

The Refining of Silicon and Ferrosilicon

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The types and origins of impurities in ferrosilicon and silicon metal, and the options in the refining of the liquid metal are reviewed.

The paper, which deals only with the chemistry of oxidative refining, focuses on carbon and oxygen solubilities in liquid iron–silicon alloys and on distribution equilibria for calcium and aluminium between the metal and ternary $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slags. The impact of these elements on dissolved oxygen in the metal phase is also discussed.

Distribution data are presented in diagrams showing isoconcentration lines for calcium and aluminium in the liquid range of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system at 1550 °C. Reaction paths and kinetic obstacles in the refining process are explained with reference to these diagrams, and the precautions to be taken to avoid the formation of oxide inclusions are mentioned.

Introduction

With an annual production 400 kt of ferrosilicon and 130 kt of silicon metal in 1989, the power-intensive Norwegian silicon industry produced about three-fifths and one-third of Western Europe's total output of these products respectively. To maintain this industry in a leading position as a reliable supplier of quality products, substantial research-and-development work on liquid- and solid-state refining has been carried out over the past few decades by the industry itself and also at research institutes. This work has not been terminated, however, and more work is still needed in order to meet the requirements of demanding customers, some of whom are asking for specifications that sometimes seem to be beyond the theoretical limitations.

Before the industry can be in a position to respond rationally to such requests, it needs to know, firstly, the theoretical limitations and, secondly, how to approach them in a reproducible way in actual production.

This paper, which deals with the oxidative refining of liquid metal only, focuses on the first point: What are the theoretical limitations in oxidative refining, and what type of supplementary data is needed to quantify them?

Origin and Control of Impurities

In any metal-production process, quality control starts with the selection of raw materials. This statement should in particular be emphasized to producers of a reactive metal such as silicon and its alloys, where the selectivity of the process itself is nearly non-existent, and where the possibilities for bulk metal refining are very limited.

Because of the nature of the metal itself, the carbothermic process for the production of silicon and ferrosilicon is in principle defined as a slag-free process. This implies that, apart from elements forming gaseous components and volatile metals or metal oxides that are lost with the off-gases, the elements entering with the charge materials are expected to be reduced and tapped as constituents of the

product metal. A variety of metallic impurities are therefore present, and those usually recorded in commercial products are listed in Table I.

However, aluminium and calcium, being the most abundant impurities in the charge, do not behave as simply as stated above. Aluminium appears as an impurity in both quartz (or quartzites) and the reductants used, the latter being responsible for the input of 60 to 70 per cent of the total aluminium and 90 to 95 per cent of the total calcium in a normal charge used for the production of standard ferrosilicon¹. The oxides of these elements present in the reduction materials are expected to be reduced fairly easily, whereas the alumina, which is diluted in the silica phase, is less available for reduction and tends to accumulate as a viscous silicate melt in the furnace. When this melt is contacted with metal sufficiently high in calcium, an exchange reaction takes place that increases the CaO content and the fluidity of the oxide phase. Occasionally, therefore, some slag is tapped together with the metal. On average, slag tapping in standard ferrosilicon production represents an outlet for 30 to 40 per cent of the total aluminium and 50 per cent of the total calcium in a charge¹.

Titanium, the third major impurity metal in standard ferrosilicon and silicon metal, originates from both the SiO_2 source and the reduction materials used, the latter being the main source. Titanium is practically absent in tapped slag, however, and nearly 100 per cent reports to the metal phase. The same applies to metallic impurities from groups V to VII of the Periodic Table, which in the case of ferrosilicon enter with the iron source, in the form of scrap iron, iron-ore pellets, or mill scale. These impurities are not usually recorded in standard ferrosilicon, but have specified maximum levels in high-purity products, as indicated in Table I.

In the reduction furnace, the metal forms in the presence of silicon carbide at temperatures in the range 1800 to 2000 °C. The carbon content of tapped metal therefore reflects the solubility of carbon in ferrosilicon at these temperatures.

