RECENT TECHNOLOGICAL DEVELOPMENTS

IN LOW AND MEDIUM CARBON

FERROMANGANESE MANUFACTURING

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INTRODUCTION

The 1st Energy Crises brought with it demands for reduced electricity consumption and, in response, the Mizushima Ferro Alloy Company introduced the energy-saving shaking ladle (often abbreviated as SL) method in 1978 for the production of medium and low carbon ferromanganese.
However, electricity costs skyrocketed even further with the onset of the 2nd Energy Crises in 1979. Here, in order to reduce our dependence on electricity, we opened a shaft-type smelting-furnace (often abbreviated as SF) shop in 1984 for the production of high carbon ferromanganese. This type of furnace does not require electricity as a main process input and is well suited to low cost production.

Even after the start-up of the shaft furnace, we continued making medium and low carbon ferromanganese by desiliconization at the shaking ladle from silicomanganese made in the No. 2 Electric Furnace. However, such a process is partially dependent on an electric furnace just as before and, with the recent appreciation of the yen, we found ourselves losing international competitiveness. We thereby embarked on an investigation of new manufacturing methods different from the conventional direct decarburization method.

In April 1987, our efforts were rewarded with the introduction of a new direct decarburization method using low-cost high-carbon ferromanganese from the shaft furnace as a raw material. The most conspicuous feature of this new process is the combination of conventional shaking with diluted oxygen blowing of oxygen and inert gas.

Generally speaking, decarburization of high carbon ferromanganese progresses smoothly down to about 2.5% carbon. However, below 2.5% carbon, the preferential oxidation of manganese becomes more pronounced and the oxygen utilization efficiency for decarburization thereby drops considerably. Here, by appropriate shaking at appropriate times, the decarburization efficiency and the manganese recovery can be increased. Still, the oxygen utilization efficiency for decarburization decreases steadily as the carbon content lowers. At low carbon contents of 2% and below, the decarburization reaction will be difficult to progress unless high temperature refining (blowing) is performed at 1800°C or above. While such high temperature refining is of course possible, one pays the price with drastically shortened ladle refractory life.

The dilute oxygen blowing process which we developed can make low-cost 0.5% C low carbon ferromanganese at temperatures below 1800°C.

TEXT

1. Manufacturing methods for medium and low carbon ferromanganese by decarburization

Figure 1 presents well known decarburization-based manufacturing methods for medium and low carbon ferromanganese.

(1) UCC Method

The UCC Method was developed by Union Carbide of the United States. It features top blown oxygen refining and has a manganese recovery of about 80%.

(2) G.f.E. Method

The G.f.E. Method was developed by Geselshaft fur Electrometallurgie of West Germany. It utilizes bottom-blown jacket gas nozzles and decarburizes at 1650 to 1900°C. Oxidized manganese phases are reduced with additions of lime and ferrosilicon.

Managanese recovery is reported to be 91.8%.

(3) Creusot - Loire Method

This method was developed by Creusot - Loire of France. This method controls the reaction temperature to 1650 to 1750°C by blowing in oxygen, steam and inert gas through the bottom. Manganese oxides in the slag are reduced after refining by additions of Fe-Si, Si-Mn, etc.

The manganese recovery of this method is 91.5%.

(4) Japan Metals & Chemicals Method

This method was developed by the Japan Metals & Chemicals Co., Ltd. of Japan. Oxygen is blown through the top and inert gases (argon gas, carbon dioxide, and nitrogen) are blown through the bottom. Refining is carried out in the temperature range of 1600 to 1830°C. Manganese in the slag is recovered by injecting silico-manganese, silicon metal, aluminum and flux into the furnace through the bottom.

Overall costs with this method are 10% lower than those for the conventional electric furnace method or the bottom-blown refining method.

