Probe into Decreasing Sulphur Contents in Medium Carbon Ferrochromium in Converter Practice

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ABSTRACT

This article probes the main factors affecting sulphur content in medium carbon ferrochromium in converter practice, and points out measures to decrease the sulphur content.

Keywords: Sulphur content, medium carbon ferrochromium, converter

Medium carbon ferrochromium produced using the converter practice (its abbreviated form is converter med-Cr) has many advantages compared with the conventional electro-silicothermic process. However, the former sulphur content (generally in 0.003~0.005%) is higher than the later sulphur content (only 0.003~0.004%). As this does not satisfy market demand, **a** solution to decrease sulphur content in converter med-Cr is urgently required.

1.0 BALANCE OF SULPHUR

In order to understand clearly the source and deportment of sulphur in converter med-Cr, the balance of sulphur is shown in Table.1 based on the product data of Zhengjiang Hengshan Ferroalloy Works in 1998.

Table: 1 the balance sheet of sulphur in converter med-Cr

Input item			Output item		
Item	Quantity /Kg	Content/%	Item	Quantity /Kg	Content/%
High-carbon Cr-Fe	1000× 0.028%=0.28	72.48	Converter med-Cr	890× 0.03=0.267	69.17
High-carbon Cr-Fe slag	30× 0.22%=0.066	18.12	Converter med-Cr slag	230× 0.032%=0.074	19.17
Lime	70× 0.04%=0.028	7.25	Dust	27× 0.08%=0.022	5.7
Si-Fe	65× 0.01%=0.0065	1.68	Gas and loses	0.023	5.96
Chrome ore	60× 0.003%=0.0018	0.47			
Total	0.386	100		0.386	100

2.0 MAIN FACTORS EFFECTING SULPHUR CONTENT IN CONVERTER MED-CR

2.1. Effect of sulphur in materials

Molten high carbon ferrochromium, the basic materials of Med-Cr in converter, is the main source of sulphur (above 70%), therefore the first guarantee to produce low-S Med-Cr in converter is to decrease sulphur content in the high carbon ferrochromium charged. Secondly the quantity of slag above the molten high carbon ferrochromium charged into converter is the next most important factor to increase the sulphur content of the converter med-Cr. The operating data from August 1998 is showed in Table 2.

Reference [1] shows that the apparent distribution coefficient of sulphur between high carbon ferrochromium and a synthetic slag is 16, 21 and 24 at 1 650, 1 730 and 1800°C respectively. However, in actual production, such high values of distribution coefficient have not been recorded. The apparent distribution coefficient of sulphur has reached 8~10 according to the sample analysis of high carbon ferrochromium at Zhengjiang Hengshan Ferroalloy Works in March 1999.

Furthermore, the sulphur content in lime, Si-Fe and chrome ore has a certain effect on the sulphur content in converter med-Cr.

Table 2 the variation of sulphur content of product according to slag quantity brought into converter /%

	Much slag quantity brought into converter					Controlling slag quantity charged
Heats No.	17-4	26-10	73-38	116-60	170-91	
S_1 (converter med-Cr)	0.047	0.054	0.048	0.053	0.046	0.027
S_2 (High-carbon Cr-Fe)	0.031	0.033	0.029	0.034	0.028	0.024
$\triangle=S_1-S_2$	+0.016	+0.021	+0.019	+0.019	+0.018	+0.003

2.2. Effect of process system

2.2.1. Low basicity

In converter smelting, the desulphurisation is a function of the distribution of sulphur between slag and hot metal. The desulphurisation reaction can be expressed as follow:

$$[S]+(O^{2-})=(S^{2-})+[O] \quad (1)$$

According to ion theory, the basicity of the slag is expressed as n_{O}^{2-} (the mole number of O^{2-}) in 100 g slag, because basic oxide generates O^{2-}, for example:

$CaO=Ca^{2+}+O^{2-}$ (2)

While acid oxide consumes O^{2-}:

$SiO_2+2\,O^{2-}=SiO_4^{4-}$ (3)

The higher N_O^{2-} concentration of the basic slags favours the desulphurisation process. So with the increasing of CaO and decreasing of SiO_2 in slag, the distribution coefficient of sulphur between slag and hot metal also increases.

From kinetic considerations, the slag basicity has an effect on the quality transfer coefficient for desulphurisation. Figure 1 demonstrates the relation between the partition of sulphur between metal and slag as a function of slag basicity. The quality transfer coefficient of desulphurisation k_m in slag will increase while the ratio of CaO/SiO_2 increases. Increasing the basicity of the slag will improve the rate of desulphurisation. Furthermore the increasing of basic oxide concentration can enhance the sulphur content in slag and it will be advantageous to desulphurisation.

