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TINJECT REFINING DURING 15 YEARS

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ABSTRACT

Tinject is a ladle process for the refining of silicon alloys based on sub-surface injection of oxygen and an inert stirring gas through a specially developed plug system, combined with the addition of slag materials on top of the metal bath.

The Tinject plug was developed at Tinfos in the early 1980's and was patented in 1986. Several ferrosilicon and silicon producers have signed licence agreements with Tinfos and utilize this technology. This paper will present the Tinject plug and some refining experiences with Tinject through 15 years of operation.

INTRODUCTION

Refining of ferrosilicon and silicon by injecting oxygen gas through top lances or through tuyeres or plugs in the ladle lining has been practised around the world. The overall reactions involved in these processes are:

$$2\,\underline{Al} + {}^{3}/_{2}\,O_2 \Longrightarrow Al_2O_3 \qquad (1)$$

$$\underline{Ca} + {}^{1}/_{2}\,O_2 \Longrightarrow CaO \qquad (2)$$

Refining by injection of silica sand and slag forming components is also used. The following reactions occur:

$$4\,\underline{Al} + 3\,SiO_2 \Longrightarrow 3\,Si + 2\,Al_2O_3 \qquad (3)$$

$$2\,\underline{Ca} + SiO_2 \Longrightarrow Si + 2\,CaO \qquad (4)$$

Tinfos' slag furnace process for refining of ferrosilicon was introduced at Tinfos in the 1950's: Quartzite, limestone and dolomite were melted in a special furnace and molten slag was mixed with liquid ferrosilicon. Refining was achieved through the exchange reactions (3) and (4). At the end of the 1970's, an increased demand for a more flexible and inexpensive refining system provided the incentive to develop a new process for the refining of ferrosilicon. This development work created Tinject, which was later adapted for the refining of silicon and has been installed by a number of ferrosilicon and silicon producers in several countries.

THE TINJECT PLUG

In ladle treatment in the steel industry the most commonly injected gases are inert gases introduced for stirring, transport or purging purposes, and there are normally no exothermic gas/metal reactions taking place.

The Tinject process, on the other hand, is based on the injection of oxygen into silicon alloys where the oxygen reacts violently with the alloy constituents, producing condensed slag phases. The amount of heat released during refining makes large demands on the plug system.

The essential part of the Tinject process is the Tinject plug through which oxygen or air, or mixtures of these, is blown into the liquid metal in a submerged position. The plug is normally positioned in the bottom of the refining ladle. The conical shaped Tinject plug as shown in Fig.1 is constructed with metallic parts in the rear and a consumable refractory front plug with tiny channels or pipes. The gases pass through a peripheral channel in the rear section of the plug, thereby cooling the plug and the surrounding refractory lining, before being injected into the melt through tiny channels, thus avoiding any leakage to the lining.

Using a plug with channels allows a wider range of flow rates than a porous plug. The capacity of the Tinject plug may be varied by choosing the number of channels and by adjusting the gas pressure. - Pressures up to 20 bar or more may be applied. Fig. 2 shows the capacity in m^3n pr. minute as a function of gas pressure for a plug with 12 channels.