2. Investigation of our new manufacturing method

(1) Theory

(1)-1 Decarburization reaction

There are two major reactions involved in the decarburization of high carbon ferromanganese. One of these reactions is the decarburization reaction [1] and the other is manganese oxidation reaction [2].

$$C + 1/2\ O_2 = CO \qquad [1]$$

$$Mn + 1/2\ O_2 = (MnO) \qquad [2]$$

From Reactions [1] and [2], we can obtain Reaction [3] which describes the equilibrium between C and Mn. The Gibbs Free Energy ($\triangle G$) of Reaction [3] can be obtained from thermodynamic tables and is also presented below.

$$(MnO) + C = Mn + CO \qquad [3]$$

$$\triangle G^\circ = 53{,}050 - 35.46\ T\ (cal/mole) \qquad [4]$$

The Equilibrium Constant (K) of Reaction [3] can be expressed as follows.

$$K = \frac{a_{Mn} \cdot p_{CO}}{a_{MnO} \cdot a_C} = \exp(-\triangle G^\circ/RT) \qquad [5]$$

Here, if we assume the activity of MnO (a_{MnO}) equals 1 and (%Mn) equals 75, then the activity of Mn (a_{Mn}) becomes 54.8%. Substituting this into [5] above, we obtain:

$$\frac{54.8 p_{CO}}{a_C} = \exp(-\triangle G^\circ/RT) \qquad [6]$$

Here we have an expression relating the temperature, (%C), and p_{CO}. (p_{CO} is the partial pressure of CO.) This relation is shown graphically in Figure 2.

From Figure 2, we see that medium carbon ferromanganese of 1.5 to 2% C can be made quite easily at 1700°C even with a p_{CO} of 1. However, for the low carbon ferromanganese with C of 0.7% or less which we intend to make, we see that at a p_{CO} of 1, a refining temperature of at least 1800°C is required. At such high temperatures, we would expect severe refractory erosion and much manganese vaporization.

Looking again at Figure 2, we see that this could be avoided if p_{CO} were able to be reduced to 0.5. In such a case, low carbon ferromanganese of 0.7% C could be made even at 1750°C.

Here, we decided to install diluted oxygen blowing equipment, with which p_{CO} can be reduced.

(1)-2 Mn vaporization

As described previously, high temperature refining is necessary for decarburization. However, manganese tends to vaporize fairly easily.

This has a considerable effect on yield.
Therefore, we also investigated the manganese vaporization rate and vaporization loss.

The vapor pressure of pure manganese (liquid) is given by the following equation.

$$\log P_o = -14{,}520/T - 3.021 \log T + 19.24 \qquad [7]$$

at 1600°C P_o = 40mmHg (0.053atm)

at 1700°C P_o = 84mmHg (0.111atm)

at 1800°C P_o = 166mmHg (0.218atm)

Approximating the activity a_{Mn} of manganese in high carbon ferromanganese as 0.77 (= a_{Mn} in a 75% Mn solution), the vapor pressure P_{Mn} of Mn in high carbon ferromanganese becomes:

at 1600°C P_{Mn} = 0.04atm

at 1700°C P_{Mn} = 0.09atm

at 1800°C P_{Mn} = 0.17atm

If we assume that gas coming out from the furnace is saturated with Mn vapor, then the following equation is valid:

$$P_{Mn} = \frac{(1)}{(1) + (2)}$$

(1) rate of manganese vaporization
(2) (CO + inert gas)

The rate of manganese vaporization does vary depending on the rate of oxygen supply and the oxygen utilization efficiency for decarburization. Therefore, it is difficult to determine quantitatively. However, if we take the rate of Mn vaporization to be 1 at 1600°C, then this rate becomes 2 at 1700°C and 5 at 1800°C.

Since the rate of Mn vaporization is so highly influenced by temperature, it is important to reduce the refining temperature in order to suppress Mn loss. Another approach is to refrain from excessive stirring in order to maintain a small contact area between the melt surface and the gas phase.

