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ON SULFUR CONTROL IN HC FeCr PRODUCTION

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ABSTRACT

Sulfur is a troublesome element in HC FeCr smelting. Although only small amounts of the total sulfur input enters the metal, the sulfur content fluctuates greatly. Sulfur behaviour was investigated in this work. It is evident that the contents of silicon and carbon in the metal as well as the slag composition may greatly affect on sulfur yield. Desulfurization of HC FeCr by vacuum treatment and slag washing were tested. Sulfur segregation in the ingots was observed and the transfer phenomena of sulfur during solidification is revealed.

INTRODUCTION

With the increasing demand for low sulfur steel, the requirement on ferrochromium of low sulfur content has been critical. As an important raw material of steel making as well as that of LC FeCr and Simplex-FeCr, HC FeCr is standing in a leading position of the quality control. A great effort has been made to reduce sulfur yield in commercial production. It is known that there is a certain relation between sulfur content and silicon and carbon contents [1-4]. It is believed that the sulfur may be controlled by adjusting silicon and carbon in metal. But, it is not easy to control carbon unless some proper chromite ores are available. In some cases sulfur often fluctuates. For some special requirement, like the raw material for Simplex-FeCr, HC FeCr with low sulfur content as well as low silicon content is required. Thus, sulfur removal is very difficult in the smelting of this grade of the products. Therefore, experimental studies on the removal of sulfur from the metal are still imperative in many plants.

In this study, the desulfurization ability of the slag was studied and the distribution of sulfur was traces during HC FeCr tapping, casting and solidifying. The aim of this work has been to find economic ways to remove sulfur from the metal. Most of the data in this paper were obtained during commercial production.

EXPERIMENTAL WORK

A great attention has been paid to the study of HC FeCr desulfurization both in the smelting and in the ladle treatment. Up until now, the following experimental and statistical work has been carried out at JFW.

The effect of silicon and carbon in the metal on the sulfur content.

It is well known that the sulfur content is related to the silicon and carbon content in the metal and it is common to control the sulfur by adjusting the metal composition. Statistical data given in Figure 1 show that an increase in silicon and carbon in the metal reduces the yield of sulfur considerably. The data were collected during an annual production record of a 12.5 MVA furnace. The data were divided into four groups according to the carbon content, e.g. 5.7-6%, 6-6.5, 6.5-7% and more than 7%. Regression lines only are given in Figure 1. It is seen that the slope value of the regression lines increases with decreasing carbon content. This means that the effect of silicon increases as the carbon content decreases.

Desulfurization ability of HC FeCr slag in smelting.

In the HC FeCr furnace, molten metal particles must penetrate a slag layer before entering the metal bath. Desulfurization takes place at the interface of slag-metal. Therefore, the slag property may greatly affect sulfur yield in the smelting. It is believed that the addition of lime or lime stone in the charge may be advantageous to desulfurization. Experimental work was carried out in a 9 MVA furnace to investigate the effect of CaO on slag properties and the influence of it on the furnace operation. Various amounts of lime was mixed with charge materials during the test and samples of metal and slag were analyzed. The results obtained showing the effect of lime addition on sulfur in produced metal are given in Figure 2.

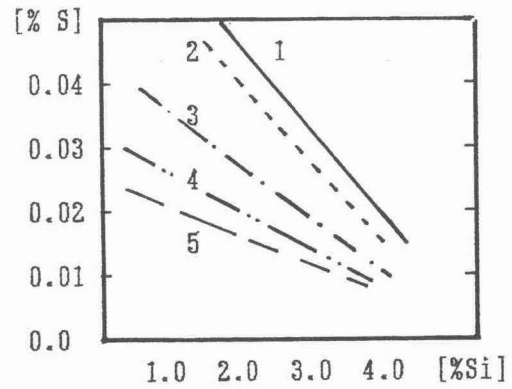

Figure 1. Sulfur variation with [Si] and [C] in HC FeCr production
1. 5.7<[%C]<6.0,
2. 6.0<[%C]<6.5
3. 6.5<[%C]<7.0
4. [%C] > 7.0
5. [%C] > 8.0 and (CaO) > 9.0