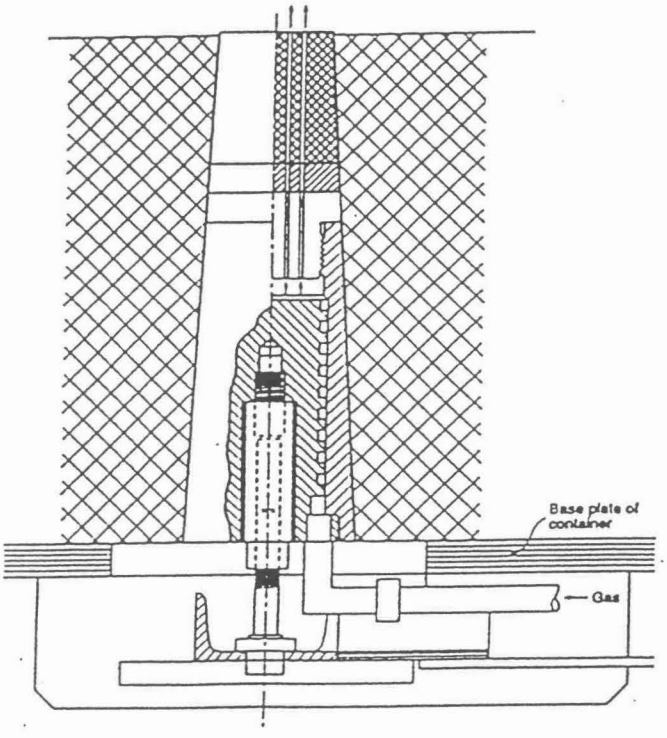

FIG. 1. The Tinject plug

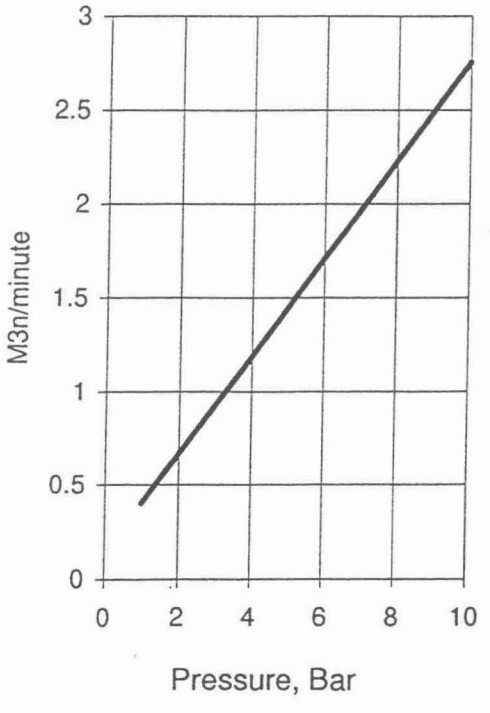

FIG. 2. The capacity of a 75 mm 12 pipe Tinject plug

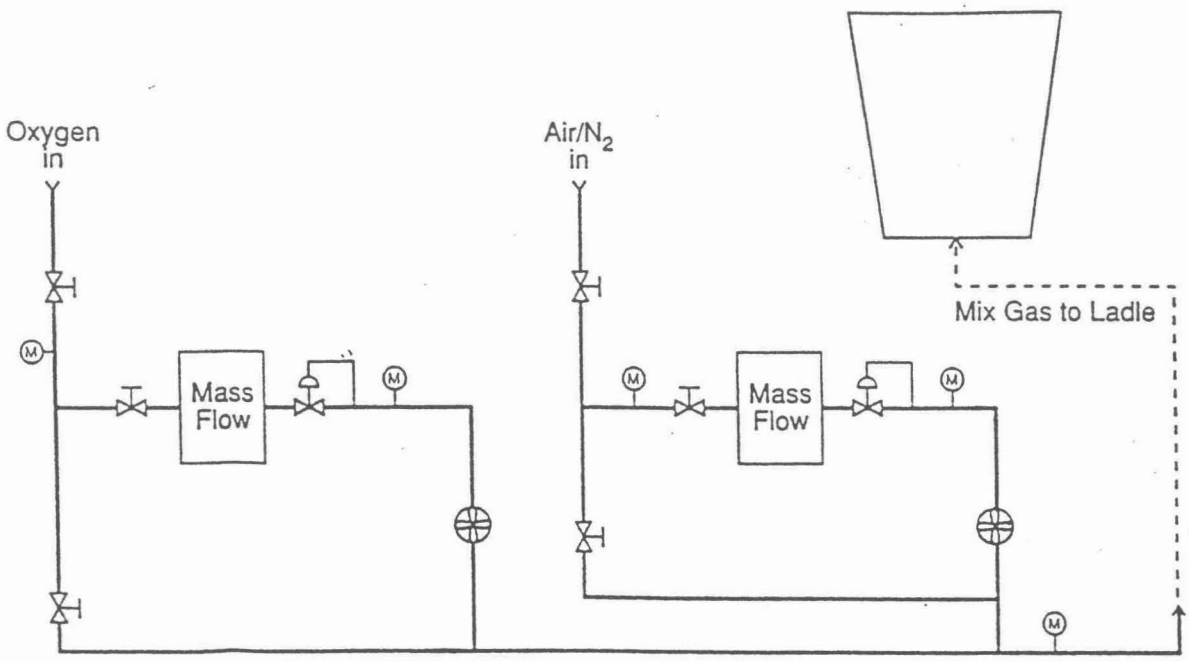

FIG. 3. Flow sheet of the Tinject gas control panel

The Tinject plug can easily be installed in the bottom lining of most ladles. The plug is supplied with gas from a control panel equipped with flow controls, manometers and valves as shown in Fig. 3. Oxygen is mixed with air in any ratio from 0-100%. The gas mixture is supplied from the control panel through a 20-40 meter long reinforced hose being connected to the plug via a quick-coupling. The control panel should be located in a position from where the casting area can be observed. The crane operator should have the freedom to choose an operating position which allows overview of the ladle spout during casting.

Tinject refining can either be carried out during tapping or in a separate refining ladle after tapping. Tinject refining of silicon is always carried out during tapping, which means that each furnace must be equipped with minimum one gas control panel. (Continuous tapping require two control panels pr. furnace). Refining time is typicaly $1^1/_2$-2 hours for a continuously tapped silicon furnace compared to 10-30 minutes refining time (depending on the analysis as refined) in a separate refining station for ferrosilicon.

The consumable front plug has a guaranteed lifetime of minimum 20 heats. However, lifetimes 4 times this figure have been achieved, particularly in silicon refining. The exchange of the consumable front plug is done by pulling out the complete plug when the ladle is in the tilted position. A new ceramic front plug is fixed and the Tinject plug is reinstalled.

HEAT BALANCE