(2) New manufacturing method

- While one would like to reduce the refining temperature in order to discourage Mn vaporization, a certain minimum temperature is necessary in order to drive the decarburization reaction.
- Since the decarburization reaction becomes more and more dependent on the carbon transport rate as the carbon content decreases, stirring of the melt is necessary.
- From experiments with steelmaking BOF's, bottom gas blowing is effective in increasing reaction efficiency. However, Mn vaporization also increases.
- With steelmaking bottom-blown BOF's, the service life of the furnace bottom is quite short and there is a possibility of sudden breakouts due to severe tuyere erosion.

From the above considerations, we decided to stay with the shaking method as our means of stirring the melt. The focal point of the shaking equipment is a 140mm eccentric shaft which can be controlled at 0 to 48rpm.

The shake-stirring method and the previously described diluted oxygen blowing method are the two prominent features of our new manufacturing method.

3. Processing

The manufacturing process we use for medium and low carbon ferromanganese is shown in Figure 3.

The primary raw material for this process is high carbon ferromanganese made in the shaft furnace. This high carbon ferromanganese is tapped into a 15 ton capacity ladle and transported approximately 700 meters by trailer. The mean tap weight is 13.5 tons.

The high carbon ferromanganese is then poured into a 20 ton capacity shaking ladle. This shaking ladle has a shaking mechanism, is lined with magnesia-carbon refractory, and is designed so that both oxygen and dilute gas can be blown in during refining. This dilute gas can be either nitrogen and argon. For ferromanganese with a restriction on nitrogen content, argon is used. For ferromangaese with no such restriction, nitrogen is used (since nitrogen is the cheaper of the two). Oxygen, nitrogen and argon are all supplied to us by pipe from the Kawasaki Steel Mizushima Works.

Secondary material charging equipment can charge cold ferromanganese, metal scrap, fluxes and other additions during refining from a set of five hoppers. Off-gas and dust are collected and filtered by 6000 Nm3/min bag filters. The gas is not recovered.

The shaking ladle has a tilting mechanism. Metal is cast on the casting floor. Slag is collected in a slag pot during deslagging for subsequent processing.

4. Manufactured products

Medium and low carbon ferromanganese products manufactured by our company are shown in Table I.

M-0	Medium carbon ferromanganese (ASTM Specifications)
M-1	Medium carbon ferromanganese (C$\leq$ 1.5%) (JIS Specifications)
M-2	JIS No. 2 medium carbon ferromanganese
LP-2	Medium carbon ferromanganese (P$\leq$ 0.12%) (Kawasaki Steel Specifications)
L-0	Low carbon ferromanganese (ASTM Specifications)
LC-0	Low carbon ferromanganese (C$\leq$ 0.7%) (Kawasaki Steel Specifications)
LC-1	JIS No. 1 low carbon ferromanganese

Products M-0, L-0 and LC-0 have a specified manganese range of 80 to 85% and are made from ASTM high carbon ferromanganese. All other products have a specified manganese range of 75 to 80% and are made from JIS No. 1 high carbon ferromanganese.

5. Operating results

(1) Optimal shaking patterns

Figure 4 shows optimal shaking patterns determined from the results of numerous operating tests. Figure 5 shows the relation between the number of shaking revolutions and the Mn yied.

Looking first at the case for medium carbon ferromanganese in Figure 4, the carbon content is high at the start of the decarburization period and refining is carried out with a hard blow. Therefore, the stirring action from the lance oxygen jet alone is considered sufficient. Shaking is thereby unnecessary.

This is also true to a degree through the middle of the decarburization period. The carbon content at this time is about 2.5% and the oxygen utilization efficiency for decarburization is still high at nearly 80%. Therefore the decarburization reaction will proceed along smoothly without the need for any shaking.

However, we found that it is advantageous to shake for about 5 minutes toward the end of the decarburization period in order to mix together any layers that may have formed within the bath.

By the time one switches to a soft blow near the end of the final decarburization period, the carbon content has become quite low and the limiting factor in the decarburization reaction is the rate of carbon transport. From the aspect of product consistency, shaking is indispensable and should be carried out for about 10 minutes.