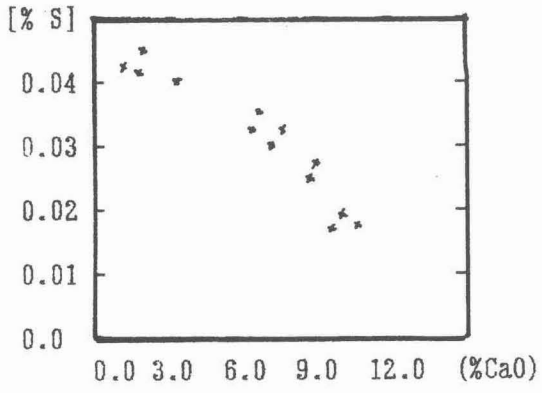

Figure 2. Sulfur variation in metal with CaO in slag.

Sulfur variation during tapping

Metal and slag together with some of the raw materials like coke and ore are intensely stirred and mixed during tapping, and finally separated in the ladle. All these actions must affect the metal properties. Samples were taken during tapping and casting. It is found that the sulfur content at tapping is lower than that at casting (Table 1).

Table 1. Sulfur variation during tapping (%)

Tap no.	54	56	78	188	199
Tapping	0.030	0.035	0.025	0.039	0.045
Casting	0.041	0.041	0.039	0.044	0.050

Sulfur variation during solidification

It has been noticed that the sulfur content varies with sampling procedure. There are usually two ways of sampling. One is taken during casting and the sample is called "hot sample". The other is taken after the metal has solidified and this sample is called "cold sample". It is very common that the sulfur content in the hot sample is higher than that in the cold sample. Table 2 gives some typical data of the samples taken at JFW in 1983. The relative deviation may be as high as 30-50%. Obviously, the deviation between the two types of samples may cause some disputation in the quality control.

Table 2. Typical sulfur content in hot and cold samples (%).

Tap no.	Hot sample	Cold sample	Delta S
1243	0.0528	0.0280	- 0.0118
1244	0.0502	0.0320	- 0.0181
1247	0.0519	0.0340	- 0.0179
1249	0.0485	0.0370	- 0.0115
1250	0.0549	0.0455	- 0.0209
1253	0.0535	0.0407	- 0.0128
1264	0.0554	0.0360	- 0.0248
2630	0.0314	0.0214	- 0..0100
2631	0.0286	0.0284	- 0.0002
2632	0.0252	0.0306	- 0.0054

A study on the solidification of HC FeCR was carried out. Positions for sampling were chosen at different locations of the ingots as marked in Figure 3, showing a section of the ingots and the sampling points.

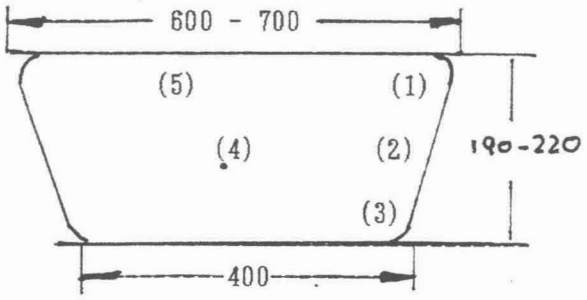

Figure 3. Sampling points in the ingot section (mm).

Table 3. Sulfur distribution in the ingots (%)

Sampling point		1	2	3	4	5	Hot sample
Ingot no.	1	0.032	0.012	0.022	0.012	0.033	0.033
	2	0.014	0.011	0.021	0.013	0.026	0.042
	3	0.063	0.050	0.062	0.042	0.048	0.059
	4	0.051	0.048	0.054	0.024	0.028	0.060

It is found that sulfur segregation takes place during the metal solidification. The sulfur content at the points close to the mould wall is higher than at the central points where the cooling rate is lower.

The samples were crushed and sized to find the sulfur distribution in the grains. It is found that there are some deviations in composition between the various size fractions. Table 4 gives the test results.

Vacuum treatment

The pilot test of vacuum desulfurization was carried out in a 50 KW induction furnace. A graphite crucible was used in the test. The charge weight is 20 kg. The charge was melted in air and sampled with a quartz tube. Then, the vessel was evacuated at a vacuum of 1.0-2.0 mm Hg for 3-5 minutes. It was observed that the melt was bubbling during the treatment. Occasionally, hot metal splashing took place. The test results are shown in Table 5.

Table 4. Element distribution in the metal particles.

