Improvement of Production Process for Medium/Low Carbon Ferromanganese

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ABSTRACT

It has been over 30 years since Shenjia Ferroalloys Co. Ltd. started to produce medium/low carbon ferromanganese (hereafter abbreviated to MC FeMn). After many improvements, the current two-step pre-smelt process was adopted. The two steps are all done in shaking ladles. The first step is to react SiMn with MC FeMn slag of the previous heat which contains rich MnO, giving SiMn with low Si content. The second step is to react the SiMn from the first step with Mn ore and lime, giving SiMn with still lower content which is used for the production of qualified MC FeMn. Since the two-step process is an improvement over the previous one-step process, the emphasis of this paper will be placed on the problems relevant to the second step and the main improvement of technical and economical indexes after upgrading the production process

1. General condition of technology

Equipment for the process includes a 10000 kVA closed SiMn furnace, a 2200 kVA MC FeMn refining furnace, 2 shaking ladles and 1 rotary kiln to preheat Mn ores. Using these equipment, the process of pre-refining outside the furnace was brought into success in 1982[1], and on this basis the two step pre-smelt process was was developed in 1991. The flow sheet of process is shown below:

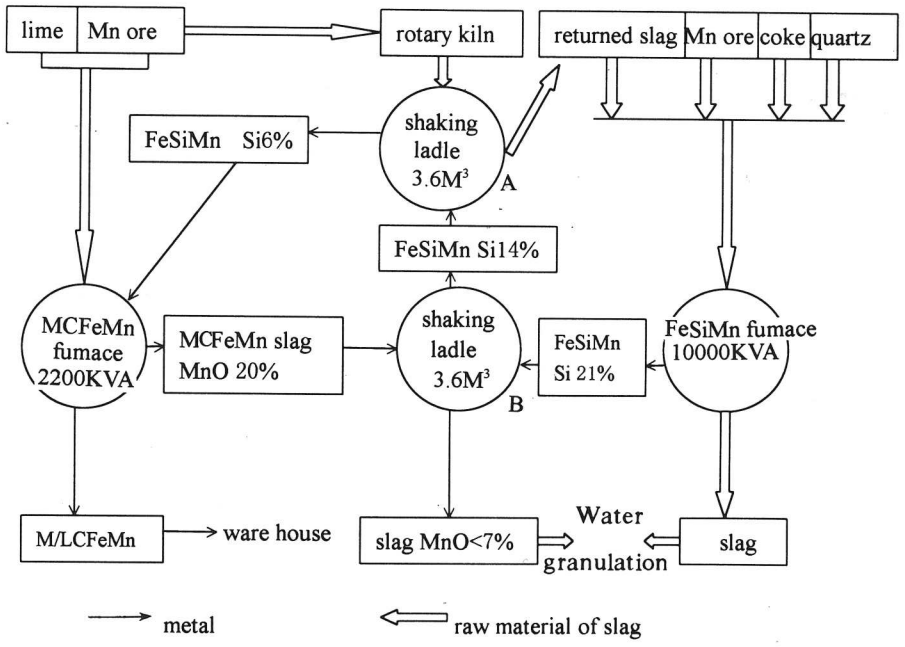

Fig.1 Flowsheet of two pre-smlet process

The first step is carried out as follows:

After tapping MC FeMn from the furnace, separate slag from alloy. The alloy is cast into moulds. The slag containing about 20% MnO is poured into shaking ladle A. After tapping SiMn from the furnace, separate slag from alloy. Treat the slag by

water granulation. Pour the liquid SiMn into shaking ladle A with MC FeMn slag inside, and then start the shaking. This is the first desiliconisation of SiMn with MC FeMn slag. After the first step, most of the Mn has been reduced and enter the alloy. The MnO in the slag is reduced from 20% to 7% or less. The Si in SiMn is reduced from 21% to 14%.

The second step is carried out as follows:

Add right amount of lime and Mn ore which has been preheated in rotary kiln into shaking ladle B. Then pour SiMn from the first step into B. After pouring, most of the Mn ore and lime will be molten, and then start shaking ladle B. After shaking for several minutes, Mn ore and lime will be molten completely, and the reaction will also end. After the second step, the Si in SiMn is reduced from 14% to 6% or so; part of MnO in the ore entered into FeMn and part is left in the slag. The slag contains 25% Mn, plenty of CaO, SiO_2 and little foreign matter (Fe, P). The slag is useful for producing SiMn. Now add the liquid SiMn which has been pre-smelted twice and contains 6% Si into the furnace together with Mn ore and lime for smelting to the final product-MC FeMn.