Experience shows that there is sufficient heat evolution during refining for Tinject to be self sufficient with energy. The temperature is often observed to increase during refining of ferrosilicon due to the exothermic reactions taking place. As a too high metal temperature may increase the refractory wear and shorten the lifetime of the ceramic front plug as well, some kind of cooling should be considered. Refining of ferrosilicon with high contents of Al and Ca, generates sufficient heat to melt up to 10 % ferrosilicon fines as coolant. Refining of silicon generates surplus energy as well. 8-10 % silicon fines has been recycled during continuous

tapping of silicon. This conversion of fines to first class lumpy material represents an added value to the production.

Due to the radiation loss from the bath surface a lid is strongly recommended during continuous tapping of silicon in order to minimise the total heat loss. The heat loss has been calculated to correspond to as much as 60 - 90 % of the total amount of heat released from oxidation during a two hour continuous refining period.

Continuous tapping of a 12 MW silicon furnace, with a tapping rate of 13-15 kg pr. minute, has been carried out successfully. This tapping rate is, however, considered to be in the lower range of what is possible without running into freezing problems or scull formation in the ladle. However, there is no problem refining silicon from a small furnace being tapped *discontinuously*.

The silicon temperature should preferably not drop below 1450-1470°C. Fig. 4 shows the weight of an empty silicon ladle during two weeks of operation. In this case the temperature was measured to 1450°C during the first taps and some scull formation occurred. This is shown as a weight increase of the empty ladle. As the temperature increased to 1470°C the sculls gradually melted.

Fig. 5 shows a typical temperature development during refining of silicon metal. In this case the furnace was tapped semicontinuously. The temperature rise during the first 25 minutes of operation is due to the heat of reaction as Al and Ca are being oxidized. The temperature loss, or the use of fines as coolant, normally brings the temperature down to 1450-1470°C which is a suitable temperature before casting.

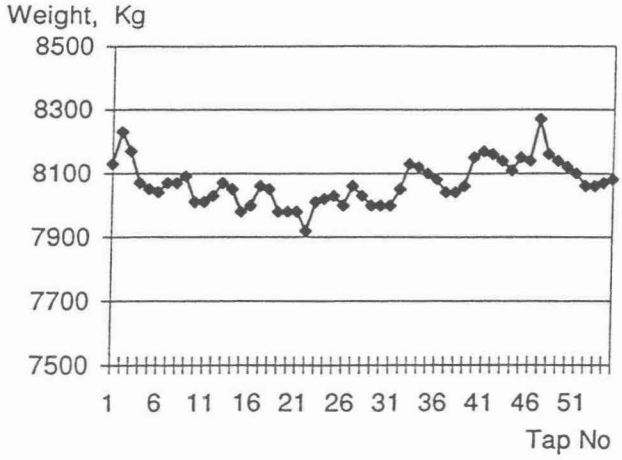

FIG. 4. Weight development of an empty silicon ladle during two weeks.