When producing low carbon ferromanganese, these shaking operations are carried out later in the decarburization period than is the case for medium carbon ferromanganese. The reason for this is that premature shaking will raise the refining temperature excessively and cause an increase in Mn vaporization and a decrease in refractory life.

When making either medium carbon or low carbon ferromanganese, additions such as FeSi, SiMn and flux are added after blow-off and shaking is performed for approximately 5 minutes. This is done in order to recover Mn from the slag.

The diluted oxygen blowing process itself is used only for making low carbon ferromanganese and only when the carbon content in the bath is 2% or less. In accordance with the drop in carbon content during refining, the oxygen flow rate is gradually decreased and the lance height is gradually increased.

Moving our discussion on to Figure 5, we clearly see that the optimal number of revolutions (rpm's) when shaking is 10 to 20. When stirring at an rpm below 10, the oxygen utilization efficiency for decarburization decreases and the amount of Mn in the slag increases (since the manganese becomes more likely to be oxidized as MnO). When stirring at an rpm above 20, the surface of the melt becomes exposed from under the slag and the amount of Mn vaporization increases (since the contact area between the bath and the air increases). As a result, the Mn recovery decreases and MgO elution from the bricks into the slag increases (since MgO equilibrium between the slag and the bricks is disturbed). This MgO elution can dramatically shorten refractory life and is to be avoided.

The shaking methods described here have raised our manganese recovery to 92% from the 85% typically obtained without shaking.

(2) Diluted oxygen blowing

Figure 6 shows the effect of diluted oxygen blowing on carbon content, oxygen utilization efficiency for decarburization, and refining temperature. We see that the oxygen utilization efficeincy for decarburization is about 40% at the start of blowing. It increases considerably upon the completion of the silicon oxidation reaction (at about 5% C) and stays around 75 to 85% until the carbon content drops to about 2.5%.

From there, however, the oxygen utilization efficiency for decarburization starts to fall dramatically. At 1.9% C, the usual blow-off point for medium carbon ferromanganese, the oxygen utilization efficiency for decarburization is only about 60%. Since the refining temperature for medium carbon ferromanganese production is limited to 1680 to 1700°C, one must continually charge cold ferromanganese once the carbon content goes below 3%.

When not utilizing the diluted oxygen blowing process, the oxygen utilization efficiency for decarburization continues to drop as the carbon content decreases down to about 0.5% C. When making low carbon ferromanganese, this utilization efficiency is only about 10% at the blow-off point. Furthermore, in order to drive the decarburization reaction further, one would have to raise the refining temperature up to around 1800 to 1840°C. Refractory life at such temperature is very short.

The diluted oxygen blowing process utilizes oxygen gas diluted with an inert gas (either nitrogen or argon). We experimented with dilution ratios (inert gas) / (oxygen + inert gas) of 20%, 40% and 60%. For all dilution ratios, the

oxygen utilization efficiency for decarburization was higher than for pure oxygen. Best results were obtained at a dilution ratio of 40%. We believe this is because the partial pressure of CO is still too high at a 20% dilution ratio, and the refining temperature is too low (and thereby refining takes a long time) at a 60% dilution ratio.

As mention before, diluted oxygen blowing is not carried out at carbon contents of 2% and above. This is because diluted oxygen blowing tends to slow down bath heating and thereby actually decreases the oxygen utilization efficiency for decarburization. This ends up lengthening the time required for refining.

From the considerations discussed above, our standard practice for diluted oxygen blowing is to blow with a dilution ratio of 40% when the carbon content is 2% or less.

Table II below presents results for test production of low carbon ferromanganese (LC-0) with and without diluted oxygen blowing.

From the table, we see that with the exception of a slightly longer refining time, diluted oxygen blowing is extremely beneficial even should one use high priced argon.