Particle size		< 160 mesh			> 160 mesh		
Element %		Cr	C	S	Cr	C	S
Sample no.	1	67.58	7.05	0.041	65.24	6.58	0.056
	2	71.52	7.14	0.037	63.35	5.70	0.070
	3	72.40	7.71	0.029	62.04	5.99	0.078
	4	71.67	7.42	0.034	63.57	5.89	0.075

Table 5. The result of vacuum treatment of the hot metal

%		Before vacuum treatment		After vacuum treatment	
		S	C	S	C
Sample No.	1	0.050	6.27	0.030	5.89
	2	0.032	9.50	0.025	9.12
	3	0.030	9.60	0.016	9.43
	4	0.028	8.93	0.013	9.22

Slag washing treatment

Slag with high basicity is a good desulfurizer. Slag washing is a common method to refine hot metal. It is reasonable to refine HC FeCr with LC FeCr slag if the slag is available in the smelting shop.

The test was carried out with the ladle treatment of a melt and slag from a 9 MVA HC FeCr furnace and a 3.5 MVA LC FeCr furnace respectively. The slag of LC FeCr was tapped into a hot metal ladle. Then, the hot metal of HC FeCr was poured onto it. After slag washing, the metal was casted. Samples were taken before and after the treatment. The basicity of the slag is around 1.8 and the slag/metal ratio is 1.5-2. The results are shown in Table 6.

Table 6. Typical desulfurization result of slag treatment

No.		[%S] in metal	Slag composition, %						
			(S)	SiO2	CaO	MgO	FeO	Al203	Cr203
1	Before	0.0138	0.0225	27.10	48.78	10.6	0.82	6.34	4.60
	After	0.0025	0.0513	27.10	47.62	11.8	0.82	6.99	4.12
2	Before	0.0312	0.0275	27.78	47.40	10.6	0.67	7.12	4.95
	After	0.0100	0.0550	28.47	42.89	13.1	0.77	8.15	5.01

DISCUSSIONS

The sulfur content in metallurgical coke may be as high as 1%. Nearly 90% of the total sulfur input comes from coke. Chromite ores and fluxes are carrying less sulfur. Sulfur in coke exists in the form of organic compounds, sulfides and sulfates [5]. FeS_2 is one of the major compounds. In submerged arc furnaces, coke descends with other reduction materials into the high temperature zone, where the organic sulfur evaporates and enters into the gas phase. Some sulfide may directly enter the slag and the metal. Statistical treatment of the production data indicate that less than 10% of the total sulfur enters the metal. Around 40-60% of the sulfur enters slag and 30-40% of the sulfur enters the furnace gas. It is advisable that

increasing the proportion of the sulfur in the slag and in the gas may contribute to the sulfur removal in the metal.

In the production process, sulfur is a very active element. It constantly transfers between the gas, the slag and the metal phase. The formation of HC FeCr inside the furnace is the result of multi-phase reactions. The reactions related to the action of sulfur are gas-solid, gas-liquid and liquid-liquid. At the upper part of the furnace hearth, chromite ores are prereduced and a great amount of metal particles with less sulfur are formed. The coke bed is the most important reaction area, where the reduction of chromium oxide is nearly completed and metal droplets separate from the slag. The partial pressure of sulfur in the gas phase varies with the hearth depth. A great deal of CO gas generated at the softening zone results in a decrease in the partial pressure of sulfur. It is indicated that sulfur in coke may evaporate at a temperature of 1500-1800°C [5]. Consequently, the coke will keep a higher sulfur content until it moves down to the coke bed, where the sulfur pressure in the gas phase may reach its maximum value. Both metal and slag have intimate contact with the gas phase during their movement downwards. Therefore, both slag and metal may easily absorb sulfur from the gas phase.

Based on the experimental work, figure 4 was drawn to illustrate sulfur variation during HC FeCr smelting. The most important equilibria relative to sulfur behaviour in the process are gas-metal and metal-slag equilibria.

