KAMATA, R., KIZU, Y., and TSUJIMURA, H. The production of special SiMn using the Gas and Powder Injection Process. *INFACON 6. Proceedings of the 6th International Ferroalloys Congress, Cape Town.* Volume 1. Johannesburg, SAIMM, 1992. pp. 139–143.

The Production of Special SiMn Using the Gas and Powder Injection Process

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The slag produced during the refining of high-carbon ferromanganese usually contains 20 to 30 per cent manganese. Several methods have been tried in the past to recover this manganese. However, there were various problems associated with these methods: use could not be made of the thermal energy in the molten slag, and the manganese recovery rate was low, etc. The Gas and Powder Injection Process was developed by Nippon Denko to solve these problems. In this process, ferrosilicon and/or silicon metal are added to the molten slag held in the ladle and are stirred by the injection of a large quantity of nitrogen, or some other inert gas, at a high flowrate from a lance immersed in the slag. Silicomanganese is thus produced by a silicothermic reaction.

The Tokushima Works of Nippon Denko are producing low-phosphorus, low-carbon silicomanganese directly from molten slag by this process.

Introduction

The slag produced during the refining of high-carbon ferromanganese contains 20 to 30 per cent manganese. In general, the following two methods are used for the recovery of this manganese.

(1) The solidified slag is crushed and screened, and is melted in an electric furnace. Manganese is reduced by carbon, and is recovered in the form of a silicomanganese metal.

(2) Ferrosilicon and/or silicon metal are added to the molten slag, the slag is stirred, and manganese is recovered in the form of silicomanganese by a silicothermic process.

The first method is simple technologically and is the method most commonly used, but it does not allow the utilization of the thermal energy contained in the molten slag.

The second method is superior to the first from the point of view of efficient energy usage. Various processes such as the shaking-ladle process, reladle process, and other methods, which differ primarily in the method of stirring the molten slag, have been proposed. However, the technologies used in these methods all embody one or more of the following problems.

(1) Owing to insufficient mixing of the molten slag with the silicon metal, the manganese recovery rate is low, and a high proportion of manganese remains in the slag and must be discarded.

(2) The amount of thermal energy becomes insufficient because the process requires a long reaction time. It therefore becomes necessary to provide a secondary supply of heat (e.g. by heating of the silicon metal and causing it to melt before being added).

(3) Wave motion in the molten slag in the ladle during mixing makes it impossible to increase the amount of material processed at one time.

In order to solve these problems, Nippon Denko developed the 'Gas and Powder Injection Process'. By means of this process, it has become possible to produce silicomanganese efficiently from high-carbon ferromanganese slag with a high manganese recovery rate, and with almost no provision of external heat. The silicomanganese produced in this way is extremely low in phosphorus and carbon.

An outline of the process as established and operated satisfactorily by Nippon Denko at its Tokushima Works is presented below.

Production Method

High-carbon ferromanganese slag (referred to as 'H slag') tapped from an electric furnace is conducted into a ladle for refining purposes. Ferrosilicon and/or silicon metal are added as the reducing agent, together with a flux when it is necessary to adjust the basicity of the slag. The slag is then stirred by the injection of nitrogen or some other inert gas, and silicomanganese is produced as the result of a silicothermic reaction. The reducing agents are added to the molten slag by means of a chute, and the flux is injected into the molten slag using the gas as carrier. Burnt lime in powder form is generally used as the flux.

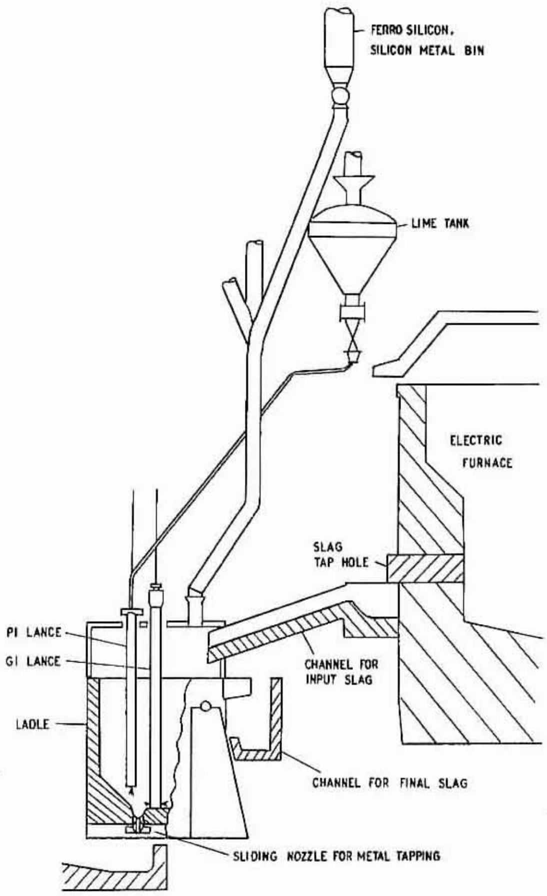

FIGURE 1. Equipment for the Gas and Powder Injection Process

Equipment

The equipment used is shown in Figure 1.