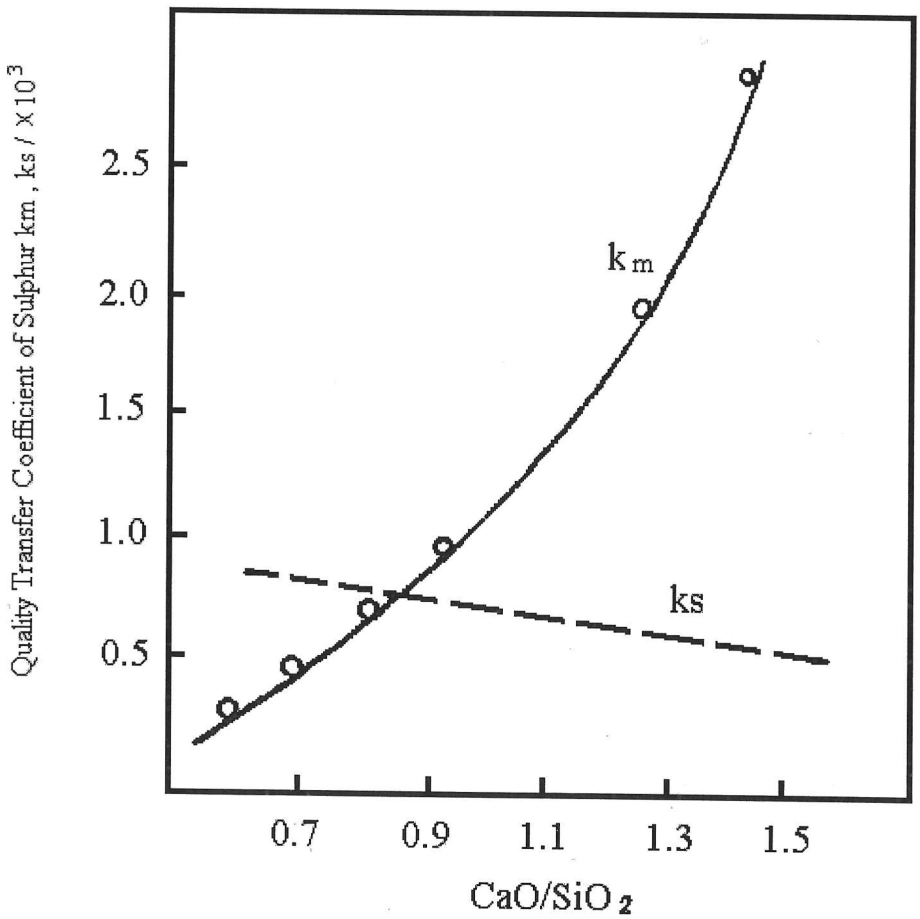

Figure 1 the relationship of between slag basicity and k_m, k_S

Higher slag basicity is necessary for satisfactory desulphurisation. In the production of converter med-Cr smelting, the adding of excess lime can result in excessive splashing, over-blowing and high slag viscosity, that will effect desulphurisation in furnace and the rate of recovery of chromium. As a consequence the slag basicity is generally controlled from 0.5 to 0.8 in practice.

2.2.2. Slag quantity

In basic oxide slag, the final sulphur content in hot metal can be expressed as follows:

$$[\%S]=100(\Sigma S_M-\triangle S_g)/(W_M-L_S \cdot W_S) \quad (4)$$

Where: [%S]—the final sulphur content in the heat;

W_S —slag quantity per 100 kg metal (kg);

W_M—quantity of metal (100 kg);

L_S —distribution coefficient of sulphur;

ΣS_M—sulphur quantity charged from all materials (metal , slag-forming), calculated according to 100 kg metal and the relevant slag-forming materials.

$\triangle S_g$ —sulphur quantity exhausted by gasification desulphurisation, calculated according to desulphurisation quantity from 100 kg metal.

According to formula (4), the larger the slag volume, the lower the final sulphur content [%S] should be in the metal. However, according to the production practice for converter med-Cr, the ratio slag/metal is constantly controlled at about 0.2~0.4.

2.3. Effect of operation

In practice, the main effect on the sulphur content of ferro-alloy product is a lower rate of temperature rise in the first stage, over-blowing in the later stage, and high slag viscosity.

Slower rate of temperature rise in first stage and over-blowing in the latter stage can result in chromium being further oxidized raising the Cr_2O_3 content in slag, so it will need more silicon reductant. As a consequence the SiO_2 content in the final slag will increase and the slag basicity will decrease, which is disadvantageous for desulphurisation.