TABLE I
IMPURITY LEVELS IN SOME TYPICAL FERROSILICON AND SILICON-METAL PRODUCTS, % BY MASS

Element	Ferrosilicon				Silicon metal	
	Standard Fe75Si	Refined Fe75Si	High-purity Fe75Si*	High-purity Fe66Si*	Standard MGSi	Refined MGSi
Si	74 – 79			65 – 67	97 – 99	> 98,5
Al	< 2,0	0,05 – 0,50	< 0,06	< 0,020	< 0,6	0,1 – 0,5
Ca	0,2 – 0,8	0,05 – 0,10	< 0,02	< 0,020	0,2	0,03 – 0,07
Ti	0,07 – 0,10	0,10 – 0,20	< 0,04	< 0,016	0,05	0,05
C†	0,05 – 0,15	0,02	< 0,02	< 0,012	0,03	0,02
Fe	(Balance)	(Balance)		(Balance)	0,3 – 0,5	0,3 – 0,5
Mn				< 0,130	0,03	0,03
V, Cr, Ni, Cu				0,01 – 0,03	0,01 – 0,03	0,01 – 0,03
Co, Mo, Zr				< 0,003	< 0,005	< 0,005
S	< 0,001 – 0,005					
P	0,015 – 0,03			0,0110	0,005	0,005
B				< 0,0005	0,005	0,004

* According to specifications by the producer (ILS). Maximum levels specified on 22 elements for the Fe66Si quality

† Mainly present as SiC inclusions (Figure 1)

The values reported for the solubility of carbon in liquid silicon vary. The data of Seace and Slack² form the basis of the solubility curve shown in Figure 1. This figure includes an enlarged portion of the Si–C phase diagram at the melting point of silicon as given by Nozaki *et al.*³ in order to show the eutectic nature of the system. For the ternary system Fe–Si–C, reliable data on carbon solubility exist only up to the stability range of SiC, which appears⁴ at around 23 per cent silicon and 0,4 per cent carbon at 1600 °C. The shape of the solubility curve from this point up to the Si–C binary, along which the activity product of carbon and silicon has to take a constant value, is not known.

Reported data⁴ from two experiments with an alloy containing 45 per cent silicon, together with preliminary results of ongoing work at the SINTEF laboratories, indicate that

the solubilities given in Figure 1 are fairly representative of commercial ferrosilicon. The carbon analysed in these products is therefore mainly present as primary particles of precipitated and suspended silicon carbide that are trapped during the solidification process.

Oxygen, which is as inevitable as carbon in the product, is not listed in Table I. It is, however, an element of growing concern to the producers of high-quality silicon and ferrosilicon.

The solubility of oxygen in liquid Fe–Si alloys in equilibrium with solid silica at 1600 and 1650 °C has been studied fairly extensively by Novokhatskiy⁵ and Shevtsov⁶⁻⁸ and their co-workers. Their results are in fairly good agreement, and are presented in Figure 2, which shows the data of Shevtsov at 1650 °C. It can be seen that there is a minimum

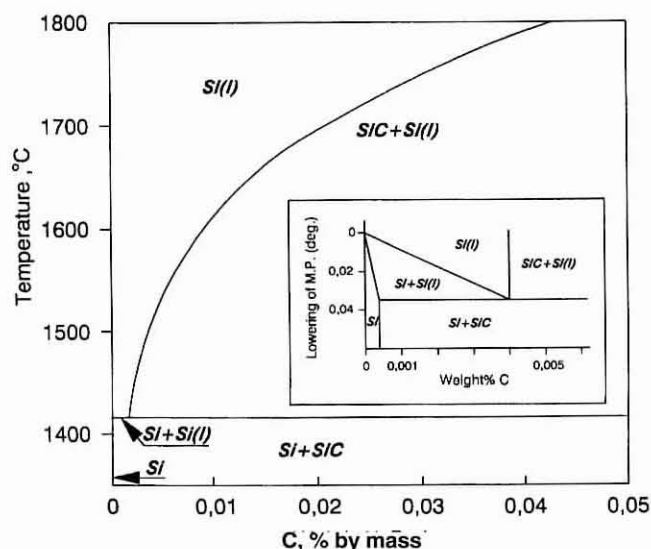


FIGURE 1. Solubility of carbon in liquid silicon, derived from the data of Seace and Slack², including the eutectic portion of the Si–C system as given by Nozaki *et al.*³