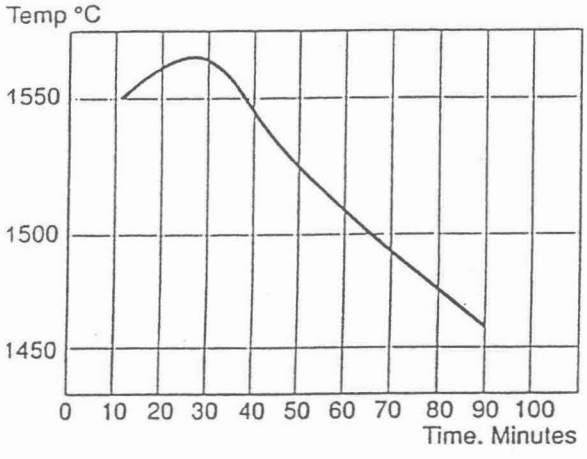

FIG. 5. Temperature development when refining silicon.

Our general experience is that surplus heat is available during refining of silicon. The amount of surplus heat varies from furnace to furnace and may vary from one day to the next as well. A variation in tapping rate between 20-60 kg pr. minute has been observed one day, whereas a stable tapping rate of 30-35 kg pr. minute was observed the next day. This means that the

metal flow and the tapping temperature may influence the heat balance significantly. A significant increase in the metal temperature may increase the refractory wear.

Tinject is in principle applicable to any furnace applying ladle tapping. The prevailing heat balance should however be carefully examined. The ladle dimensions for silicon refining should be adjusted to the size of the furnace and the tapping stream flow rate measured in order to balance scull formation and lining wear.

A useful guiding relationship seems to be the tapping rate (q = kg/minute), versus the bottom area of the ladle. A suitable inner diameter (ϕ = mm) of the ladle bottom used for continuous tapping of silicon may be expressed as:

$$\phi = 2 \cdot \sqrt{\frac{a + b \cdot q}{\pi}} \quad , \quad \text{where a = 135000 and b = 32500} \qquad (5)$$

The heat loss depends on tapping time, shape of the ladle, type of refractory and insulation. Normally, a high alumina refractory material is recommended for Tinject. Other refractory materials have also proved successful. However, graphite materials do not work together with Tinject! Refractory lifetimes in the range of 400 - 600 taps have been experienced, even 800 have been recorded. In general we have experienced the same lining life after having Tinject installed compared to the situation without refining. Sometimes the lifetime has increased.

METAL ANALYSES

Ferrosilicon with aluminium levels in the range of 1.0 - 2.5 % Al as tapped, has been refined down to 0.05 % Al. The corresponding range of calcium is 0.3 - 1.0 % Ca as tapped and 0.01 - 0.02 % Ca as refined. Some magnesium and carbon are also removed.

There has been a tendency towards lower levels of Al and Ca in refined ferrosilicon during the later years. At most, we have been down to a level of about 0.02-0.03 % Al. The 0.05 % Al level is however the lowest *guarantee* we have given. Besides, the question of low aluminium and calcium is also a question of silicon yield! Normally the silicon yield is about 95-99 % of the silicon units being tapped from the furnace.

Silicon, having calcium levels in the range of 0.3 - 1.0 % Ca as tapped, has been refined down to 0.01 % Ca. Even refining of silicon from 1.6 Ca % down to 0.02 % has been demonstrated. The aluminium content of silicon as refined is normally preferred to be in the range of 0.1 - 0.2 % Al.

Some years ago the silicon producers mainly focused on the aluminium content only without paying much attention to calcium. Since 1990 the silicon producers have been mainly concerned with lowering the calcium content while keeping aluminium at a stable and moderate level.

Fig. 6 and 7 show some analyses of calcium and aluminium respectively in ferrosilicon during one week of operation. Dashed lines refer to the analyses as tapped and continuous lines refer to the analyses as refined.. The calcium content as tapped was easily lowered to 0.01 % Ca. During this period the aluminium content as tapped was relatively high and varying.