With respect to the kinetics of desulphurisation, higher slag viscosity can slow the diffusion of sulphur. As the diffusion of sulphur ion S^{2-} in slag phase side is the rate limiting step, the rate of desulphurisation can be expressed as follows:

$$V_S = D_S(C_b - C_i)/X_b \quad (5)$$

Where: D_S: Diffusion coefficient of sulphur in slag;

X_b: The effective thickness of boundary in slag phase side;

C_i, Cb: The interface and internal concentration in slag phase side.

From formula (5), lower slag viscosity is not advantageous to the diffusion of sulphur ion S^{2-} so much as improving the stirring of metal melt to attain better desulphurisation.

2.4. Effect of other factors

The relationship "low sulphur with high carbon and high silicon" in converter med-Cr smelting is similar to that experienced in high-carbon Cr-Fe smelting. High [C] and [Si] content can obviously increase the activity coefficient of sulphur $f_{[S]}$ in hot metal, the higher $f_{[S]}$ is, the higher is the distribution coefficient of sulphur L_S. Furthermore there is a reduction reaction between [Si] and Cr_2O_3 in slag in the casting process that will reduce the slag basicity, so sulphur content in final production will increase in casting process when much slag is above hot metal.

The comparison of production composition from two different furnaces at our works in March 1999 is shown in Table 3. Thus to control a higher content of [C] and [Si] has a certain effect on decreasing the sulphur content in the range of composition shown.

Table 3 Composition in converter med-Cr with high [C] and [Si] and [S] content in high [C] Cr-Fe

Heats No.	C	Si	Cr	P	S	[S] in high [C] Cr-Fe
173-24	3.17	2.00	67.19	0.019	0.018	0.022
191-30	2.89	1.76	68.11	0.018	0.020	0.021

3 MEASUREMENT OF DECREASING [S] CONTENT IN CONVERTER

Taking into account the factors previously described, some measures were taken to decrease sulphur content in converter med-Cr and a marked effect has been achieved. The ratio of first-grade product (S≤0.025%) increased from 18.46% in 1998 to 32.54% and the ratio of quality product (S≤0.025%) from 59.17% in 1998 to 92.44%. These results were obtained implementing the following steps.

3.1 Control of S in high-C CrFe and slag above high-C CrFe charged to converter

Sulphur content in high-C Cr-Fe originated from coke, and makes up 90 percent of the total S brought into converter. The operating conditions for several coke sources used in our works during March and April in 1999 are shown in Table 4.

Table 4 Sulphur content in High-C Cr-Fe with different kinds of cokes

Used date	Composition %		
	Fixed carbon	S content in coke	S content in hot metal
1~29 March	85.17	0.412	0.024
29 March~5 April	85.36	0.689	0.041

5 April ~	84.90	0.330	0.023

According to Table 4, it is critical to use low-S coke to control sulphur content in high-C Cr-Fe, in order to control the sulphur content in converter med-Cr. In addition to selecting ore and slag composition, increasing converter temperature will also result in decreasing sulphur in high-C Cr-Fe. The consumption of O_2 and the age of the converter in smelting process of converter med-Cr, limit the C and Si in high-C Cr-Fe (the optimum composition is about 8.5%C and 0.8%Si).
From Table 1, slag quantity above high-C Cr-Fe charged to the converter will adversely influence sulphur to converter med-Cr, so this is strictly controlled in Zhengjiang Hengshan Ferroalloy Works. Operations work to decrease top slag flow into converter while taking hot metal into the converter.

3.2 Adding CaO, CaF_2 in hot metal ladle

After ferro-alloy is reduced from converter slag by the addition of Si, slag basicity will decrease sharply. During this process sulphur in slag will transfer into ferro-alloy. In order to avoid the impact of lime addition to the converter, this addition is made to the ladle. In order to make full use of thermodynamic and kinetic potential Si, CaO and CaF_2 (quantity rate 5:1) are added into hot metal ladle to promote final slag basicity and decrease SiO_2 concentration in the slag. This reduces the reversion of S while adding the silicon reductant. Though adding CaF_2 improves fluidity of slag it protects against the reversion of S. CaF_2 plays the role of de-sulphuriser and flux. It facilitates the absorption of lime, promoting slag basicity and promoting the reduction of Cr.
The relationship among final slag basicity, S in ferro-alloy and Cr_2O_3 in final slag are shown in Figure 2. From this figure, in order to control sulphur in ferro-alloy below 0.030% , final slag basicity should not be below 0.8 , it is fit to control it between 1.0 and 1.2 in practice.