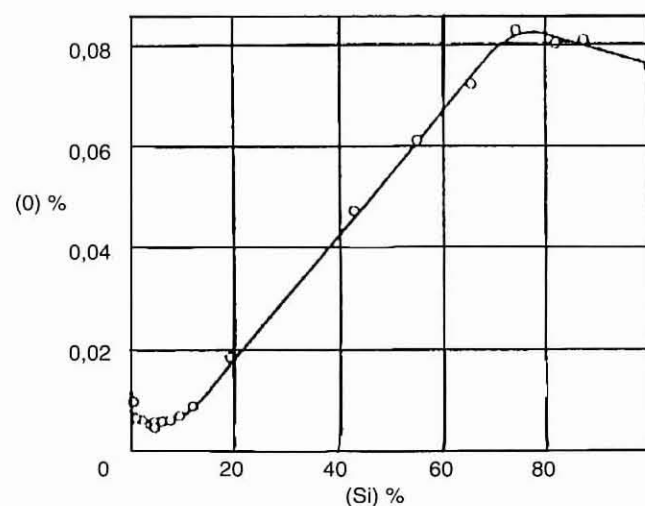


FIGURE 2. Oxygen solubility in Fe–Si melts at 1650 °C (after Shevtsov⁸)

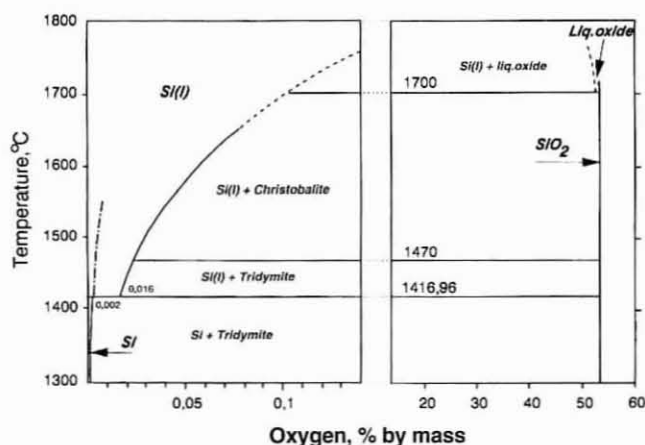


FIGURE 3. The system Si-O with solubility curves as given by Novokhatskiy⁵. The dash-dotted curve represents the liquid solubility as given by Hirata⁹

in oxygen concentration at low silicon contents, as can be recognized from the known deoxidation equilibria of liquid steel, whereas a maximum in oxygen solubility appears at around the composition of Fe75Si. The solubility value at 100 per cent silicon as given in this diagram is consistent with data for the system Si-SiO₂ taken from the work of Novokhatskiy *et al.*⁵. Their data were used in the construction of Figure 3, which shows the silicon-rich part of this system. The uncertainty in these data is illustrated by the solubility curve, which was calculated from the recent work of Hirata and Hoshikawa⁹.

It is worth noting that the diagram shows the feature of a eutectic system. One would expect this binary eutectic to extend towards a ternary eutectic in the system Si-Fe-O. The location of this eutectic, which is not known, is assumed to be fairly close to the Fe-Si eutectic appearing at 58.2 per cent silicon and 1207 °C. The level of oxygen at this ternary eutectic will probably be of the order of 50 p.p.m. Therefore, in commercial alloys containing more than 50 to 80 p.p.m. of oxygen, the excess oxygen would be expected to be present as primary oxide inclusions.

Options in the Refining of Liquid Metal

Apart from sophisticated methods like electrolytic and vacuum refining, both of which are considered to be of interest in connection with the production of solar-grade silicon, there are only two options of practical interest in the bulk liquid-metal refining of silicon metal and ferrosilicon:

- methods based on the oxidation and slagging of impurities.
- methods based on chlorination and the removal of impurities as volatile chlorides.

Both types of method are effective for the same types of reactive elements such as the alkali and alkaline-earth metals and aluminium. The chlorination process, being the more effective of the two for these elements, appears to also have a certain purification effect on other elements such as chromium, manganese, and copper. The process is, however, of less industrial interest owing to the environmental and material problems associated with the use of chlorine and the emission of corrosive metal chlorides. The silicon industry therefore uses only methods that are based on the oxidation and slagging of impurities.

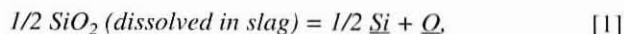
The oxygen needed for the refining reactions in oxidative refining can be introduced

- as a gas in the form of oxygen or air at the metal surface, or by gas-blowing through a lance, a nozzle, or plug in the bottom of a refining vessel
- in the form of an oxidizing agent, such as Fe₂O₃ in the case of ferrosilicon, or SiO₂ in the case of silicon metal
- or by slag treatment combined with mixing.

