

## Desulfurization ability of refining slag with medium basicity

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**Abstract:** The desulfurization ability of refining slag with relative lower basicity ( $B$ ) and  $\text{Al}_2\text{O}_3$  content ( $B = 3.5\text{--}5.0$ ;  $20\text{wt}\%\text{--}25\text{wt}\% \text{Al}_2\text{O}_3$ ) was studied. Firstly, the component activities and sulfide capacity ( $C_S$ ) of the slag were calculated. Then slag–metal equilibrium experiments were carried out to measure the equilibrium sulfur distribution ( $L_S$ ). Based on the laboratorial experiments, slag composition was optimized for a better desulfurization ability, which was verified by industrial trials in a steel plant. The obtained results indicated that an MgO-saturated CaO– $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ –MgO system with the basicity of about 3.5–5.0 and the  $\text{Al}_2\text{O}_3$  content in the range of  $20\text{wt}\%\text{--}25\text{wt}\%$  has high activity of CaO ( $a_{\text{CaO}}$ ), with no deterioration of  $C_S$  compared with conventional desulfurization slag. The measured  $L_S$  between high-strength low-alloyed (HSLA) steel and slag with a basicity of about 3.5 and an  $\text{Al}_2\text{O}_3$  content of about  $20\text{wt}\%$  and between HSLA steel and slag with a basicity of about 5.0 and an  $\text{Al}_2\text{O}_3$  content of about  $25\text{wt}\%$  is 350 and 275, respectively. The new slag with a basicity of about 3.5–5.0 and an  $\text{Al}_2\text{O}_3$  content of about  $20\text{wt}\%$  has strong desulfurization ability. In particular, the key for high-efficiency desulfurization is to keep oxygen potential in the reaction system as low as possible, which was also verified by industrial trials.

**Keywords:** high-strength steel; low alloyed steel; refining; slag; basicity; desulfurization; thermodynamic calculations

### 1. Introduction

Sulfur in steel is required to be reduced as low as possible for most steel grades because it deteriorates the properties of ductility, low-temperature toughness, welding, anti hydrogen-induced cracking (HIC), etc. For example, the sulfur content should be controlled lower than  $0.005\text{wt}\%$  for most high-grade pipeline steel and  $0.001\text{wt}\%$  for anti-HIC pipeline steel [1–3]. To realize high-efficiency desulfurization, the desulfurization ability of slag was studied by some scholars. Calculated formulas of sulfide capacity ( $C_S$ ) based on optical basicity were obtained by Sosinsky and Sommerville [4], Young *et al.* [5] and Taniguchi *et al.* [6], and the Kungliga Tekniska Högskolan (KTH) model was developed by Nzotta *et al.* [7]. The effects of slag components on desulfurization were also investigated [8–12]. For example, an increase in the content of free CaO for slag that contained  $15\text{wt}\%\text{--}40\text{wt}\% \text{Al}_2\text{O}_3$  can obtain good desulfurization, and the  $\text{Al}_2\text{O}_3/\text{CaO}$  mass ratio of refining slag has a great influ-

ence on the equilibrium sulfur distribution ( $L_S$ ). In addition, refining slag usually used in industrial production was studied. Nippon Ko-Kan (NKK) proposed the concept of a slag parameter (S.P.) and pointed out that the optimized slag composition as far as desulfurization is concerned is around  $60\text{wt}\%\text{CaO}\text{--}30\text{wt}\%\text{Al}_2\text{O}_3\text{--}10\text{wt}\%\text{SiO}_2$  [13], while the report of Dillingen Company mentioned that slag with a composition of  $60\text{wt}\%\text{CaO}\text{--}30\text{wt}\%\text{Al}_2\text{O}_3\text{--}8\text{wt}\%\text{SiO}_2$  was better based on the analysis of the lime saturation index of slag in their production [14]. Usually, the main parameters of ladle furnace (LF) slag for X80 in Baosteel are  $B > 7$ ,  $\text{Al}_2\text{O}_3 > 30\text{wt}\%$ , and  $(\text{FeO} + \text{MnO}) < 0.5\text{wt}\%$  [15]. Therefore, the main feature of conventional desulfurization slag is high basicity ( $B > 6$ ) and  $\text{Al}_2\text{O}_3$  content ( $30\text{wt}\%$  or even higher).