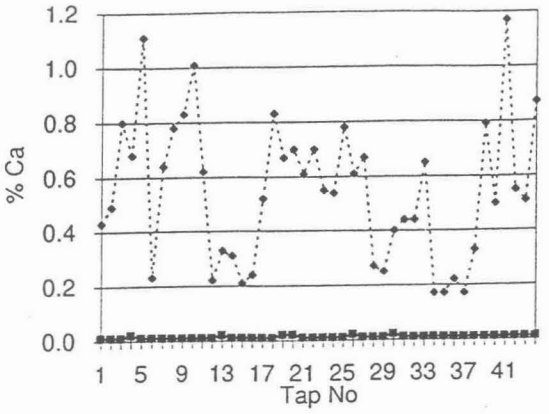

FIG. 6. Ca analyses of ferrosilicon as tapped(dashed) and as refined.

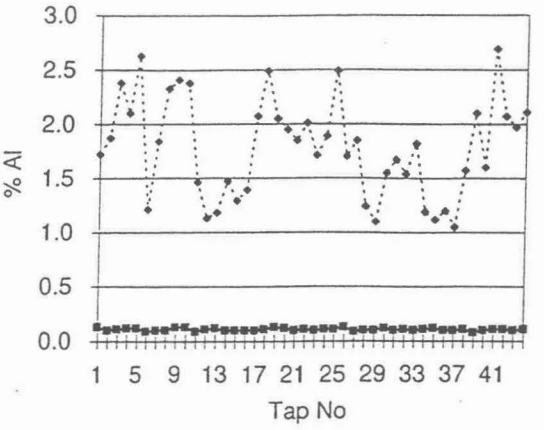

FIG. 7. Al analyses of ferrosilicon as tapped (dashed) and as refined.

Nevertheless,a stable level of about 0.1 % Al was reached after refining in a separate refining station after tapping. Titanium, phosphorus and iron are not influenced significantly during Tinject refining, while magnesium is lowered from 0.04 to 0.02 % Mg.

Fig. 8 and 9 show some analyses of calcium and aluminium respectively from the refining of silicon. The calcium level as tapped tends to fluctuate between 0.4 - 0.8 % Ca, whereas the calcium level as refined stabilizes between 0.01-0.02 % Ca. The aluminium was stabilized in the range of 0.1 - 0.2 % Al, being brought down from 0.3 - 0.5 % Al as tapped. No significant change was observed for titanium or iron.

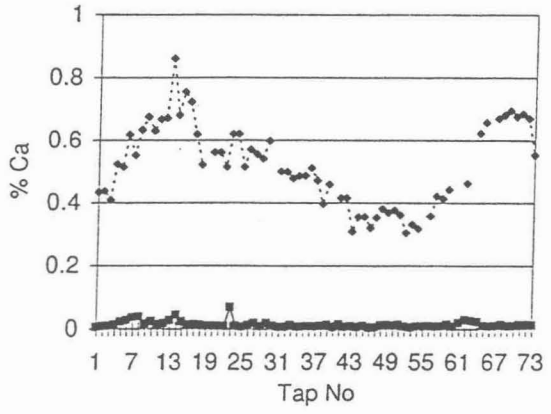

FIG. 8. Ca analyses of silicon as tapped (dashed) and as refined.

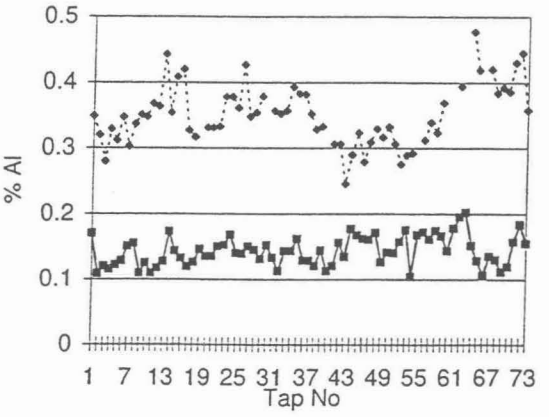

FIG. 9. Al analyses of silicon as tapped (dashed) and as refined.

The silicon level (% Si) is usually stable during refining of ferrosilicon, but may increase when refining ferrosilicon from high levels of aluminium and calcium. This is partly due to the weight reduction obtained as aluminium and calcium are oxidized and partly due to the exchange reactions (3) and (4) between silica sand and the elements to be refined. The relative silicon content (%Si) in silicon normally rises during refining, even when having a poor yield of silicon. Thus, a rise in % Si during refining is no criteria for a high silicon yield.

