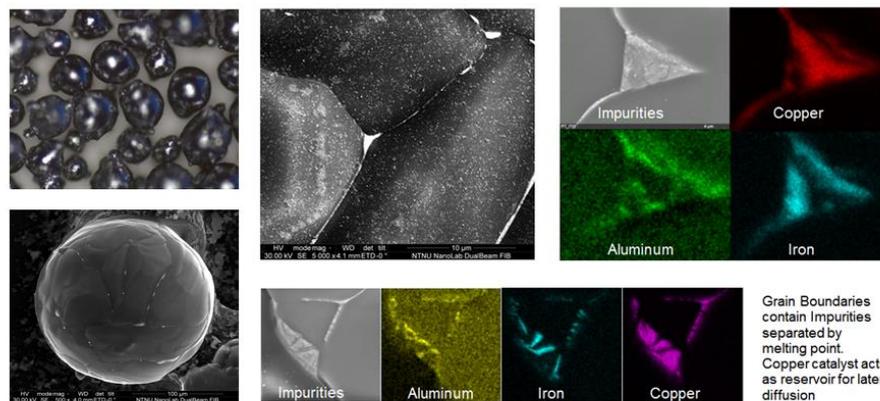
segregation rate of Copper in Silicon have not been validated.

Figure 9: Previous work by author on copper in grain boundaries of gas atomized Silicon

Many works on the subject emphasize that the effect of the Cu_3Si catalysis for TCS-HC or MCS is limited to the surface leading to the inference that Copper buried inside the particle as in atomized Silicon would not be as effective. However, this inference has not been fully evaluated and remains unclear if a distributed network of catalyst evenly distributed in a fine grain Silicon particle with surface negatively impacts the reaction in HC-TCS or MCS. The authors believe the segregation front, as described in literature, would be enhanced as it moves from the surface of the particle and encounters additional reservoirs of catalyst, thereby actually improving the performance of the reaction.

Adaptation of Søderberg electrodes

Catalyst addition in the smelting process

It is known that at least one Silicon producer has experimented with adding Copper to at the refining stage in order to achieve high Copper content in the final product for use at

a specific Polysilicon customer. The same experiments were performed at difference Silicon producer with the goal us adding Copper for eventual MCS consumers. The results from these experiments were mixed as the volatility of the distribution of the Copper in the mgSi ground mgSi was less than ideal. Given the high segregation rates and the cooling methods for Silicon ingots, this result would be expected. Silicon smelters are generally reluctant to add Copper to silicon due to possible contamination into other product grades for customers that are sensitive to Copper content. Therefore, any serious strategy to add Copper to Silicon would likely be limited to smelters who have exclusive production contracts with TCS or MCS customers that would allow for the management of this risk. Another option is for fully integrated MCS and TCS producers who own and operate mgSi smelters, to have production protocols that allow for Copper addition.

The main method for adding Copper to mgSi is simply the addition of copper source to the ladle before tapping ensuring the dissolution of the Copper during the refining step. Once Copper has been added, the subsequent casting of the Copper doped Silicon occurs normally. The authors propose that a different route for Copper addition is possible in combination with the use of 100% Søderberg electrodes for Silicon production.

Introduction of Copper in the Alternative Søderberg electrode column

As discussed in the previous section, the Alternative Søderberg electrode consists of the casing, the fins and the paste itself. It is feasible that the internal fins of the column are made with different materials. This component of the electrode column could be designed based on a Copper based material, i.e. Copper metal or a Copper alloy, that could be used as catalyst in the downstream application for Chemical processes. The mechanic strength and electrical conductivity of that specific fin design as well as the complete assembly characteristics (thermal, mechanic and electrical) must be carefully evaluated with careful consideration of the safety limits of the flexural strength, conductivity and tension support. Various fin designs are possible based on evaluation of the stresses on the electrode during production.

Figure 11: Example of substitution of one fin with Copper based material

The substitution of one or more of the find with Copper material will affect various aspects of the electrode column, namely:

Thermal Conductivity	Higher thermal conductivity is expected which supports and improved baking process of the column.
Electrical Conductivity	Higher electrical conductivity of the electrode from the Copper fins will reduce the heating of the electrode
Thermal Expansion	Due to disparate expansion coefficients of the two fin materials, adjustments in the fin thickness and dimensions of the Copper fin will be required.
Melting Point	The lower melting point of Copper is a detriment to the structural aspect of the column, but should not impact to a large degree as the temperature of the fins at the contact plate region will be below the melting point and the engineering of the column should be made with these limits in mind to avod failures

The addition of Copper in the Alternative Søderberg electrode column must be considered in regards to the eventual transference of the Copper to the final Silicon project. The internal furnace composition which consists of various forms of SiC, Si and other phases represent a complex environment that is not easily estimated without extensive testing. Kamfjord 2012 and Myrhaug in 2003 afirm that 79% to 80% of the Copper added to the furnace will be carried to final product (Silicon), which considers no segregation due to the high temperatures of the middle and lower reaction zones and indicate that high levels of Copper would reach the tapped Silicon. Additionally no Copper will be lost via oxidation in the refining process based on the Elligham Diagram. Synthetic slagging of Silicon with high Copper content is not recommended to avoid equilibrium dislocation during the refining process.