Gas-blowing is usually combined with the addition of some kind of slag-forming compounds that may also act as oxidizing agents. The addition is usually carried out by injection when a lance is used for gas-blowing, or by direct charging to a top slag in the case of the nozzle-blowing technique, where intimate mixing associated with air-blowing can be obtained. The various sources of oxygen listed are therefore effective in a real process, but their relative importance may differ from one type of operation to the other. The way the oxygen is introduced does, in fact, strongly affect the heat balance and the kinetics of the refining process, but has in principle no influence on the chemical equilibria controlling the process.

Distribution Equilibria in Oxidative Refining

No matter how the oxygen is introduced, a boundary-layer film of oxide forms at the metal surface as a result of the reaction between the oxygen and the most abundant element, which is silicon. The reaction defining the oxygen potential in the metal at this interface is, then

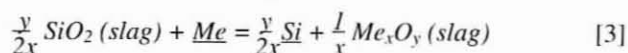


where the underlining indicates elements that are dissolved in the metal phase.

A dissolved metal impurity, $\underline{\text{Me}}$, present at the interface may now react as follows:



If both reactions are at local equilibrium at the interface, with the same activity of dissolved oxygen (a_0), then this quantity can be eliminated if equations [1] and [2] are combined. Multiplication of the resulting expression by the factor y/x yields the following equation:



with the equilibrium constant

$$K_{\text{Me,Si}} = \frac{(a_{\text{Si}})^{y/2x} \cdot (a_{\text{Me}_x\text{O}_y})^{1/x}}{a_{\text{Me}} \cdot (a_{\text{SiO}_2})^{y/2x}}. \quad [4]$$

This is equivalent to stating that the oxidation of a dissolved impurity is coupled with the oxidation of silicon, since both reactions appear to be under the control of the same rate-limiting step, here assumed to be the rate at which oxygen is supplied to the metal-slag interface. If this is true, it is also evident that the oxidation of the various dissolved elements is mutually coupled through reactions similar to those shown in equation [3]. At low impurity levels, however, the transport of the impurity elements from the bulk of the metal to the slag-metal interface may very well take over as a rate-controlling step, and the resulting distribution will deviate from the equilibrium values discussed below.

Table II lists the set of distribution reactions obtained when $\underline{\text{Me}}$ is substituted for $\underline{\text{Al}}$ and $\underline{\text{Ca}}$ in equation [3]. The

TABLE II
DISTRIBUTION EQUILIBRIA IN THE OXIDATIVE REFINING OF LIQUID FERROSILICON AND SILICON METAL

Distributing equilibria and corresponding expressions for impurity concentrations	ΔG , kJ		Calculated k values			
			Fe75Si as solvent		Si metal as solvent	
			$k_1^* = \frac{(a_{Si})^{y/2x}}{K} M_{Me} \left[\frac{75}{M_{Si}} + \frac{25}{M_{Fe}} \right]$		$k_2^* = \frac{(a_{Si})^{y/2x}}{K} \frac{100 M_{Me}}{M_{Si}}$	
	1550 °C	1600 °C	1550 °C	1600 °C	1550 °C	1600 °C
[3.1] $\underline{Al} + \frac{3}{4} (SiO_2) = \frac{3}{4} \underline{Si} + \frac{1}{2} (Al_2O_3)$ $[\%Al] = k \frac{1}{\gamma_{Al}} \frac{(a_{Al_2O_3})^{1/2}}{(a_{SiO_2})^{3/4}}$	-107,307	-106,742	6,09 10^{-2}	7,63 10^{-2}	8,06 10^{-2}	1,01 10^{-2}
[3.2] $\underline{Ca} + \frac{1}{2} (SiO_2) = \frac{1}{2} \underline{Si} + (CaO)$ $[\%Ca] = k \frac{1}{\gamma_{Ca}} \frac{a_{CaO}}{(a_{SiO_2})^{1/2}}$	-145,017	-140,306	7,89 10^{-3}	1,38 10^{-3}	9,94 10^{-3}	1,74 10^{-2}

