Industrial Trials on Basic Fluxes in SiMn Smelting

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Abstract

SiMn is produced in a mechanism of smelting reduction. The properties of the slag, such as melting temperature, conductivity, fluid ability, surface tension and the ability of superheating, affects on the process greatly. Generally speaking, the slag properties depend on the addition of fluxes. The production practice indicates, however, that the slag behavior is also related to the mineralogy of the Mn ores and operation parameters. One can not make furnace operation well merely by adjusting the basicity or the constituents of the slag. High MgO slag is acceptable for small furnaces, as a certain amount of MgO in slag improves Si reduction. The measurement of the running slag indicates that hearth temperature of larger furnaces is higher than that in smaller ones. The slag may often get superheated in large furnaces, which promotes the reduction process. Therefore, the slag behavior in furnaces is much more important than its chemical constitutions. In order to improve furnace operations, it is essential to balance the constituents of the slag, melting and reduction behaviors of the ores according to the furnace characteristics.

Introduction

Basic oxides play an important role in improving slag behaviors, such as conductivity, fluidity, and surface tension in metallurgical process. MC FeMn slag, dolomite, limestone, magnesite and other industrial waste slag with high basic oxides content are often taken as fluxes in SiMn smelting.

The term of basicity is defined to evaluate slag function and properties. The definitions of the slag basicity, depending on the practices and the amounts of the constituents, are as the following:

Binary basicity $B_2 = (\%CaO)/(\%SiO_2)$ (1)

Ternary basicity $B_3 = (\%CaO + \%\ MgO)/(\%SiO_2)$ (2)

Since the molar weight of CaO is 1.4 times of MgO a unit weight of MgO almost plays a role as 1.4 times of that as CaO. Therefore, the ternary basicity is sometimes defined as the following:

$$B_M = (\%CaO + 1.4\%MgO)/(\%SiO_2) \quad (3)$$

Many people believe that 0.5-0.7 of the binary basicity or 0.6-0.8 of the ternary is preferable in SiMn smelting. Due to SiO_2 reduction in smelting, B_2 or B_3 of the tapped slag differs from the initial slag.

It is common that Al_2O_3 input in the charge varies substantially in the operation. High Al_2O_3 content makes slag viscous and deteriorate furnace operation. In the case of high Al_2O_3 input, the operator has to adjust slag constituent by charging basic fluxes. Regarding no Al_2O_3 loss occurs during smelting, it is reasonable to define the term of slag basicity as[1,2]:

$$B_{Al} = (\%CaO + \%MgO)/(\%\ Al_2O_3) \quad (4)$$

It is certain that B_{Al} keeps constant during smelting. Fu[1] recommended that the charge proportioning be made based on the input Al_2O_3 in the charge. He named it as "low slag volume operation", in which the addition of fluxes is controlled at the value of

$$B' = 0.8(\%CaO + 1.4\%MgO)/(\%\ Al_2O_3) = 1.5$$

As the constituent of the raw materials changes time by time, it is found that the concept of basicity could not explain all what happens in the process sometimes. It is obviously necessary to investigate the relations between furnace characteristics and slag behaviors, to study the effects of the slag constituents on furnace operation.

Industrial Trials

It has been found that suitable chemistry of SiMn slag varies greatly with furnace rating, parameters and raw materials. A complete contrary operation was resulted in as the same charge proportion was applied in two furnaces with different ratings.

Table 1 shows that the operating parameters of the furnaces in JFC vary with the rating and furnace geometry data.

Tab.1 Typical Parameters of SiMn Furnaces in JFC

Rating MW	Electrode Diameter mm	P. C. D. mm	Operating Resistance mΩm
8.0	950	2900	1.69
10.5	1000	2800	1.29
14.2	1150	3000	0.94
14.5	1300	3400	0.77

The fluxes used in the tests were limestone, dolomite, magnesite, MC slag, MgO rich waste slags. The trials were divided into 3 groups, CaO-based, MgO-based and composite fluxes.

Tab. 2 shows some production results as MC FeMn slag was charged in the trials of CaO-based fluxes during smelting SiMn with 18% silicon. It is reasonable to use MC FeMn slag not only because of its high CaO-content but also because of its low phosphor content.