(3) Operating data

Table III presents operating data for LP-2 and LC-0, our two primary products, from April to September of 1988.

(3)-1 Molten high carbon ferromanganese is the primary raw material for both grades. 13.5 tons is charged for LP-2, and 13.0 is charged for LC-0. In order to raise production efficiency, high carbon ferromanganese cold-charge is also added when making LP-2. High carbon ferromanganese cold-charge is not added when making LC-0 since this makes refining time excessively long.

High carbon ferromanganese consumption units are 1,126 kg/t for LP-2 and 1,228 kg/t for LC-0.

(3)-2 Medium and low carbon ferromanganese cold charges are added when making both medium and low carbon ferromanganese each. Specifically, these charges are used to control the temperature during refining and to reduce the tapping temperature to 1600°C in order to preserve cast for casting.

(3)-3 Refractories in areas exposed to severe erosion are replaced when necessary. Refractory life is defined as the interval between replacement for these eroded sections. Refractories at other areas are not replaced as frequently.

(3)-4 Furthermore, since the price of Fe-Si was very high during this period, we did not use any silicon deoxidizing agents to recover Mn from the slag.

(4) Refractories

The shaking-ladle refractory-arrangement is shown in Figure 7. The inner course is composed of magnesia carbon brick, and the two outer courses are composed of magnesia brick and high alumina brick.

Note that the inner and outer courses are composed of different types of brick. The inner course serves to prevent leakage from erosion. The outer courses are made of insulating brick to protect the ladle shell from heat. The cover is protected with castable.

Initially, refractory life was only about 50 heats for even medium carbon ferromanganese production. However, at present refractory life is approximately 200 heats. This improvement was brought about by the following measures:

(4)-1 Improvements in materials properties of magnesia carbon brick
- Optimization of the fused magnesia ratio (to match the erosion line)
- Optimization of the carbon ratio
- Addition of oxidation preventive agents

(4)-2 Improvements in operating practices
- Optimization of slag composition
- Adoption of the self lining method
- Reduction of refining temperature and time

with the above measures, we were able to reduce refractory costs by 80% for cost of plan for medium carbon ferromanganese production. This has contributed much to reducing production costs.

6. Conclusion

In April 1987, we adopted a new direct decarburization method which works in place of the conventional electric furnace shaking ladle method. This new method utilizes shaking to stir the bath and diluted oxygen blowing to decarburize the bath at low carbon ranges. Compared to conventional methods, this method

is very economical and leads to a large reduction in costs.

(1) By shaking at appropriate times and at an appropriate number of revolutions, the manganese recovery has been increased by approximately 7% for the manufacture of medium carbon ferromanganese.

(2) By carrying out blowing with a 60% oxygen 40% inert gas mixture at low carbon ranges of 2% and below, the refining temperature can be lowered just as suggested by theory. By this, Mn recovery and refractory life are conspicuously improved for the manufacture of low carbon ferromanganese.

(3) Various improvements have greatly reduced refractory costs for the manufacture of medium carbon ferromanganese.

ACKNOWLEDGEMENTS

Our new direct decarburization method has allowed us to produce medium and low carbon ferromanganese economically and thereby regain our international competitiveness. Here, we would like to express our appreciation to the following organizations for their valuable assistance in relation to technical development and equipment design:

Kawasaki Steel Corporation
Steelmaking Research Section
Steelmaking Department
Engineering Department

Kawasaki Refractories, Ltd.