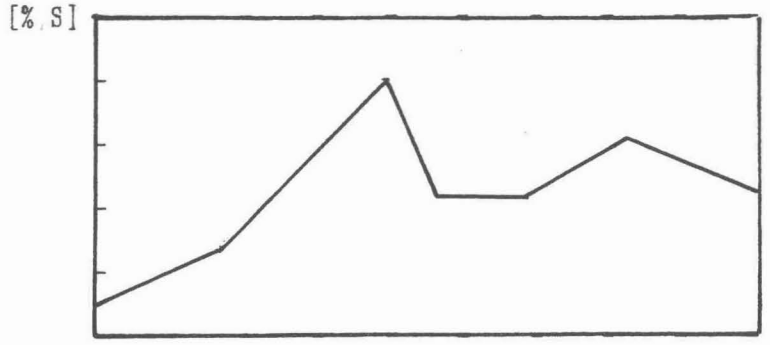

Figure 4. Tentative variation of sulfur in metal during HC FeCr smelting

Sulfur transfer between metal and slag

The equilibrium distribution of sulfur between metal and slag is expressed as

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

It is obvious from Eq. 1 that the elements which decrease the activity or the concentration of oxygen in the metal may promote desulfurization. Silicon and carbon are typical ones for HC FeCr. The presence of Si and C in the metal lowers the oxygen potential and increases the sulfur activity. It is favourable for sulfur transfer to the slag phase.

$$\partial [s] = f_s * [\%S] \quad (2)$$

$$d\partial_{[s]} = f_s * d[\%S] + [\%S] * df_s \quad (3)$$

In the case of a certain sulfur activity,

$$d\partial[s] = 0$$

therefore,

$$\frac{d[\%S]}{[\%S]} = -\frac{df_s}{f_s} \tag{4}$$

It is clear that the increase of sulfur activity must result in a decrease of sulfur in the metal. With the intersection factors of silicon and carbon in iron melt, the calculation shows that one percent increase in silicon content may decrease the total sulfur in the metal by 14.5%. This agrees well with the production data.

The production experience shows that the proportion of sulfur entering the slag varies with temperature and slag properties as the slag-metal reaction plays an important role in sulfur transfer. The concept of sulfur capacity is used to evaluate the ability of desulfurization [6]. Sulfur capacity which is an inherent property of the slag is defined by the equation

$$Cs = (\%S) * (Po_2/Ps_2)^{1/2} \tag{5}$$

A slag with a high Cs will clearly hold sulfur more strongly than one with low Cs. An empirical expression of sulfur capacity as function of the basicity of a slag is as follows

$$lg\ Cs = -5.57 + 1.39B \tag{6}$$

$$B = \frac{N_{CaO} + \frac{1}{2}N_{MgO}}{N_{SiO_2} + \frac{1}{3}N_{Al_2O_3}} \tag{7}$$

It is apparent that the Cs values increase with the mole fraction of metal oxides. Consequently, the lime addition in the charge in order to get a slag with a high basicity is applicable in desulfurization of HC FeCr. In the furnace, desulfurization takes place when the metal particles penetrate the slag layer. The HC FeCr slag has a strong ability of desulfurization. Reference [7] points out that apparent ratios of sulfur in slag/metal at 1650, 1730 and 1800°C, respectively, are 16, 21 and 24. These data were obtained in a laboratory study. The actual ratios obtained in the commercial production are only 5-10 (see Table 6). It seems that the slag still has some potential of desulfurization.

A high temperature is favourable for the sulfur removal from the metal. It is considered that the silicon content reflects the hearth temperature. Usually, the HC FeCr has less sulfur when the tapping temperature is high.

It is believed that even though the slag and the metal does not reach the equilibrium state in the smelting, the slag with a high sulfur capacity still has a strong tendency of desulfurization. This effect may be considered as a driving force of desulfurization. It may be written in the following form:

$$\Delta G = \Delta G^0 + RT * \ln(fs * (\%S) * (Po_2/Ps_2)) \quad (8)$$

$$\Delta G = RT * \ln((\%S)/(\%S_0)) \quad (9)$$

where (%S) is the actual sulfur content in the slag and ($\%S_0$) is the sulfur content at equilibrium, fs is the activity coefficient of sulfur.

Table 6. Typical sulfur distribution in slag and metal

No.	(%S)	[%S]	L_s
1	0.215	0.0266	8.08
2	0.221	0.0420	5.26
3	0.251	0.0320	7.84
4	0.296	0.0335	8.84
5	0.264	0.0436	6.06
6	0.251	0.0485	5.18
7	0.276	0.0463	5.96
8	0.251	0.0460	5.46
9	0.256	0.0370	6.92
Average	0.253	0.0395	6.41

Attention must be paid, however, to the disadvantage of lime addition in the smelting. Too much CaO in the slag may change the conductivity of the slag and the furnace operation. Therefore, the smelting parameters should be adjusted as well.