In the case of deficiency of MC FeMn slag, dolomite, magnisite and other MgO containing materials were used in the production. The results of monthly trials of MgO-based fluxes are shown in Table 3. In the trials at a 10.5 MW furnace Mn content in the input were controlled at 42% and 32% respectively.

In order to investigate the best flux composite for SiMn

Tab. 2 Trails Results in SiMn Smelting with Flux of MC FeMn Slag

Rating MW	Mn	SiO_2	CaO	MgO	Al_2O_3 (% in Slag)	Mn yield %	Si yield %	Power Consumption kWh/t	B_2	B_M
8.5	12.3	42.0	24.8	4.3	9.8	80	37.9	4631	0.69	0.73
10.5	9.4	43.0	27.9	4.7	10.9	80	45.1	4703	0.76	0.80
14.0	11.8	43.6	20.4	4.8	12.4	82.3	53.3	3836	0.58	0.62
14.5	7.0	43.0	26.7	7.5	14.1	82	55	3850	0.80	0.87

Note: the results were monthly average.

Tab. 3 Trial Results on MgO fluxes in SiMn Production

No	Rating MW	Mn	SiO_2	CaO	MgO	Al_2O_3 (% in Slag)	Mn yield %	Si yield %	Power Consumption kWh/t	B_2	B_M
1	3.5	7.1	44.2	3.6	12.9	17.4	82	45	3700	0.37	0.49
2	8.0	13.1	43.0	5.8	13.9	16.6	82	51.7	3888	0.46	0.58
3	10.5	12.8	42.0	6.1	17.6	16.6	82.2	48.8	4122	0.56	0.73
4	10.5	12.2	41.2	9.5	13.6	17.3	80.0	50.0	4566	0.56	0.69

Note: Trails of No. 3 and 4 were at the same furnace with 40% and 32% of Mn in the input ore.

Tab. 4 Trail Results on fluxes at a 10.5 MW furnace

Fluxes	Mn	SiO_2	CaO	MgO	Al_2O_3 (% in Slag)	Mn yield %	Si yield %	Power Consumption kWh/t	B_2	B_M
D+LS	8.4	42.3	19.9	9.9	12.6	84	49.2	4201	0.70	0.80
D	10.7	42.0	17.0	7.0	13.4	80.2	42.2	4413	0.57	0.63
M	9.7	43.8	12.6	13.9	11.7	80.7	48.8	4562	0.61	0.73
LS	9.9	42.5	21.9	5.1	12.8	70.0	37.2	5567	0.64	0.68
Mn S	9.4	43.0	27.9	4.7	10.9	80.0	45.1	4707	0.76	0.80

Note: D- Dolomite, LS- Limestone, M- Magnesite, Mn Slag- MC FeMn Slag.

production, several fluxes were chosen in the trails. Table 4 gives the monthly results of trials with composite fluxes.

The melting points of industrial slag with high MgO content were measured with high temperature microscope. The result as well as sectional curves of diagram of CaO-MgO-SiO_2-Al_2O_3 system[3] with certain CaO/MgO ratio are shown in Fig.1.

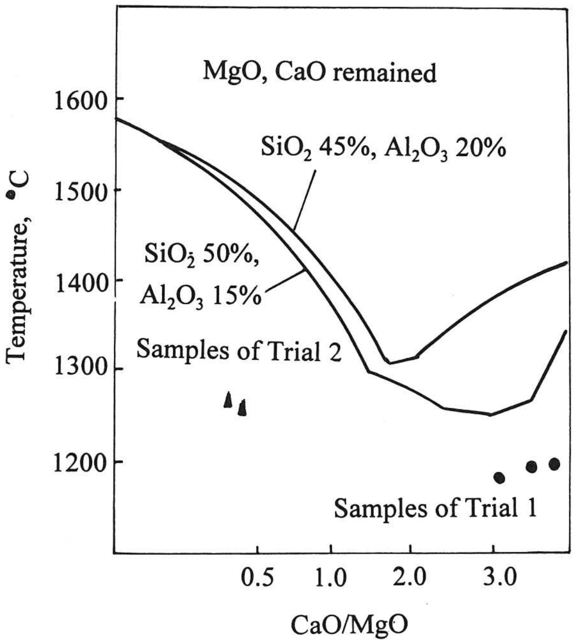

Fig. 1 Melting Temperature of CaO-MgO-SiO_2-Al_2O_3 system via. CaO/Mgo Ratio

In order to invetigate the effects of MnO content on slag conductivity, four electrodes cell method was applied in a previous measurement at JFC. The result is given in Fig. 2.

