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Experimental Determination of Sulfur Partition Ratio in the CaO-Al_2O_3-SiO_2-CaF_2-MgO Slag and Liquid Iron

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Abstract. The external desulphurization of molten iron has become an important step in the production of steel and iron. The desulfurization degree of the high calcium slag, which was mainly taken from Shougang Shuicheng Iron and Steel (Group) Co. Limited, was investigated on basis of the fundamental theory of slag metal equilibrium reaction. The initial content of sulfur in the slag was adjusted to 2.60% mass perdent by adding analytical reagent CaS. The results show that the desulfurization degree of the high calcium slag increases obviously with the increase of temperature in the range 1593-1743K, and so the sulfur partition ratio. When the holding time of the hot metal and slag at controlled temperature was extended from 120 min to 180 min in the furnace, both the sulfur partition ratio and the desulfurization degree increased markedly.

1. Introduction
The external desulphurization of molten iron has become an important step in the production of steel and iron. It is meaningful for Shougang Shuicheng Iron and Steel (Group) Co. Ltd feeded with a wide and unstable iron ores to apply the ladle desulphurization. The average time of iron ladles from blast furnace to converter is about 4 hour in which the temperature drop of the liquid iron in 90 ton ladle is 130K or so (from about 1735K to 1605K averagely). Lower melting temperature is a basic and necessary characteristic of high calcium slag in the ladle desulfurization process. Acidic silicon dioxide can significantly lower the melting temperature of high calcium slag with a basicity decreased and against the desulfurization [1-2]. It is the reason that the weakly acidic aluminium sesquioxide is used to lower the melting temperature of high calcium slag [3,4]. Moreover, the CaF_2 with a lower melting point is a general selection to lower the melting temperature of high calcium slag [4,5]. The higher the sulfur partition ratio, the less the amount of the high calcium slag used in the ladle desulfurization process, and the lower the consumption of the process cost. Based on both the chemical composition of the blast furnace slag and the iron ladle situation of the ShouGang ShuiCheng Iron and Steel (Group) Co. Ltd, the CaO-Al_2O_3-SiO_2-CaF_2-MgO slag with the lowest flowing temperature reported by literature [4-9] is selected for the sulfur partition ratio to be measured experimentally in the temperature range 1593-1743K and to discuss the effects on the sulfur partition ratio in high calcium desulfurization slag and liquid iron by temperature in this study.

2. Experimental
The high calcium desulfurization slag are mainly prepared by the blast furnace (BF) slag taken from Shougang Shuicheng Iron and Steel (Grope) Co. Limited. The main chemical composition of the BF

slag after crushed, ball milled, magnetic separation and iron removal is shown in table 1. Based on the content requirements of the CaO-Al_2O_3-SiO_2-CaF_2-MgO slag with the lowest flowing temperature [4], analytical reagents $Ca(OH)_2$, Al_2O_3 and CaF_2 were added to the BF slag powder (see table 2). Mixed equally, the modified mixture was placed in a graphite crucible and heated in an electric resistance furnace to 1773K, maintained at the temperature for 30 min to ensure the mixture was fully melted, and then the high calcium slag was taken out and cooled by water.

The dried high calcium slag was ground to less than 200 mesh in an agate mortar, adding in an appropriate amount of analytical reagent CaS to make the sulphur content up to 2.60%Wt, and mixed equally, then the powder was pressed in a cylindrical sample mold to obtain testing samples, the size of which was φ3mm*3mm. The melting temperature of the slag was determined using a melting temperature measurer (model CQKJ-II). The temperature of the sample was directly measured by PtRh30-PtRh6 thermocouple. The accuracy of sample melting temperature was about ±3K. The temperature, at which the height of the sample is reduced to one half of its original height, is defined as hemisphere temperature; at a quarter of its original height is flowing temperature [3].

The main chemical composition of the pig iron pieces taken from Shougang Shuicheng Iron and Steel (Grope) Co. Limited is shown in table 3. Based on the mass of the iron about 210 grams, the high calcium slag powder with 2.60% sulphur was weighed according to a 12.0% mass ratio of iron (see table 4), placed in the graphite crucible with an inner size φ40mm*65mm under the iron pieces, and covered with a graphite cap; then, put the crucible into the well-type resistance furnace, heated up to 1773K and holding for 30 min, and lowered to the controlled temperature in 30 min as shown in the figure 1. The graphite crucible was taken out of the heating furnace according to the selected holding time 120 min or 180 min and poured out the hot metal and slag to cool rapidly. The samples were taken to analyze sulfur content.

Table 1. Main chemical composition of the BF slag (%Wt).

FeO	T.Fe	CaO	MgO	SiO_2	Al_2O_3	TiO_2	S	Ig
1.79	1.37	37.95	9.12	29.4	11.87	6.13	0.823	1.59

Table 2. Main chemical composition of the high calcium slag (%Wt).

CaO	Al_2O_3	SiO_2	CaF_2	FeO	MgO	TiO_2	S
47.0	20.0	13.48	10.0	0.82	4.18	2.75	0.38

Table 3. Main chemical composition of the pig iron (%Wt).

C	Si	Mn	Ti	P	S
4.87	0.18	0.36	0.24	0.087	0.026

3. Results and discussion

The analyzed sulfur contents in the hot metals and the slags are fully summarized in Table 4. The sulfur content in the iron decreased with temperature increase or holding time extension. But the sulfur content in the slag increased with temperature increase or holding time extension.

3.1. Hemisphere temperature and flowing temperature

The melting temperature of the high calcium slag was determined as 1606K for hemisphere temperature and 1613K for flowing temperature. The hemisphere temperature and the flowing temperature of the high calcium slag with 2.60% sulphur was determined as 1647K and 1670K respectively. The hemisphere temperature raises 41K with the sulphur content increased from 0.38% to 2.60%, and the flowing temperature raises 57K. It is evident that the melting temperature of the high calcium slag raises with the sulphur content increase.