The authors estimate that the substitution of three thicker fins of the Alternative Södeberg electrode with Copper would add approx. 0.0920% ppm to the Silicon final product. Additionally, Copper contamination of the Silica Fume is expected to be minimal based on literature references that approximately 20% of the Copper added to the furnace would reach the Micro Silica. This is clearly not sufficient in terms of the targeted 3% Copper addition as stated previously, however, such an addition of Copper in the fins of the Søderberg electrode would provide a base level of Copper that would reduce the future addition of Copper catalyst at the Polysilicon and MCS site and would reduce minor amounts of Iron contamination from the Stainless Steel fins. Additional work on the subject is required to examine the full range of benefits of adding Copper catalyst via Søderberg electrode in combination with gas atomization to provide a high performance Silicon material for end use applications.

Acknowledgements

Conclusions

Søderberg electrodes have been used extensively in the production of Ferrosilicon due to the lower operational costs compared to Prebaked carbon electrodes. Adaptation of Søderberg electrodes for Silicon has been successful in Brasil as an alternative to Prebaked and Composite electrodes and has seen a resurgence of interest. Søderberg electrodes can provide an easy method for adding catalyst to Silicon via the substitution of one of the fins of the electrode with a catalyst bearing materials, namely Copper. The use of Copper as a catalyst for the Polysilicon and MCS production processes is well established and Copper based catalyst are routinely added to Silicon material at the site to increase performance. The authors propose the addition of Copper catalyst to the Søderberg electrode column as a manner to provide a baseline level of Copper to the Silicon that can bring benefits to the vertically integrated Polysilicon or MCS producers by reducing the need to add excess Copper catalyst, reduce the addition of Iron the Silicon via the removal of some of the Stainless Steel fins in the electrode, and providing a highly homogenous Silicon material via the use of extreme rapid cooling of Silicon such as gas atomization that can be a marked improvement over standard casting methods due to segregation effects. Further work on the subject is needed to validate the effects of the Copper addition in the electrode column and the phases present in the final Silicon.

References

[1] Ward, W. J.; Ritzer, A.; Carroll, K. M.; Flock, J. W., Catalysis of the Rochow Direct Process, J. Catal. 1986, 100, 246.

[2] Dow Corning Patent US 4,898,960.

[3] A. Crawford, Cost saving of using a metallurgical grade silicon with higher trichlorosilane yield in the hydrochlorination based polysilicon process, Silicon for the Chemical and Solar Industry XIII, L. Nygård, B. Pachaly, H. Rong, M. Tangstad, H. Tveit, I. Page Eds., (Kristiansand, Norway), 2016, p. 201-218.

[4] John M. Bablin, Larry N. Lewis, Aqueous Leaching Technique for the Determination of Eta Phase (Cu3Si) in MCS Beds, Silicon for the Chemical and Solar Industry V, H.A. Øye, H.M. Rong, L. Nygaard, G. Schtissler, J.Kr. Tuset (Trondheim, Norway), 2000, p. 347-364.

[5] A. Crawford, et al

[6] Ward, et al

[7] W. Banholzer and Micheal C. Burrell, Characterization of Reactive Areas in the Direct Process for the Production of Methylchlorosilanes, GE Research and Development Center, p. 269

[8] Maria Førde Møll, KH Berget, E Myrhaug, M Onsoien, and H Tveit, The Main Reasons to develop an improved casting process for silicon, Proceedings of INFACON XIII, Almaty, Kazakhstan, p. 763.

[9] Jose Joaquim Cardoso, Eletrotermia - Fornos Eletricos a Arco., Volume I and II. 1987.

[10] Engineering ToolBox, (2005). Thermal Conductivity of Metals. [online] Available at: https://www.engineeringtoolbox.com/thermal-conductivity-metals-d_858.html [Accessed 02 05 2018].

[11] Aleksandar Mitrašinovic, Characterization of the Cu-Si System and Utilization of Metallurgical Techniques in Silicon Refining for Solar Cell Applications, Department of Materials Science and Engineering, University of Toronto, 2010

[12] W. Kurz, D.J. Fisher., Fundamentals of solidification, Uetikon-Zuerich, Switzerland ; Enfield, N.H. : Trans Tech Publications, 1998

[13] V.D. Oliveira, et all, Electrode Technology comparison for Silicon production – a brief overview, Infacon XV: International Ferro-Alloys Congress, Cape Town – South Africa, 2018