* Inserted for $a_{Si} = 0,82$ in Fe75Si and $a_{Si} = 1$ in Si metal. M_{Me} = mole mass

† The calculations were based on data from JANAF¹⁰, except for the free energy of formation of cristobalite, where the data of Rein and Chipman¹¹ were used

standard free energies of these reactions at 1550 and 1660 °C are also listed. All the data used in these calculations are from JANAF¹⁰, except for the standard free energy of cristobalite, which was derived from the equation given by Rein and Chipman¹¹:

$$\Delta G_{crist}^{\circ} = -226,500 + 47,5 T \text{ (kcal/mol)}. \quad [5]$$

This expression yields values that deviate slightly from the JANAF values at 1550 and 1600 °C, but it was chosen to obtain consistency with the slag-activity data of Rein and Chipman¹¹. Furthermore, it has to be pointed out that the ΔG values given for reaction no. 3.2 in Table II are not the proper standard values, since liquid calcium was chosen as the reference state in these calculations, not gas at a pressure of 1 atmosphere.

The equilibrium constants are calculated from the well-known expression

$$K = \exp \left(\frac{-\Delta G^{\circ}}{RT} \right) \quad [6]$$

When these values are used as shown in Table II, two sets of distribution constants are obtained. One set of values refers to Fe75Si, and the other to silicon metal as the solvent for impurities. In both cases, the constants given are correct only for impurities present at infinite dilution. This depends on the silicon activity values used (0,82 and 1,0 for Fe75Si and silicon metal respectively¹²) and the correction factors used for the change in concentration from mole fractions to percentage by mass.

With this limitation in mind, the given constants can be used in the calculation of the equilibrium concentration of each of the two elements listed provided that their activity coefficients

(γ_{Me}) in the metal solutions, as well as the impurity oxide activity and the SiO_2 activity of the slag phase are known.

These constants, as well as similar expressions for equilibria involving the other impurities appearing in standard products, can also be used in the calculation of the expected activities of the oxides formed from these impurities when the SiO_2 activity is equal to 1, which represents the most oxidizing conditions that can be realized in this system. The use of estimated and conservative γ -values for the metal impurities leads to the conclusion that, apart from the silicon itself, aluminium and calcium are the only metals among those present that will contribute significantly to the formation of slag during the oxidation process. A relevant slag is therefore the ternary system $CaO-Al_2O_3-SiO_2$.

When the accepted activity data for this system were used as given in the comprehensive work of Rein and Chipman¹¹, together with experimental data on the equilibrium distribution of calcium and aluminium between Fe75Si alloys and synthetic slags located within the liquid region of the system at 1500, 1550, and 1600 °C, good correlation between the experimental and the calculated values was obtained when the following values were inserted in the expressions given¹³ in Table II:

$$\gamma_{Ca} = 2,1 \cdot 10^{-3} \text{ and } \gamma_{Al} = 0,45. \quad [7]$$

Isoconcentration lines for calcium and aluminium, drawn on the basis of both experimental and calculated data at 1550 °C, are shown in Figures 4 and 5 respectively. A diagram similar to Figure 5, which shows good agreement, has been published by Ageev and his co-workers¹⁴, who studied the distribution of aluminium between Fe75Si alloys and synthetic slags at 1600 °C.

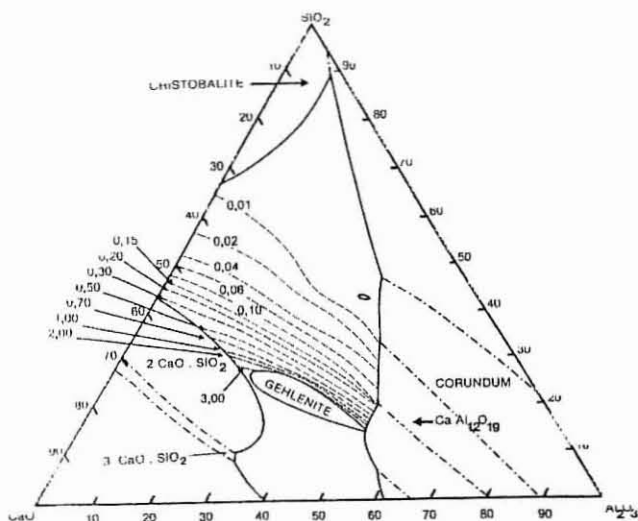


FIGURE 4. Isoconcentration lines for Ca in Fe75Si alloys in equilibrium with $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ -slags at 1550 °C, in percentages by mass (after Tuset¹³)