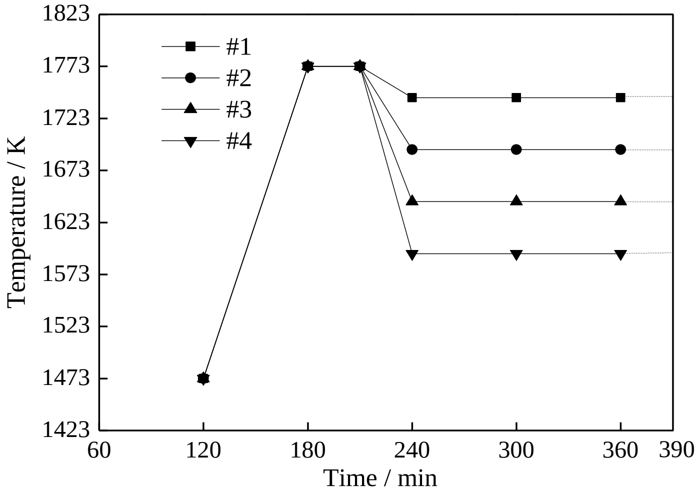

Figure 1. Heating and holding time of samples versus temperature.

Table 4. Sulfur content in samples and initial masses of both iron and slag.

Sample	1	2	3	4	5	6	7	8
Iron mass/g	206.19	225.24	208.63	204.24	201.95	204.22	240.32	225.24
Slag mass/g	24.74	27.03	25.04	24.51	24.23	24.51	28.84	27.03
holding temperature/K	1743	1693	1643	1593	1743	1693	1643	1593
holding time/min	120	120	120	120	180	180	180	180
sulfur in iron/ppm	90	130	190	220	60	80	130	170
sulfur in slag/%Wt	2.71	2.71	2.62	2.54	2.73	2.64	2.59	2.56

3.2. Effect of temperature on the desulfurization degree
When the holding time of the hot metal and slag at controlled temperature was 120 min in the furnace, the desulfurization degree of the high calcium slag increased correspondingly with temperature increase (see figure 2). Similarly, the desulfurization degree of the high calcium slag increased correspondingly with temperature increase in the range 1593-1743K when the holding time of the hot metal and slag at controlled temperature was extended from 120 min to 180 min in the furnace(see figure 2). Moreover, the desulfurization degrees of the samples increased correspondingly with the holding time extended from 120 min to 180 min at the same temperature (see figure 2). The higher desulfurization degree of the high calcium slag may be mainly correlated with the higher basicity or higher CaF_2 content [1,5].

3.3. Effect of temperature on sulphur partition ratio
When the holding time of the hot metal and slag at controlled temperature was 120 min in the furnace, the sulfur partition ratio of the sample increased correspondingly with temperature increase (see figure 3). Similarly, the sulfur partition ratio of the sample increased correspondingly with temperature increase when the holding time of the hot metal and slag at controlled temperature was extended from 120 min to 180 min in the furnace(see figure 3). Moreover, the sulfur partition ratio of the samples increased correspondingly with the holding time extended from 120 min to 180 min at the same temperature, and the increasing range of the sulfur partition ratio increased correspondingly with temperature increase in the range 1593-1743K (see figure 3). The higher sulfur partition ratio of the sample may be related to the multicomponent characteristics of the slag such as lower flowing

temperature and better liquidity [1,3-5,8-10], and mainly correlated with the higher basicity and higher CaF_2 content[1,5-9].

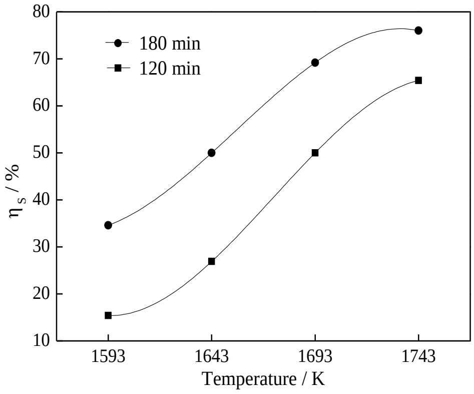

Figure 2. Effects of both temperature and holding time on the desul furization degree of the samples.

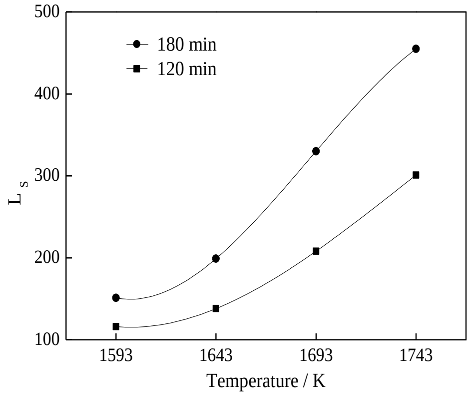

Figure 3. Effects of both temperature and holding time on the sulfur partition ratio of the samples.

4. Conclusions

The melting temperature of the high calcium slag raises with the sulphur content increase, the flowing temperature raises 57K from 1613K with the sulphur content increased from 0.38% to 2.60%.

The desulfurization degree of the high calcium slag increased correspondingly with both the temperature increase in the range 1593-1743K and the holding time extension from 120 min to 180 min. The sulfur partition ratio of the sample increased correspondingly with both the temperature increase in the range 1593-1743K and the holding time extension from 120 min to 180 min. The higher sulfur partition ratio of the sample may be related to the multicomponent characteristics of the slag, and mainly correlated with the higher basicity and higher CaF_2 conten.

5. References

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