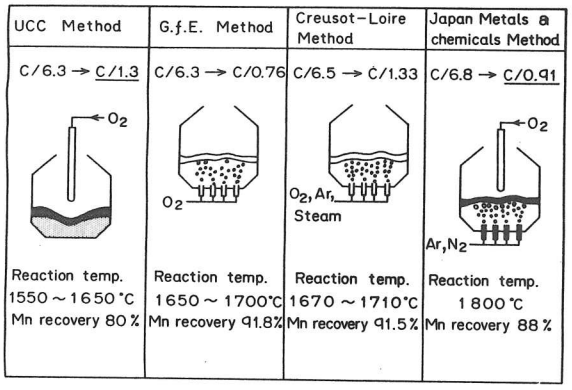

Fig. 1 Methods for medium and low carbon ferromanganese manufacturing using decarburization

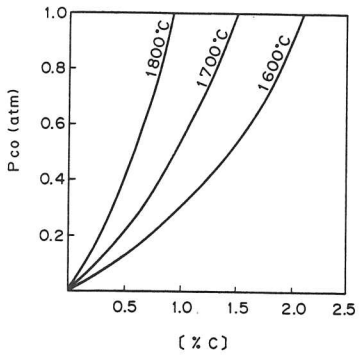

Fig. 2 Equilibrium relation between [% C] and Pco

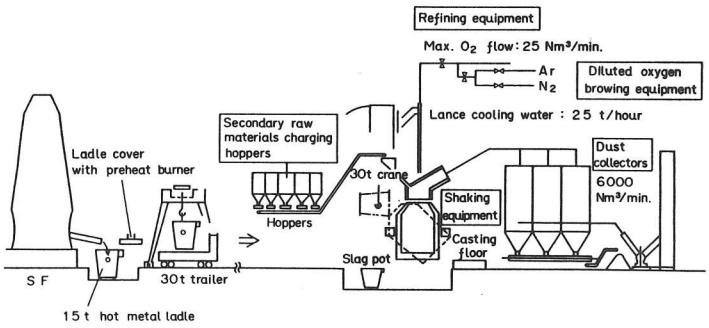

Fig. 3 Manufacturing process for medium and low carbon ferromanganese

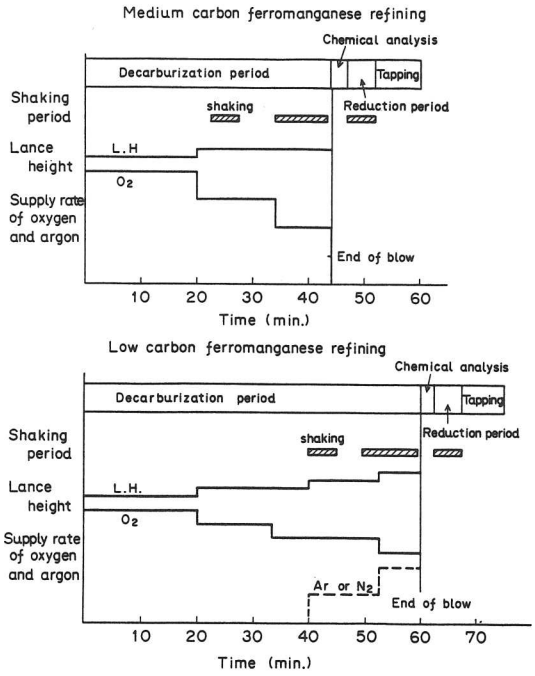

Fig.4 Optimal refining patterns

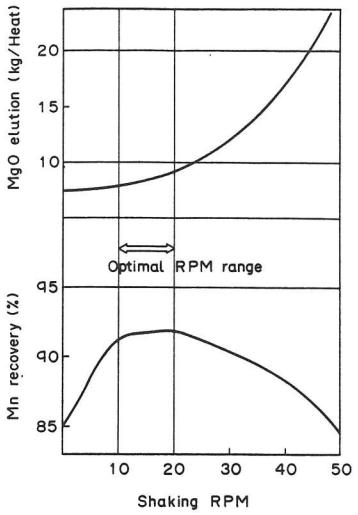

Fig.5 MgO elution and Mn recovery as affected by shaking RPM

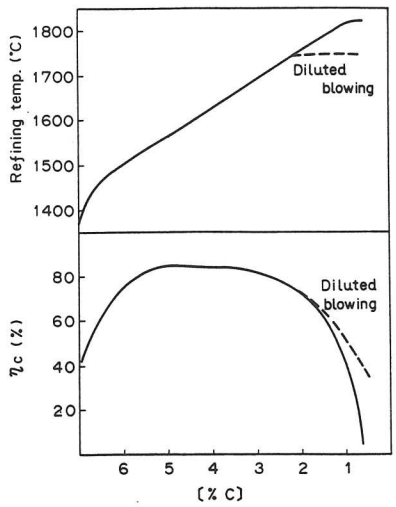

Fig.6 Relation between [% C] and oxygen utilization efficiency for decarburization