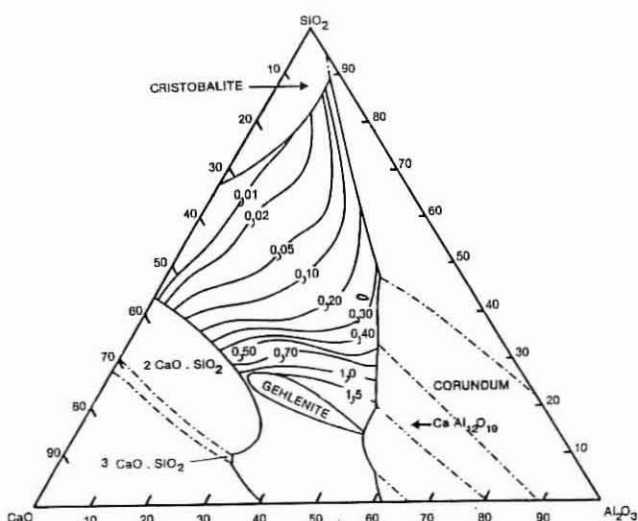


FIGURE 5. Isoconcentration lines for Al in Fe75Si alloys in equilibrium with $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ -slags at 1550 °C, in percentages by mass (after Tuset¹³)

When the data in these diagrams are applied to silicon metal in equilibrium with the same slags, the impurity concentrations have to be corrected relative to the given values for ferrosilicon as follows, with k values taken from Table II:

$$[\% \text{Ca}]_{\text{Si}} = [\% \text{Ca}]_{\text{FeSi}} \frac{k_2}{k_1} \frac{\gamma_{\text{Ca}}^{\text{FeSi}}}{\gamma_{\text{Ca}}^{\text{Si}}} = 1,26 [\% \text{Ca}]_{\text{FeSi}} \frac{\gamma_{\text{Ca}}^{\text{FeSi}}}{\gamma_{\text{Ca}}^{\text{Si}}} \quad [8]$$

$$[\% \text{Al}]_{\text{Si}} = [\% \text{Al}]_{\text{FeSi}} \frac{k_2}{k_1} \frac{\gamma_{\text{Al}}^{\text{FeSi}}}{\gamma_{\text{Al}}^{\text{Si}}} = 1,32 [\% \text{Al}]_{\text{FeSi}} \frac{\gamma_{\text{Al}}^{\text{FeSi}}}{\gamma_{\text{Al}}^{\text{Si}}} \quad [9]$$

The γ -ratios appearing in these expressions are correction factors for the change in the activity coefficients of calcium and aluminium respectively during the transition from iron-containing to iron-free alloys. The γ -ratios are both expected to be greater than unity, owing to the stronger interaction between the iron and the silicon than that between the iron and the dissolved impurities.

For calcium in silicon, the value

$$\gamma_{\text{Ca}}^{\text{Si}} = \gamma_{\text{Ca}}^{\infty} = 8 \cdot 10^{-4} \quad [10]$$

can be used. This value was derived from the work of Schürmann *et al.*¹⁵, and leads to the relationship

$$\frac{\gamma_{\text{Ca}}^{\text{FeSi}}}{\gamma_{\text{Ca}}^{\text{Si}}} = 2,1 \cdot 10^{-3} / 8 \cdot 10^{-4} = 2,6. \quad [11]$$

The use of this value as the correction factor for an alumina-free silica-saturated slag, yields the following expression for the equilibrium concentration of calcium:

$$[\% \text{Ca}]_{\text{Si}} = 1,26 [0,006] \cdot 2,6 = 0,02. \quad [12]$$

This value agrees fairly well with the experimental values obtained at 1550 °C.

A correction factor that is applicable for aluminium in liquid silicon is unfortunately not available at present, but work on this is in progress.

Oxygen in Refined Alloys

No reliable information is currently available on dissolved oxygen in real silicon alloys containing calcium, aluminium, and carbon. However, this should not prevent speculation on this topic.