SLAG ANALYSES AND EQUILIBRIUM

It is absolutely necessary to create a slag with a chemical composition allowing the oxides of aluminium and calcium being formed to be picked up in the slag phase. When the oxide concentration of aluminium in the slag reaches a level being in equilibrium with the aluminium content in the metal, no more refining of aluminium will take place. The temperature also effects the equilibrium distribution between aluminium and aluminium oxide, according to Agev et al. [4]. This has been experienced with Tinject during refining of ferrosilicon to low levels of aluminium: The 0.05 % Al level is more easily reached at moderate temperatures.

The equilibrium distributions of aluminium and calcium between slag and metal, carried out by researchers, represent valuable information for refining operations. Figures 10 and 11, showing the isoconcentration lines for Al and Ca in ferrosilicon at 1550°C, are taken from a presentation by J. Kr. Tuset. [2]. Similar diagrams have been presented for silicon [3].

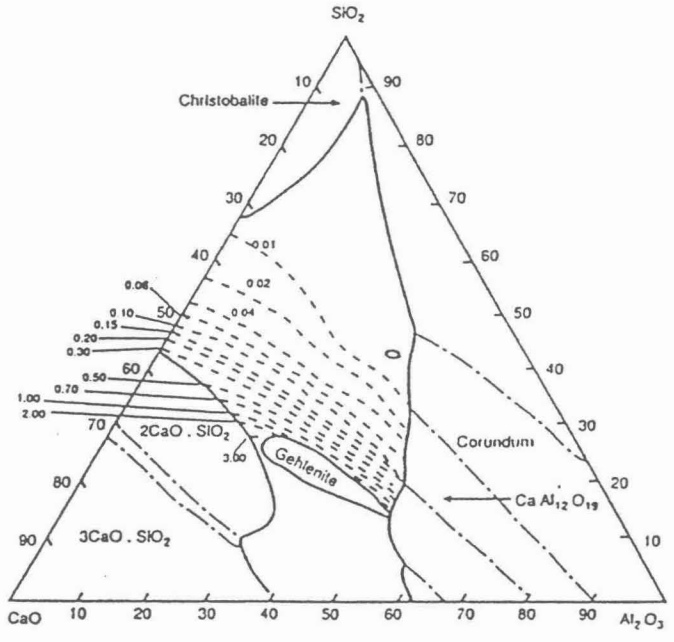

FIG.10.Isoconcentrational lines for Al in Fe75Si in equilibrium with $CaO-SiO_2-Al_2O_3$ slag. at 1550°C. Concentrations in weight % [2].

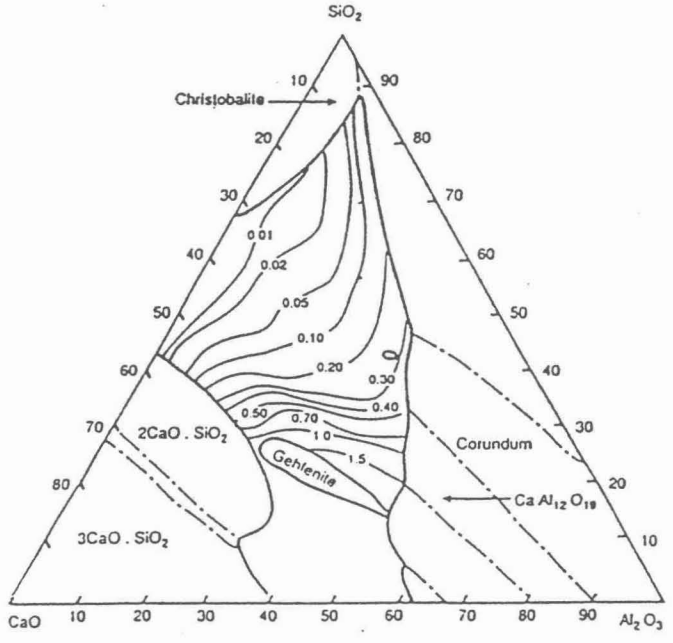

FIG.11.Isoconcentrational lines for Ca in Fe75Si in equilibrium with $CaO-SiO_2-Al_2O_3$ slags at 1550°C Concentrations in weight % [2].