2. Two-step pre-smelt process

2.1 Control of calorific value of charge

The main content of the improvement is the supplement of the second step of pre-smelting which consists of a reaction taking place between Mn ore, lime and liquid SiMn. Just as the thermite process for producing other ferroalloys, this process requires that the calorific values of charge be high enough so that the reaction will occur spontaneously and the slag can be separated completely from the alloy. Zhemchuchnil in the former Soviet Union[2] pointed out that in thermite process the calorific value should be 2299 kJ/kg or more; Volkert[3] suggested a value of 2717 kJ/kg or more. The difference between the reaction of preheated , lime and liquid SiMn and the thermite process is that in the former, the sensible heat of raw materials is higher, the kinetic condition is better and the heat loss is smaller, and therefore the required calorific value can be lower. Through studies and tests over a long period, it was found that under the present conditions of raw materials and equipment, the second pre-smelt will run smoothly at the calorific value of 2090 kJ/kg per unit charge . The larger the scale of production, the lower calorific value will be demanded.

The preheating temperature of Mn ore is closely related with the calorific value of the charge. Therefore, the calorific value of charge can be adjusted through preheating temperature. Since the Mn ore used are all oxides containing 45～50% Mn, being mainly MnO_2. With the increase of preheating temperature, the high valent Mn oxide decomposes stagewise, and the calorific value of charge also decreases stepwise.

$$MnO_2 \xrightarrow{480℃} Mn_2O_3 \xrightarrow{950℃} Mn_3O_4 \xrightarrow{1177℃} MnO$$

Silicothermic reaction	Calorific value per unit charge (kJ/kg)
$MnO_2+Si=Mn+SiO_2$	−3336
$2/3\ Mn_2O_3+Si=4/3\ Mn+SiO_2$	−1998
$1/2\ Mn_3O_4+Si=3/2\ Mn+SiO_2$	−1471
$2MnO+Si=2Mn+SiO_2$	−459

It will be noted from above that the calorific value of charge is very low when the preheating temperature of Mn ore exceeds 950℃. Without additional energy, the reaction can not take place spontaneously.

Preheating temperature lower than 480℃ is also undesirable. Since Mn ore contains 3～5% crystal water which can be eliminated at 400～650℃, the preheating temperature of Mn ore should be higher than 650℃ to remove completely the crystal water. Otherwise, there will be bad results. Besides, if the calorific value of charge is too high, the reaction will become so violent that the metal loss will be serious.

From consideration of raising Si utilization rate, lowering consumption of silico-manganese and the sensible heat of Mn ore, the higher the preheating temperature of Mn ore, the better will be the result, and the best will be over 1177℃. However, from the consideration of the feasibility of the process, the preheating temperature should be within 650～950℃.

A large number of tests on the reaction between liquid SiMn and Mn ore, lime in ladle under conditions of various preheating temperature of Mn ores were carried out with the following results:

When the pre-heating temperature of Mn ore is 200 ~ 400℃, the reaction occurs easily. As soon as liquid SiMn is added into the ladle, a violent reaction takes place. With the full addition of SiMn, the Mn ore and lime are almost completely molten.

Table 1 Result of various preheating of Mn ore

Preheating temperature(℃)	Reaction state	Desiliconisation result	SiMn consumption
200—400	violent splashing, flame is long and strong, high temp. of alloy ferroalloy temperature	good	high
700—900	high stable, flame is short and weak, low temp. of alloy and slag	good	low
1000—1200	most of charges are not molten no reaction occurs	very poor	very low

Smelting will be finished in a short time of shaking. Being at high temperature, both slag and alloy have good flowability and are easy to separate. The main problems are generation of considerable amount of fumes and dusts, high consumption of SiMn and poor economic index. If the amount of addition of SiMn is reduced, the Si content in alloy will be less than 2%, namely, MC FeMn can be produced directly in the shaking ladle by this process, but this is uneconomical. Under the condition of small production scale and insufficient calorific value of charge, addition of small amount of Mn ore at low preheating temperature or dry ore to make up the calorific value is feasible.

When the preheating temperature of Mn ore is above 1000℃, part of Mn ore has already begun to melt. Although the sensible heat of charge is high, the reaction will hardly occur after the addition of liquid SiMn. Most of the Mn ore and lime will not melt and react even after starting the shaking ladle.