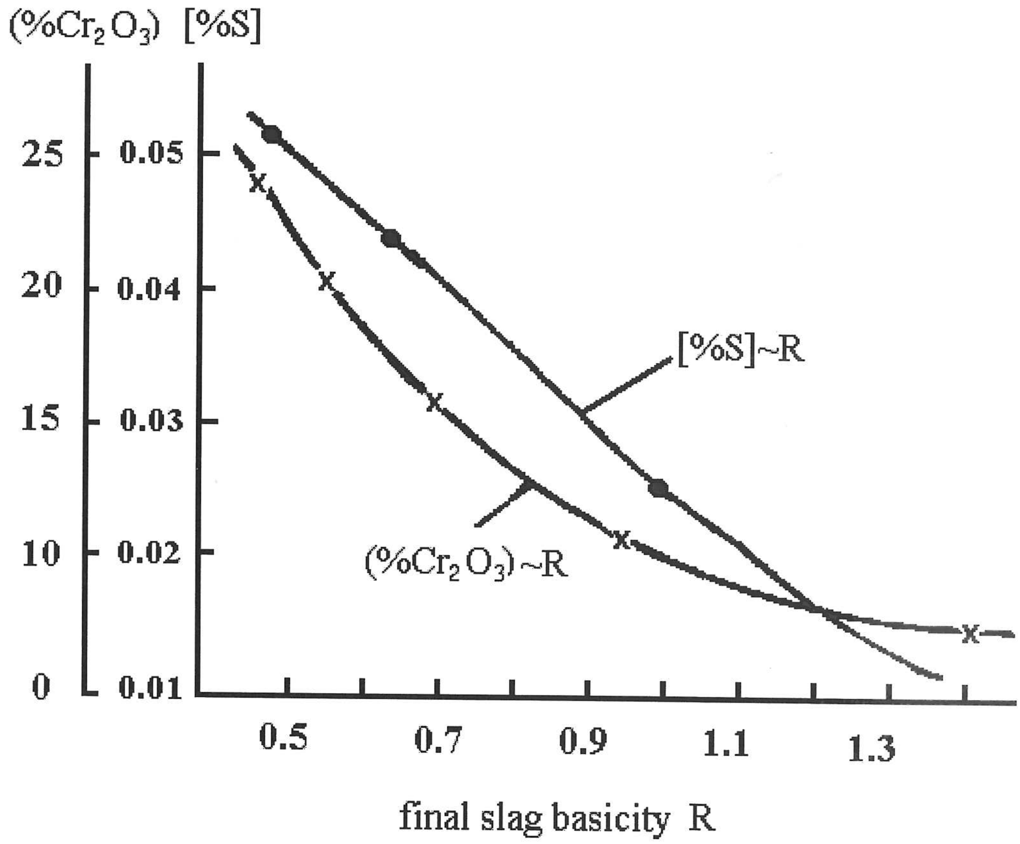

Figure 2 The relationship among final slag basicity, S in ferroalloy and Cr_2O_3 in final slag

3.3 Smelting operation

Increasing temperature rapidly during the early stage is critical to guarantee a fluid slag. It is necessary that the molten iron temperature of high carbon ferrochromium be high and that the content of silicon be controlled at 0.8%~1.6%. During blowing, if the splashing is not excessive, the operator may increase the flow of oxygen. After initial blowing, the volume of the consumed oxygen must be calculated and according to the volume, the operator may make adequate arrangements for the whole operation sequence. To be sure of the fluidity of the slag and for the sake of the normal finishing control, the slag-forming material should be put in regularly and in small amounts. When the carbon content is stable in hot metal of high carbon ferrochromium, the operator may rely on oxygen volume to judge the endpoint of smelting.

3.4 Other factors

Skimming slag before casting and reduce the slag cover over hot metal, will reduce resulphurisation and guarantee physical quality of alloy, little slag must cover the molten iron. Considering the composition of product and the cost of production, high carbon and silicon are not used to reduce the sulphur content of alloy.

4.0 CONCLUSION

From the analysis of theory and practice, the main measures to decrease sulphur content in medium carbon ferrochromium in converter practice have been established:

- Decreasing the total sulphur content of raw materials;
- Increasing slag basicity and slag quantity adding lime and fluorspar out of the converter;
- Taking some reasonable methods, for control reaching technological level of high—temperature, rapidly and reasonably controlling endpoint;
- Casting and decreasing resulphurisation in casting process after skimming slag.

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