Ferrosilicon and silicon metal

Three 4 m^3 bins contain the ferrosilicon and silicon metal. The amount to be introduced into the slag is adjusted according to the mass measured by the load cells attached to the bins. The bins are discharged by means of a roll feeder, and the discharged metal is conducted along a chute into the ladle.

Flux

One 6 m^3 tank contains the flux. The amount to be introduced is adjusted according to the mass of a load cell attached to the tank. The discharged flux is conducted along a flexible chute, together with the carrier gas, and is injected into the molten slag within the ladle through the powder-injection lance.

Lances

The lances for both gas injection (GI) and powder injection (PI) are covered with refractory material. The total length of the GI lance is approximately 5 m, and the lance has two holes facing sideways on its forward edge. The PI lance has a total length of approximately 4 m, and has one downward-facing hole on its forward edge.

Electric furnace

The electric furnace is a closed-type submerged-arc furnace with a 40,5 MVA transformer. It has two tapholes, one for metal and one for slag. The H slag discharged from the taphole into the slag pool is supplied to the ladle after the coke that is discharged at the same time has been removed.

Refining ladle

The ladle, which is lined on the inside with refractory material, is capable of holding approximately 20 t of slag. The contents of the ladle are discharged through a sliding nozzle.

Changes in lance and ladle refractory

As the cost of the refractory accounts for a large proportion of the refining costs, various materials were tested in order to reduce this expense. A summary of changes in lance refractory is shown in Table I, and a summary of changes in ladle refractory in Table II.

TABLE I
CHANGES IN LANCE REFRACTORY

Step	Refractory
1	Al_2O_3–MgO castable
2	Al_2O_3–MgO–SiC castable
3	High-Al_2O_3 castable

TABLE II
CHANGES IN LADLE REFRACTORY

Step	Refractory
1	MgO–CaO brick
2	High-Al_2O_3 castable
3	MgO–C brick

Refining Method

Raw materials

Representative compositions of the ferrosilicon, silicon, metal, and lime used in the process are shown in Table III.

TABLE III
ANALYSIS OF RAW MATERIALS

Material	Si %	C %	P %	Fe %	CaO %	Size mm
Ferrosilicon	74	0,2	0,02	22		0 – 10
Silicon metal	97	0,05	0,008	0,5		0 – 10
Lime		0,15	0,008		97	0 – 1

TABLE IV
REFINING SCHEDULE

Time, min (0 – 16 min)	Duration
Slag input	5 min
Si charge	3,5 min
Gas injection	6 min
Powder injection	4 min
Separation	5 min

Refining schedule

A representative refining schedule for the process is shown in Table IV.

After GI has been completed, the mixture is allowed to settle for approximately 5 minutes, and is then tapped after the slag has been separated from the metal during settling.

Conditions of injection

Representative injection conditions for the process are shown in Table V.

TABLE V
CONDITIONS OF INJECTION

Parameter	GI	PI
Gas pressure, kg/cm^2	5 – 6	6 – 7
Gas volume, Nm^3/min	7 – 12	2 – 4
Gas speed, Nm/s	1200 – 2200	
Ratio of powder/gas (mass)		50 – 300

Results

Refining

The silicomanganese produced by this process has far lower phosphorus and carbon contents than the silicomanganese produced in an electric furnace. Some production examples are shown in Table VI.

In example 1, ferrosilicon is added to the H slag, and GI is carried out while lime is injected by PI. Silicomanganese with a silicon content of 12 per cent is produced.

In example 2, both silicon metal and ferrosilicon are added to the H slag, and GI is carried out concurrently with lime addition by PI. Silicomanganese with a silicon content of 18 per cent is produced.

In example 3, silicon metal is added to the H slag and only GI is carried out; silicomanganese with a silicon content of 22 per cent is produced. In this example, because the basicity of the H slag is comparatively high and the silicon grade of the metal produced is also high, it is unnecessary to control the basicity by the PI of flux.