Sulfur-uptaking during tapping is an unnegligible phenomenon. As Table 1 indicates the uptaking of sulfur during tapping may amount to as much as 24% of the total content in the products. This phenomenon may be attributed to slag-metal mixing and to temperature variations during tapping. As the metal and the slag move out of the furnace, the temperature drops rapidly. There exists a tendency of sulfur transfer from slag to metal during tapping since sulfur capacity of the slag decreases with decreasing temperature. Besides, the unreacted coke with some absorbed sulfur may transfer its sulfur to the metal in the mixing during tapping. In this case, the slag with higher sulfur capacity may prevent sulfur transfer from the slag to the metal. Consequently, it is helpful to reduce the sulfur content in the metal.

Applying the principle of slag-metal equilibria experimental work has shown that basic slag washing is a simple way to remove sulfur from the metal. Around 40-60% of the sulfur in the metal may be removed by slag treatment. But, the temperature decrease may cause metal loss in the slag. The feasibility of the process depends on the availability of slag, and the metal yield of the treatment.

Sulfur Transfer between Metal and Gas

The solubility of nitrogen in liquid chromium is as high as 5%. But the solubility of sulfur, nitrogen and other gases in liquid and solid HC FeCr metal is still unknown [8]. It is observed in this work that sulfur escapes from the metal during its solidification. An interesting phenomenon was observed during HC FeCr casting. When the hot metal is poured into the mould, bubbling occurs all over the whole surface of the ingot. A great deal of gas escapes from the metal before the metal solidifies. The bubbling may last as long as one minute. This phenomenon occurs in many other metal castings as well. It was found that it has nothing to do with the mould and the coating materials of the mould. It was also observed that a great deal of pores and holes appeared all over the section of the ingot after the metal was crushed.

The gas dissolution in the metal may be expressed as:

$$S_2 = 2[S] \tag{10}$$

According to Sievert's law, the solubility of the gas varies with its partial pressure

$$[\%S] = K\sqrt{Ps_2} \tag{11}$$

In vacuum or in a gas phase where the sulfur pressure is very low, sulfur may transfer from the metal phase to the gas. This is the basic reason of vacuum and gas desulfurization. The gas solubility in metal varies with temperature and phase transformations. It is known that there is a turning point at the solidification temperature of Fe, Cr and Mn. The gas solubility in the metals sharply drops. The escape of the dissolved gas makes molten metal bubbling. Vacuum and low sulfur pressure in the gas are favourable to sulfur removal. Tables 2 and 3 reveal that the gas dissolved in the metal promotes sulfur escape. This is especially evident when the sulfur in the metal is high. Desulfurization by vacuum treatment and bottom blowing of inert gas is feasible if the device is available.

Metallographic studies show that the main phase of HC FeCr is (Fe,Cr)7C3 with small amounts of α-(Fe,Cr) solid solution. (Fe,Cr)7C3 is brittle and easily crushed. It is believed that the fine particles contain more (Fe,Cr)7C3. Table 5 indicates the segregation of carbon, chromium and sulfur in the different size fractions. In the fine particles, the carbon and chromium contents are higher and the sulfur content is lower. This may indicate that sulfur is less soluble in (Fe,Cr)7C3 than in α-(Fe,Cr) solid solution [7]. The fact also remind us that care must be taken in sample preparation in order to obtain a reliable chemistry.

CONCLUSIONS

(1) Sulfur in HC FeCr mainly comes from coke during smelting. Sulfur is an active element. It transfers easily among the gas, the slag and the metal depending on the conditions of smelting.

(2) Increasing silicon and carbon in the metal, or addition of CaO in the charge are effective ways to remove sulfur from HC FeCr. But, some operation parameters should be adjusted to ensure a stable operation.

(3) Bubbling phenomena in the mould of the hot metal were observed and are explained by the escape of the gas dissolved in the hot metal. Sulfur segregation in the ingots takes place during solidification. It is especially evident when the sulfur content in the ingots is high.

(4) Vacuum treatment and slag washing are applicable in HC FeCr desulfurization. However, the application depends on the process economy.

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