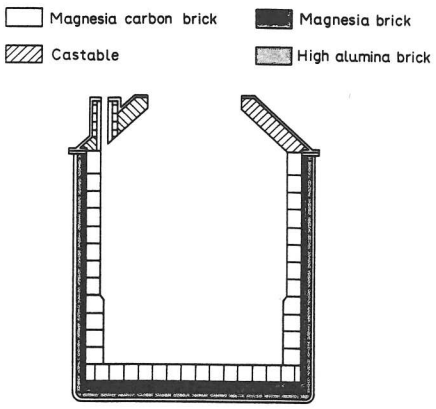

Fig.7 Refractory arrangement in shaking ladle

Table 1 List of specifications for medium and low cabon ferromanganese products

Type	Mizushima Ferroalloy Specifications	Corresponding JIS Specifications	Chemical composition				
			Mn (%)	C (%)	Si(%)	P (%)	S (%)
Medium carbon ferromanganese	M − 0	FMnM 0	80~85	≦ 1.5	≦1.5	≦0.40	≦0.02
	M − 1	FMnM 2	75~80	≦ 1.5	≦2.0	≦0.40	≦ 0.02
	M − 2		75~80	≦ 2.0	≦2.0	≦0.40	≦ 0.02
	LP − 2	FMnM 2	75~80	≦ 2.0	≦2.0	≦0.12	≦ 0.02
Low carbon ferromanganese	L − 0	FMnL 0	80~85	≦ 1.0	≦ 1.5	≦0.35	≦0.02
	LC − 0	FMnL 0	80~85	≦ 0.7	≦ 1.5	≦0.20	≦0.02
	LC − 1	FMnL 1	75~80	≦ 1.0	≦ 1.5	≦0.40	≦ 0.02

Table 2 Production test results for low carbon ferromanganese with and without diluted oxygen blowing

Item	Units	Without diluted oxygen blowing	With diluted oxygen blowing	
Refining time	min./heat	52	55	
Refining temp.	°C	1836	1754	
Oxygen utilization efficiency for decarburization	%	57	66	
Mn recovery	%	78	83	
Refractory life	heats	35	64	
Ar consumption	Nm^3/t	0	18	n=10

Table 3 Operating record for midium and low carbon ferromanganese production

Item	Units	LP−2	LC−0
High carbon ferromanganese			
Hot charge	kg/tap	13,550	13,070
Cold charge	kg/tap	1,070	0
Hot charge temp.	°C	1,368	1,365
Mn	%	74.53	78.21
Si	%	0.32	0.31
C	%	6.96	7.03
P	%	0.098	0.112
Medium cabon ferromanganese			
Production	kg/tap	12,980	10,640
Tapping temp.	°C	1,596	1,606
Mn	%	77.44	81.47
Si	%	0.25	0.23
C	%	1.86	0.66
P	%	0.106	0.132
Cold charge	kg/tap	1,880	3,540
Slag volume	kg/t	43	148
Dust quantity	kg/t	55	80
Oxygen consumption	Nm^3/t	75	110
Argon consumption	Nm^3/t	0	19
Refining temp.	°C	1,690	1,755
Refining time	min.	38.4	56.6
Shaking time	min.	15	18
Oxygen utilization efficiency for decarburization	%	75.3	68.4
Mn recovery	%	92.2	84.8
Refractory life	heats	236	73