The phosphorus content in all of the above examples is around the 0,01 per cent level, which is far lower than that of any material produced in an electric-furnace process.

Manganese and Silicon Yield

The main reducing reaction that takes place in the ladle is given by

$$2\,MnO + Si \rightarrow 2\,Mn + SiO_2. \qquad [1]$$

The manganese content of the slag produced when refining has been completed (when reaction [1] has reached equilibrium) is determined from the silicon content of the metal produced and the basicity of the slag generated. Formula [2] is used in the calculation of the basicity:

$$B = \frac{(CaO) + 1{,}39(MgO)}{(SiO_2)}, \qquad [2]$$

TABLE VI
PRODUCTION EXAMPLES

Ex.	Component		Analysis (%)							Quantity kg/batch
			Mn	SiO_2	CaO	MgO	Si	C	P	
1	Input	Hslag	24,5	25,3	23,1	5,4		0,008	0,003	19 270
		FeSi					74,2	0,217	0,018	1 730
		Lime			97,8			0,148	0,007	1 070
	Output	Metal	76,1				12,3	0,187	0,018	3 870
		Slag	9,6	35,9	30,2	5,7				18 200
2	Input	Hslag	26,3	25,5	20,5	3,2		0,005	0,003	17 640
		Si metal					97,1	0,048	0,006	1 180
		FeSi					73,7	0,189	0,021	1 040
		Lime			97,4			0,162	0,010	1 350
	Output	Metal	76,6				17,8	0,122	0,014	4 850
		Slag	5,5	40,0	30,1	3,4				16 380
3	Input	Hslag	21,6	26,2	26,4	3,5		0,010	0,003	19 030
		Si metal					97,5	0,063	0,008	2 180
	Output	Metal	76,1				22,4	0,055	0,012	4 800
		Slag	2,8	42,5	30,6	4,1				16 420

where B represents the basicity of the slag,

(CaO), the CaO content of the slag,

(MgO), the MgO content of the slag, and

(SiO_2), the SiO_2 content of the slag.

The relationship between the manganese content of the slag, the silicon content of the metal, and the basicity of the slag obtained in approximately 500 refining runs is shown in Figure 2. The regression formula is

$$(Mn) = -6{,}9[Si]^{0{,}5} - 8{,}1\ B + 42{,}1, \qquad [3]$$

where (Mn) represents the manganese content of the slag produced,

[Si] is the silicon content of the metal produced, and

B is the basicity of the slag produced.

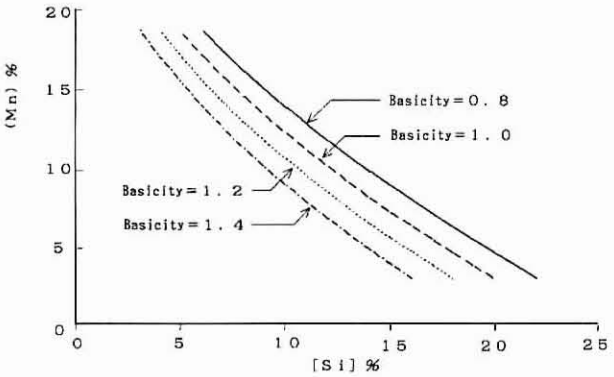

FIGURE 2. Relationship between (Mn) in slag and [Si] in metal

A comparison of the results of refining by this method with those obtained by other methods is shown in Table VII.

The manganese content of the slag produced by the Gas and Powder Injection Process is lower than that of slag produced by the former methods, owing to the strong stirring during the process. The manganese yield achieved is high.

The silicon efficiency ratio is defined as

$$A = \frac{0{,}256 \times Mo + So}{Si} \times 100 \text{ (expressed as \%)} \qquad [4]$$

where A represents the silicon efficiency,

Mo, the amount of Mn that is transferred to the metal reduced from H slag,

So, the amount of Si that is transferred to the metal, and

Si, the amount of Si inserted.

The silicon efficiency ratio of the method approaches approximately 95 per cent. This means that, of the total amount of silicon added, 95 per cent contributes to the reduction of MnO or is transferred to the metal produced.

Change in Temperature and Heat Balance

Examples of the change in temperature during refining are shown in Figure 3.