Discussion

It is essential to high light the characteristics of FeMn smelting process in submerged arc furnaces.

(1) Smelting reduction takes place in the process and manganese is extracted from manganese containing slag. The final slag chemistry is completely different from that of the initial slag.

(2) The reduction rate, the slag behavior and slag superheating are greatly affected by the hearth temperature. The hearth temperature, however, is controlled by the distribution of electric current inside the hearth and by furnace parameters.

(3) The power distribution in the hearth is related to the slag behavior and coke bed volume.

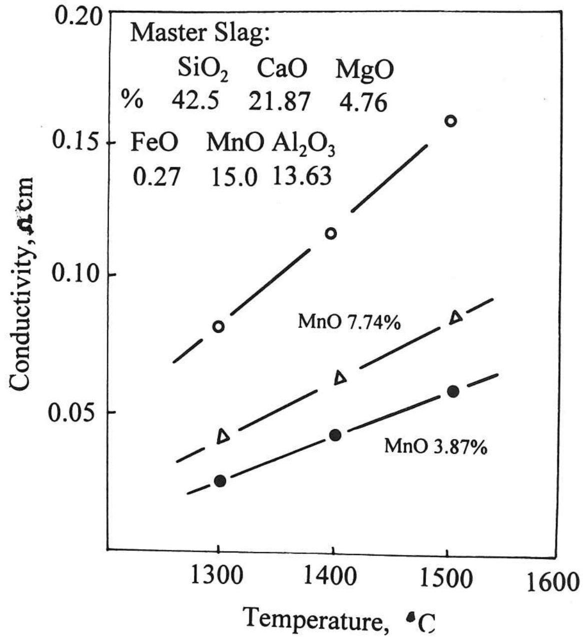

Fig. 2 Effect of MnO Content on Conductivity of the Melt

Silicate Stability

Figure 3 shows the free energy of some silicate formation[4], which described the chemical stability of these silicates. Compared with CaO, the bond force of SiO_2 with MgO is much weaker. Consequently, MgO presence in the slag is favorable to silicon reduction[5]. It is found from Tab. 3 that Si yield is increased as MgO fluxes were used in the trials. In practice it is easier to get higher silicon content as the final slag contains higher MgO.

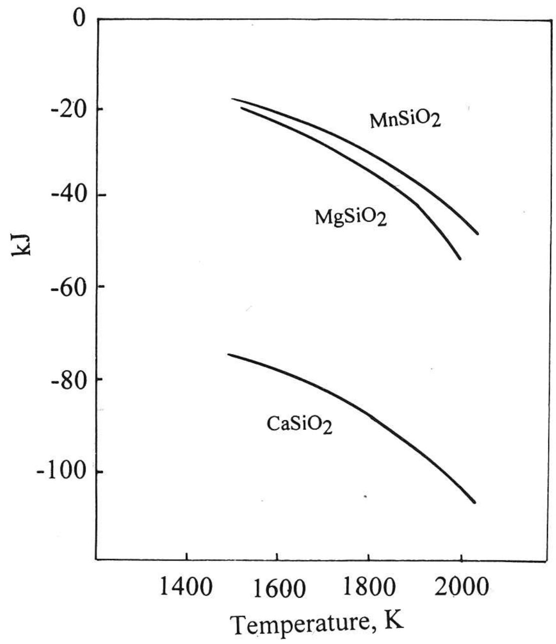

Fig. 3 Free Energy of Silicate Formation

The molecular weight of MgO is less than CaO. The application of MgO fluxes reduces slag volume in the production. As a result, the electricity consumption and metal loss in the slag should be reduced.

Both CaO and MgO increase MnO activities in silicate melt. CaO function is greater than MgO[6].

Hearth Temperature and Furnace Rating

Experience shows that increasing temperature promote the reduction of silicon oxides. It has the same function as to vary melt chemistry in reducing the free energy of the reaction. Tapped slag temperature at the furnaces with different rating is given in Tab. 5.