Thus, the metal analyses of aluminium and calcium as refined depends on the initial amount of those elements in the metal as tapped and the amount of slag being used during refining. The amount of slag is normally adjusted by adding quartz sand, preferably 2-10 mm. Refining of ferrosilicon may require some use of lime or dolomite as fluxing agents, depending on the calcium content in the metal. Fluxing improves slag formation as well. The use of dolomite is observed to effect the Mg refining. Limestone has been used successfully instead of burnt lime. Fluorsbar may be used to obtain early slag formation, particularly when the metal temperature is low. As an alternative source of SiO_2, instead of adding quartz sand, SiO_2 could be created

by oxidizing silicon (5). The silicon yield will decrease, of course, and the bath temperature will rise. Thus, additional cooling may be necessary. Oxidation of Si can also be used as an energy source when having very low tapping temperatures.

$$Si + O_2 \Longrightarrow SiO_2 \qquad (5)$$

The slag materials should be added to the bath over some period of time, e.g. through a feeder, particularly when doing refining during tapping. Provided proper stirring in the bath, Tinject refining normally creates a siliceous and sticky slag that can easily be removed from the surface of ferrosilicon. The slag analysis, particularly the concentrations of Al_2O_3 and CaO, should be watched and slag analysis may have to be adjusted depending on the present metal analysis as tapped.

When refining silicon to low levels of calcium, the corresponding level of CaO in the slag may be so low that the slag will float on top of the silicon bath. This phenomenon is due to the low density of SiO_2 compared to the higher density of CaO. Acceptable separation of slag and metal has been obtained with a slag composition of approximately 69% SiO_2, 18% Al_2O_3 and 13% CaO giving a level of 0.026% Ca in the metal. When refining silicon to 0.01% Ca, we have sometimes experienced difficulties because of having a floating slag. A floating slag is in general very difficult to avoid being mixed with the metal during casting, causing slag inclusions in the silicon. A very thin slag layer may sometimes freeze and stick to the ladle wall as the silicon is being cast.

STIRRING AND KINETICS

In order to reach the theoretical equilibrium between metal and slag, an optimal kinetic situation is required. Kinetics means stirring in this context, which is found to be as important as the slag composition discussed above. «Proper stirring» is observed at the surface as an extensive «rolling around» of the melt without creating too much splashing.

Oxygen being injected into the bath is observed to react very fast and efficiently at the tip of the plug as Al, Ca, and Si are oxidised. -The injection of pure oxygen at a rate of 2 m^3n/minute into 8 tonnes of ferrosilicon containing 1.8% Al, causes hardly any visible circulation on the bath surface and the oxygen seems to be consumed totally. However, the vibrations of the ladle is felt and sounds like thunder coming from the inside of the vessel. This is observed as long as the contents of Al and Ca are above certain minimum levels. The absence of stirring led to the introduction of compressed air, or an inert gas, to improve the circulation of the liquid metal bath.

Stirring is vital for the silicon yield because the reactions between the metal and the created slag phases bring about a reduction of the produced SiO_2 through the reaction with Al and Ca. This becomes especially important when operating with top additions of slag forming materials. Tinject refining of ferrosilicon requires a considerably lower slag volume compared to the amount of slag used in the slag furnace process. -Typically, the amount of slag to be used for refining of ferrosilicon from 1.8% Al down to 0.6% Al was lowered by 70%, mainly due to a more optimal kinetic situation.

Tinject is normally operated with a mixture of oxygen and compressed air being adjusted to the size of the ladle and the refining situation: During refining of 8 tonnes of ferrosilicon at a separate refining station, 2.5-3.0 m^3n gas pr. minute has been blown through the bottom of the ladle. During refining of 2.5 tonne of silicon being tapped continuously, we have been blowing 200-250 litres pr. minute. Pure oxygen may also be used, bearing in mind the consequences of somewhat less efficient stirring. Refining may also be carried out with injection of compressed air only, as the balance of oxygen is picked up from the surroundings. About 20 - 70 % of the total oxygen consumed is observed to come from the surrounding air, depending on the amount of compressed air being used. However, oxygen is always recommended to be available, as a mixture of oxygen and compressed air is found to give the best operation of Tinject.