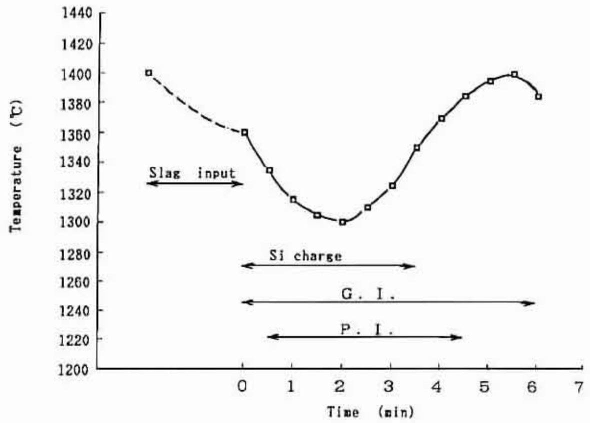

FIGURE 3. Change in temperature during refining

The temperature of the molten slag during refining drops initially because of the the addition of silicon metal at room temperature and the PI of the flux. It increases with the progress of the silicothermic reaction, and then decreases again owing to the radiation of heat after the reaction has reached equilibrium.

The heat balance for this example is shown in Figure 4. The heat of reaction and the heat of formation of the slag and metal serve to preserve the latent heat of the raw materials, the sensible heat of the gas, and the radiation.

As the refining time is short, the amount of heat radiated is small, which makes it possible to introduce the silicon metal and flux at room temperature.

Refractories

Lifetime of ladle inner-lining bricks

The area of the ladle inner-lining bricks that exhibits the heaviest corrosion is the slag line at the time of refining. If a certain thickness of brick remains in other areas, the corroded area is repaired with castable and re-used. When the average remaining thickness of the inner-lining bricks has been reduced to approximately one half its value at the time the ladle was put into operation, the ladle is regarded

TABLE VII
COMPARISON OF REFINING RESULTS

Process	Mn in final slag, %	Si in metal, %	Basicity	Mn yield, %
GI, PI process	4,3	18,8	0,94	84
Shaking-ladle process	9,5	18,8	0,95	66
Re-ladle process	16,1	18,8	0,94	39

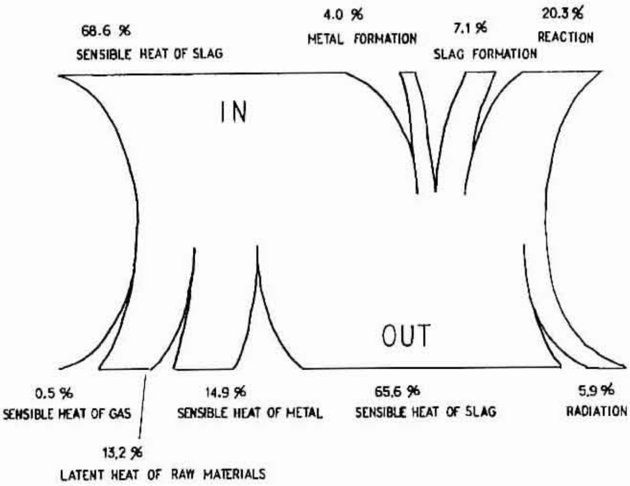

FIGURE 4. Heat balance

as having reached the limits of usability, and is relined. The average time a ladle can be used before relining is that for approximately 400 heats, with repairs being carried out once or twice during this period. Corrosion is limited to the side areas of the ladle, and hardly any erosion of the bottom lining occurs. The average loss of refractories per heat is approximately 22 kg.

Lifetime of GI lance castable

The part of the GI lance castable that undergoes the severest corrosion is the area that is immersed in the slag at the time of refining. When the thickness of the remaining castable has been reduced to half its initial value when the lance was first put into operation, it is considered to have reached the limits of usability, and repair work is carried out. A lance can be used for approximately 12 heats, and the average amount of material lost per heat is approximately 25 kg.

Conclusions

(1) It is possible to produce silicomanganese without external heating by the addition of ferrosilicon and/or silicon metal to molten ferromanganese slag, and vigorous stirring by means of gas injection.

(2) The silicomanganese produced in this way can have a phosphorus content of 0,02 per cent or less and a carbon content of 0,1 per cent or less, provided that suitable grades of ferrosilicon and/or silicon metal and suitable production conditions are used.

(3) There is a correlation between the manganese content of the generated slag, the silicon content of the metal produced, and the basicity of the slag generated. The regression formula for this correlation is

$$(Mn) = -6{,}9[Si]^{0,5} - 8{,}1\,B + 42{,}1,$$

where (Mn) represents the Mn content of the slag produced,

[Si], the Si content of the metal produced, and

B, the basicity of the slag.

(4) Approximately 95 per cent of the silicon added in the process contributes to the reduction of MnO or is transferred to the produced metal.