Table 5 Temperature of Tapped Slag in SiMn Production

Rating, MVA	25	16.5	12.5	9.0
Temperature °C	~1600	~1550	~1500	1450
Melting Range, °C	1160 - 1250			
Superheating, °C	350	300	250	200

It was found that the tapping temperature at bigger furnaces is usually higher than that at smaller ones. Practically, the power density and the heat efficiency in bigger furnace are higher. Therefore, as the slag chemistry is similar the tapped slag from the bigger furnace has been much superheated. This is confirmed by silicon yields indicated in Tab. 2. Obviously, the higher temperature of the hearth is more favorable to silicon formation both in thermodynamics and in kinetics of reduction process.

Slag superheating usually depends upon melting behavior of raw materials, power density and the operation. The higher melting temperature of the slag is, the hotter furnace hearth will be. Increase of 1% MgO in slag brings 10 °C increase of tapped slag[7]. Fig. 1 shows that melting temperature of the slag varies with CaO/MgO. The replacement of MgO with CaO may increase the melting temperature of the slag as high as 50 - 100 °C. One must keep in mind, however, that SiMn smelting requires a suitable temperature range in the hearth. Overheating the slag will lead the evaporation of manganese and reduce Mn yield. The relation of Mn vapor pressure and temperature is as following:

$$lg\, P\ (\text{mm Hg}) = -12548/T + 10.483$$

Mn vapor pressure increases twice as temperature growth in the scale of 100 °C at 1400-1600 °C.

The descending burden may absorb certain amount of Mn vapor and partly recover the Mn loss. If electrodes exceed normal operating position, however, Mn yield will drop dramatically.

It is unnecessary to make the slag much superheated. As appropriately hearth temperature is easily attained in big furnace, extra MgO addition or increase slag basicity seems needless. Some reports even recommended slag basicity of 0.39 in a 48 MVA furnace as appropriate one[5].

Influence of Basic Oxide on Slag Properties

The conductivity of the burden varies as the slag chemistry changes. The addition of basic oxides in the slag increases the electric current passing through the burden. The results of trials 2 and 3 indicate that the hearth temperature in a 7.5MW furnace increased as CaO-based fluxes were replaced by MgO-based fluxes and silicon yield was increased subsequently. The addition of MgO fluxes in the charge of a 14.5 MW furnace seemed no positive reaction at all. On the contrary, Mn yield was reduced in some extent.

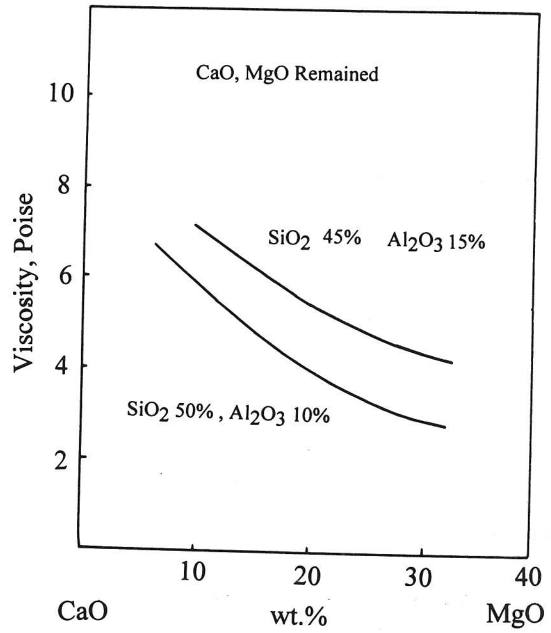

Fig. 4 Effect of CaO and MgO Contents on Viscosity of CaO-MgO-SiO_2 -Al2O3 Melt at 1500 °C

Basic oxides improve slag conductivity and reduce its viscosity. Fig. 4 shows the viscosity of melts with the same content of SiO_2 and Al_2O_3 but various CaO and MgO contents[7]. It is evident that the replacement of CaO with MgO decreases slag viscosity. The comparison of the conductivity of SiO_2 - MgO - Al_2O_3 system and SiO_2- CaO - Al_2O_3 system indicates that MgO improves melt conductivity better than CaO.

It seems that the basicity extent does not affect on furnace operation much as the hearth temperature and slag fluidity are kept in appropriate range.