Some calcium analyses of silicon as refined have been compared to theoretical values presented by Tuset [3]. This comparison is shown in Fig. 12 as a function of the CaO content in a silica-lime-alumina slag. The content of silica and alumina (and other minor slag constituents as well) have been disregarded in this comparison. The calcium analyses from practical operations came out at about the same level as the theoretical values. The low levels of calcium (0.01-0.03% Ca) were reached from calcium levels as tapped between 0.8-1.6 % Ca.

The circulating metal bath also acts as an effective coolant for the tip of the plug which is protected by a mushroom of frozen SiO_2 and metal being formed during refining. The size of this mushroom depends on the metal temperature, the stirring of the bath and the flow of oxygen and air. A suitable size is about ϕ100 mm in diameter and a height of about 150 mm.

Good stirring further provides a more homogeneous bath temperature showing a favourable effect on scull formation inside the ladle. Thus, the ladle lining is kept clean at relatively low metal temperatures and a reduced demand for jack hammering has been observed. During periods having low tapping temperatures or long tapping times the bath stirring enables a more flexible operation. Thus, it has been found profitable to operate Tinject just in order to reduce scull formation and improve operation flexibility without specifically aiming at low levels of aluminium and calcium.

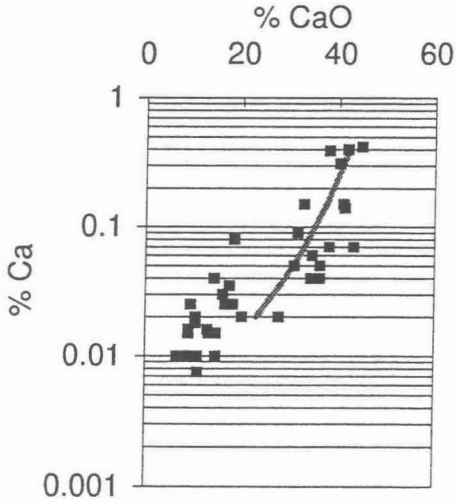

FIG.12.The relation between Ca in the silicon and CaO in the slag.
Square = Tinject refining.
Line = J. Kr. Tuset [3]

Item	Unit	Amount	USD pr. unit	Value
Ferrosilicon as refined	tonne	0.975	600	585.00
Scale premium	%	2.50	8	20.00
Losses	%	2.00	-6	-12.00
SUM SALES VALUE				593.00
Ferrosilicon as tapped	tonne	1.000	550.00	550.00
Ceramic front plug	plug	0.007	160.00	1.12
Silica sand	tonne	0.075	25.00	1.88
Lime	tonne	0.005	180.00	0.90
Oxygen	m3n	1.500	0.30	0.45
Compressed air	m3n	12.000	0.07	0.84
Misc. spare parts				0.40
SUM PRODUCTION VALUE				555.59
Net profit operation:				37.42
SUM PROFIT AND COSTS				593.00

TABLE 1. Operating costs based on Tinject refining of 7.5 tonnes Fe75Si taps.

OPERATING COSTS

The operating costs are estimated to be about USD 5 pr. tonne. This includes consumption of Tinject plugs and Tinject spare parts, slag forming material and gas. In Table 1 the operating costs for a 7.5 tonne ferrosilicon tap has been calculated to USD 5.59 pr. tonne, assuming a fairly high consumption of slag due to the high level of aluminium as tapped (1.8 % Al). The silicon content is expected to increase by about 2.5%, mainly due to the removal of aluminium and calcium, giving a scale premium of USD 20 pr. tonne. Losses are assumed to be 2 %. Assuming a sales price of refined ferrosilicon being USD 50 pr. tonne higher than for standard ferrosilicon, a net profit operation of USD 37.42 pr. tonne is obtained. Using ferrosilicon fines as coolant usually improves this margin.

CONCLUSION

The Tinject system has been installed and operated under a variety of refining conditions, and has proved to satisfy the requirements as to reliability, efficiency and flexibility.

Successful refining of aluminium, calcium, magnesium and carbon requires correct slag composition and efficient stirring. The economic value of reduced scull formation, lower casting temperatures, conversion of fines and better operation flexibility must be taken into account.

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