Calcium, aluminium, carbon, and silicon are known to act as deoxidizing agents in liquid steel, despite the fact that they all lower the activity of dissolved oxygen in steel, as reflected by the negative values of their interaction coefficients, i.e. $\epsilon_{\text{O}}^{\text{X}} < 0$. The addition of a deoxidizer should, owing to this effect, increase the oxygen level provided the oxygen potential is kept constant. The opposite is experienced, however. The explanation is, of course, that it is the deoxidizer itself that now defines the oxygen potential of the system, and this takes place almost right from the beginning of the addition. This phenomenon is clearly reflected in the oxygen-solubility curve for the Fe-Si alloys shown in Figure 2.

When silicon or a silicon-rich ferroalloy is the solvent for oxygen, the situation is somewhat different. In that case, the oxygen potential is defined by the stability and activity of the oxide of the solvent itself, and it will even remain constant, independent of the level of calcium and aluminium, as long as solid silica forms as a stable phase. As the interaction coefficients of these elements on dissolved oxygen are expected to be negative, although less negative than in steel, higher levels of dissolved oxygen would be expected in metal in equilibrium with silica-saturated calcia-alumina slags than in the calcium- and aluminium-free systems. However, the actual values have yet to be determined experimentally.

For a metal containing higher levels of calcium and aluminium in equilibrium with unsaturated slags of decreased silica activity, an overall decrease in the concentration of dissolved oxygen might be expected, since it is believed that the opposing effect, caused by the increase in the content of deoxidizer, is more than counterbalanced by the decrease in the oxygen potential of the system.

Equilibrium Reaction Paths and Their Kinetic Interpretations

In the refining of silicon, the density of the slags formed is nearly the same as that of the metal. A silica-rich slag of the ternary type considered will float on the silicon-metal bath, whereas the more basic and alumina-rich slags tend to sink¹³.

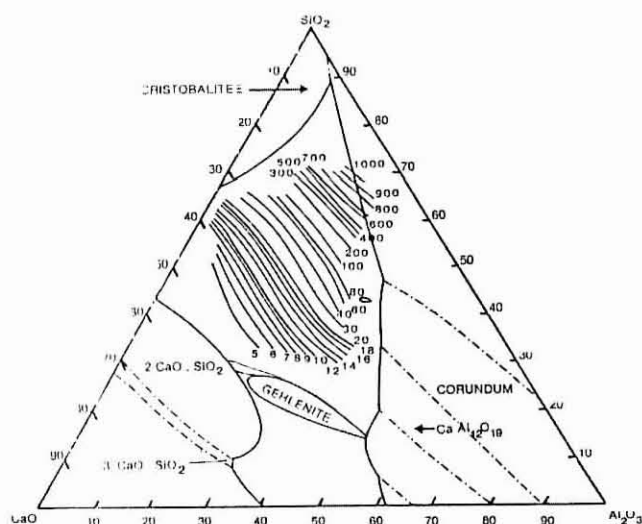


FIGURE 6. Isoviscosity lines (poise) in the CaO-SiO₂-Al₂O₃ system at 1500°C (after Elliott *et al.*¹²)

This problem does not occur in the refining of ferrosilicon. The viscosity of the slag is important in the refining of both silicon and ferrosilicon; its variation with composition at 1500 °C is shown by the isoviscosity lines in Figure 6.

Consider now the refining of ferrosilicon containing 1,5 per cent aluminium and 0,5 per cent calcium being blown with oxygen or air in a ladle at 1550 °C. It is assumed that a boundary slag layer forms at the metal-gas interface of the gas bubbles being created deep in the ladle, and that this slag reaches equilibrium with the bulk metal before the bubbles burst at the surface, leaving their slag content behind as a top-layer slag. The composition of the slag formed in the initial stage of the refining process is indicated by the letter A in Figure 7. This slag, which has nearly the same composition as those reported for tapped slags from ferrosilicon furnaces¹, has a calcium-to-aluminium ratio larger than that of the metal. Consequently, the metal