MnO in slag affects slag conductivity considerably. Fig. 2 shows the changes of slag conductivity with MnO content in slag. As the other oxide ratios keep constant, the higher MnO content in slag is, the bigger the conductivity of the slag will be. The high grade of MnO in a batch of the charge will result in an initial slag with high MnO content and high conductivity. In addition more coke is required to proceed the reduction of rich Mn slag. The conductivity of the burden in this case would be much higher than that in normal production. Unsuitable flux addition will lead to unstable electrode immersion.

Initial Slag in the Process

In submerged arc furnace, initial slag forms at the upper part of the hearth and the reduction of silicon and manganese completes in the molten state of the oxides.

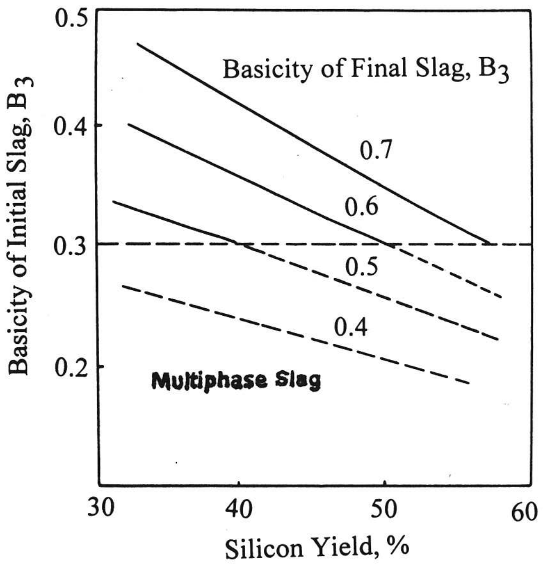

Fig. 5 Relationship of Silicon yield and B_3 of Initial Slag

Fig. 5 shows the relationship between silicon yield and the calculated basicity of initial slag. Though the chemistry of the initial slag may be carefully composed, the final slag varies much with the silicon yield. In normal production, the basicity of initial slag is so low that silicon is saturate in the slag. The presence of solid SiO_2 in slag keeps high SiO_2 activity. It is certainly favorable to silicon reduction.

The basicity is an ındication of slag properties in some extent. The behavior of a slag during its descending in the hearth, however, may be more important. The optimum behavior of a slag may be achieved by carefully adjusting its constituents, coke volume and operation parameters.

Therefore, adjusting the behavior of the initial slag according to the characteristics of furnaces and raw materials is the most important in SiMn smelting.

Conclusions

(1) SiMn formation proceeds in smelting reduction. The variation of physical and chemical properties of slag directly affects silicon and manganese reduction.

(2) Substitution of CaO with MgO in the fluxes may increase SiO_2 activity and the fluidity of the slag. It is favorable to silicon reduction. The practice in some furnaces of small and middle sizes shows both silicon yield and Si content has been improved by adjusting slag constituents.

(3) Solid silica presented in the initial slag with low bisicity improves Si reduction in smelting.

(4) It is suggested that the melting temperature of the initial slag be controlled at a reasonable level. Over superheating slag will make Mn evaporation and increase Mn loss in vapor form.

Reference

1.Fu W.: On Proportioning of Raw Materials in SiMn Smelting with Low Volume Slag Operation. Ferroalloys, 1(1988), 13~15.

2.Wang, J.; Zhu, Z.: A Study on the Ratio of (CaO + MgO)/ Al_2O_3 in SiMn Slag. Ferroalloys, 2(1990) 15~19.

3.Zhang, J.: Phase Diagrams and Slag Properties. Beijing: Metallurgy Press, 1990, China.

4. Barin I. ; Knack O. : Thermochemical Properties of Inorganic Substançe. Berlin: Springer-Verlag, 1973.

5.Bezemer, K.: The SiMn Production Process at Translalloys. INFACON 7 Proceedings,1995, Trondheim, 573~580.

6.Cengizler H.; Eric, R. H.: Thermodynamic Activity of Manganese Oxide in Mn Slag and the distribution of Manganese between Metal and slag phase. INFACON 6 Proceedings, 1992, Cape Town, 167-175.

7.Zhang, H.: The Economic Practice of HC FeMn Production in Blast Furnace. Ferroalloys, 1982(2), 1~6.