When the preheating temperature is between 700~800℃, the Mn ore and lime will gradually melt. Reaction is stable and smooth; fumes and dusts are few. Most of the charge will be molten after the full addition of liquid SiMn. Shaking for several minutes will completely melt the charge. The temperature of slag and metal is rather satisfactory; consumption of SiMn is comparatively low. It has been found from tests that this range of temperature is suitable. Under this condition, the calorific value per unit charge will be 1807. 83 kJ/kg. In order to improve the reliability of the process, addition of small amount of Mn ore at preheating temperature lower than 400℃ or dry ore to keep the calorific value per unit charge over 1881 kJ/kg is necessary. However, if the calorific value exceeds 2090 kJ/kg, consumption of SiMn will increase.

2. 2 Material balance and heat balance

The calorific value per unit charge can be calculated through material balance and heat balance. The condition for calculation is as follows:

Mn ore 100kg, amount of desiliconisation in the second pre-smelt accounting for one third of the total amount of Si in SiMn, the temperature at which Mn ore is added being 700℃, the temperature at which liquid SiMn is added being 1450℃. Material balance and heat balance are listed in Table 1 and Table 2:

According to our experience in tests and production over a long period, the control of calorific value of charge at 1881~2090 kJ/kg is suitable. In addtion to the preheating temperature of Mn ore, the composition and sizes of Mn ore and lime, parameters of equipment and operating practice will exert great influence on the production quota.

Table 2 Material balance
(preheated manganese ore)

Input	(kg)	Output	(kg)
SiMn	200	FeMn	209. 109
Manganese ore	100	Slag	103. 588
Lime	30	Volatiles	14. 913
		Tolerance	2. 39
Total	330		330

Table 3 Heat balance

(Fully heated manganese ore)

Input KJ	%	Output KJ	%
From SiMn alloy (1450 ℃) 328489.10	39.24	heat of decomposition $1.2Mn_2O_3 \rightarrow 4MnO+O_2$ 83802.98	28.72
From Manganese ore (700 ℃) 56759.13	6.79	$2.2MnO \rightarrow 2Mn+O_2$ 128805.36	
Reaction heat $Si+O_2 \rightarrow SiO_2$ 403416.31	48.19	$3.2Mn_2O_3 \rightarrow 4MnO+O_2$ 7871.48	
$SiO_2+CaO \rightarrow CaO\ SiO_2$ 48411.92	5.79	$4.2FeO \rightarrow 2Fe+O_2$ 17426.92	
		$5.CaCO_3 \rightarrow CaO+O_2$ 2544.41	
		total 240451.16	
		In volatiles 5764.643	0.69
		In molten metal 308773.59	36.89
		In slag 221414.56	26.45
		Thermal losses 60673.62	7.25
		Total 596626.40	
Sum 7077.56	100	837077.56	100

Calorific value of charge : 1807.83kJ/kg

3. Technical and economical indexes of the improvement of production process

The improvement of the technology has yielded good results. Before improvement, in one step pre-smelt process, one third of desiliconisation is accomplished bypre-smelt outside the furnace, two thirds are accomplished inside the furnace. After improvement by the two step pre-smelt process, two thirds of desiliconisation are accomplished by the two steps of pre-smelting without consumption of electric energy. The electric furnace is just required to accomplish one third of desiliconisation. The greatest advantage from the improvement of the technology is a significant reduction of power consumption and an increase of daily output, thereput reducing production cost. Some chief indexes, both technical and economical, are listed in table 3:

Afetr improvement of technology, power consumption for MC FeMn furnace is reduced by 32. 3%, daily output is increased by 33. 3%. In spite of slight increase of SiMn consumption, the production cost is markedly lowered in general.

$$\text{Calorific value per unit charge} = \frac{\text{(Sensible heat of raw materials + heat evolved by reaction - heat of decomposition}}{\text{total amount of charge}}$$

$$= \frac{200257.79-57524.20}{330} = 432.5\text{kJ/kg}$$

Table 4 Comparison of indexes before and after improvement

Item	Unit	Before improvement	After improvement	+(−)
Daily output	t/d	42	56	+14
Power consumption	Kwh/t	854	578	−276
Mn recovery	%	81	81	——
SiMn consumption	t/t	0. 96	0. 98	+0. 02

References

(1) 《Development of production technology of refined ferromanganese in China》, Zhou Jinhua, INFACON 6 Proceedings, p. 145

(2) 《Ferroalloys》, Elutin, translated by Chu Jue, p. 163

(3) 《Metallurgy of Ferroalloys》, G. Volkert, K. D. Frank; translated by Yu Hui, Gu Jinqing; pp 52～53