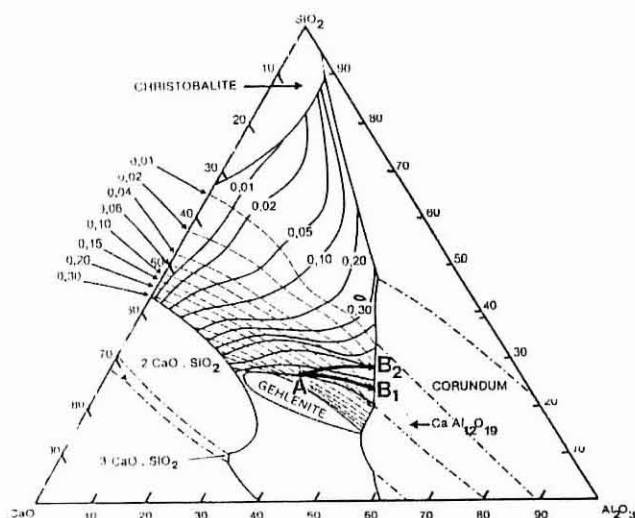


FIGURE 7. Isoconcentration lines for Ca (broken lines) and Al (solid lines) in Fe75Si at 1550 °C as reproduced from Figures 5 and 6. Path A-B₁ represents the change in the composition of the product slag when an alloy containing 1,5 per cent aluminium and 0,5 per cent calcium reacts to equilibrium with oxygen, provided the top slag is inactive. Path A-B₂ represents the same data for an active top slag, i.e. equilibrium has been established throughout (after Tuset¹³)

becomes depleted in calcium.

If the top-layer slag does not participate in the reaction, the resulting slag changes its composition from A towards B₁ in Figure 7 as the metal changes its composition from 1,5 to 1,1 per cent aluminium and 0,5 to 0,05 per cent calcium.

If the top-layer slag also participates in exchange reactions with the metal, the resulting equilibrium slag composition is shifted towards point B₂ in Figure 7, and the concentrations of aluminium and calcium in the metal will change to 0,7 per cent and 0,04 per cent respectively.

Along these paths from A to B there is a large increase in slag viscosity. Furthermore, for the removal of aluminium to continue beyond the above limits, a highly viscous and partly solidified alumina-silicate slag has to form. One would therefore expect that the efficiency of the oxidation process will decrease gradually as the calcium concentration of the metal decreases, and that the aluminium content will tend to level off at a concentration much higher than predicted for a silica-saturated slag.

This agrees with observations made during industrial trials and bench-scale tests. The process is running with nearly 100 per cent oxygen utilization in the initial stage when calcium is present and a liquid slag is formed, but becomes inefficient as soon as the calcium is consumed and a crusty, nearly dry oxidation product of silicon starts to form. This usually takes place at around 0,05 to 0,06 per cent calcium in silicon metal, and at 0,03 to 0,04 per cent calcium in ferrosilicon¹⁶.

Calcium deficiency at the site of oxidation will not only influence the oxygen yield as described, but will also have a dramatic effect on the oxygen in the product metal, owing to the formation of crusty silica films that do not easily dissolve or separate from the liquid metal. Such tiny particles, being difficult to identify under the microscope, will, of course, result in oxygen levels far in excess of the liquid solubility values.

If oxygen lancing is used and the degree of mixing is limited, the flux should preferably be injected with the oxygen. This is, however, not necessary in an air- or oxygen-blown process using a bottom plug, as described for the Tinject process¹⁷, where the top slag appears to participate throughout the reaction owing to intimate mixing. In that case, a direct addition of flux to the top slag is sufficient.

The carbon removal that takes place in oxidative refining is not considered here, since such refining is not based on chemical reactions but is a separation process based on differences in densities and interfacial energies.

From reported measurements of contact angles, it is clear that liquid silicon wets silicon carbide better than quartz or fused silica¹⁸. This does not mean, however, that silicon carbide is wetted better by silicon metal than by silicate slags. On the contrary, all the observations made during the melting of silicon or ferrosilicon in graphite or silicon carbide crucibles in the presence of slags support the conclusion that the slag wets silicon carbide better than it does the metal. Slags are always found enveloping the metal in these crucibles, and particles of silicon carbide are always seen concentrated in the slag phase. The question of relative wetting is therefore not critical, at least in the case of acidic slags with low surface energies, but it may be for more basic slags.

The extent to which suspended particles of silicon carbide can be effectively removed in an oxidative refining process therefore depends primarily on the fluidity of the slag and the degree of intermixing of metal and slag, as well as on the conditions under which the phases separate.

Acknowledgment

The author gratefully acknowledges the financial support received from the Research Association of the Norwegian Ferroalloy Producers (FFF) and the Royal Norwegian Council for Scientific and Industrial Research (NTNF).

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