HSLA steel has a strict requirement for sulfur content. Therefore, high basicity and  $\text{Al}_2\text{O}_3$  content slag is used in secondary refining, and the steel usually contains more than  $0.015\text{wt}\%$  [Al] [2,13,15]. As a result, the low-melting-point inclusions of CaO– $\text{Al}_2\text{O}_3$  systems with large size can

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probably be formed and have been frequently blamed as the reason for the deteriorated properties of HSLA steel plates or the downgrade of the coils [16–18]. Research [16–21] has indicated that the formation of such inclusions is closely related to high-basicity slag refining. Therefore, methods should be found to effectively prevent such kinds of inclusions, at the same time ensuring the desulfurization. Under this background, a new concept was proposed to avoid these low-melting-point inclusions by reducing the basicity of refining slag, but the premise is that the new slag has strong desulfurization ability. Some industrial practices have shown that refining slag with a relatively lower basicity could obtain good desulfurization; for example, satisfactory desulfurization was achieved at Jigang Corporation, who refined by CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–MgO system slag with  $B = 3$ – $3.5$  and Al<sub>2</sub>O<sub>3</sub> = 11wt%–17wt% [22] and at Anyang Steelmaking Plant by CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system slag with  $B = 3$ – $5$  and (TFe + MnO) < 1.5wt% [23]. Li *et al.* [24] and Chen and Wang [9] investigated the desulfurization ability of CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–MgO–CaF<sub>2</sub> system slag. According to their results, the optimum composition obtained by Li *et al.* was  $B = 3$ , CaF<sub>2</sub> = 7wt%, MgO = 6wt%, and Al<sub>2</sub>O<sub>3</sub> = 24wt% but that obtained by Chen *et al.* was  $B = 4$ , CaF<sub>2</sub> = 9wt%, MgO = 8wt%, Al<sub>2</sub>O<sub>3</sub> = 13wt%, and FeO < 0.5wt%. Both slag samples had a relatively higher content of CaF<sub>2</sub>. Thus, it is not clear whether the CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–MgO system with a relatively lower basicity has strong desulfurization ability. The practice of Kawasaki Steel Corporation, Japan [25] and Ovako Steel AB, Sweden [12] indicated that both basicity and Al<sub>2</sub>O<sub>3</sub> content in slag had a great influence on desulfurization, but the proper basicity and Al<sub>2</sub>O<sub>3</sub> content of refining slag were not reported. For these reasons, the desulfurization ability of CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–MgO system slag with the basicity less than 5.0 was studied in this paper.

## 2. Methodology

### 2.1. Thermodynamic calculations

(1) Calculation of  $a_{\text{CaO}}$ . The activity of CaO ( $a_{\text{CaO}}$ ) in slag with different compositions was calculated using the thermodynamic commercial software Thermo-Calc Version TCCR, which was released in 2007 [21]. At present, the main components are CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and MgO in slag commonly used in secondary refining. Thus, the calculated slag system was set as CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–MgO in the present work, and the conditions were as follows: temperature ( $T$ ), 1873 K;  $B$ , 2–7; Al<sub>2</sub>O<sub>3</sub>, 20wt%–35wt%; MgO saturated, which was set as the activity of MgO ( $a_{\text{MgO}} = 1$ ) in thermodynamic calculations. All compositions in this paper are

given in mass percentage unless specifically stated.

(2) Calculation of  $C_S$ .  $C_S$  represents the desulfurization ability of slag under a certain temperature. In this paper, the  $C_S$  of slag was calculated using the Young's model [5] and the KTH model [7], and the formulas are as follows.

The Young's model follows [5]: when the optical basicity of slag  $A < 0.8$ ,

$$\lg C_S = -13.913 + 42.84A - 23.82A^2 - \frac{11710}{T} - 0.02223(\% \text{SiO}_2) - 0.02275(\% \text{Al}_2\text{O}_3) \quad (1)$$

but when the optical basicity of slag  $A \geq 0.8$ ,

$$\lg C_S = -0.6261 + 0.4808A + 0.7197A^2 + \frac{1697}{T} - \frac{2587A}{T} + 0.0005144(\% \text{FeO}) \quad (2)$$

The KTH model is shown below [7]:

$$C_S = \frac{K_1 \cdot a_{\text{O}^{2-}}}{f_{\text{S}^{2-}}} \quad (3)$$

$$K_1 = \exp\left(-\frac{\Delta G^\ominus}{RT}\right), \quad \Delta G^\ominus = 118535 - 58.8157T \quad (4)$$

$$\frac{a_{\text{O}^{2-}}}{f_{\text{S}^{2-}}} = \exp\left(-\frac{\xi}{RT}\right) \quad (5)$$

$$\xi = \sum X_i \xi_i + \xi_{\text{mix}} \quad (6)$$

where  $A$  is the optical basicity;  $C_S$  is the sulfide capacity;  $T$  is the temperature (K); (%SiO<sub>2</sub>), (%Al<sub>2</sub>O<sub>3</sub>), and (%FeO) are the contents of components in slag;  $K_1$  is the reaction equilibrium constant;  $a_{\text{O}^{2-}}$  and  $f_{\text{S}^{2-}}$  are the activity of O<sup>2-</sup> and the activity coefficient of S<sup>2-</sup>, respectively; and  $R$  is the gas constant. In a multicomponent system,  $\xi$  is described as a function of both temperature and composition. In Eq. (6), the subscript  $i$  denotes component  $i$ ,  $X_i$  is the mole fraction of this component; the first term  $X_i \xi_i$  represents the variation of  $\xi$  from the pure components in the absence of the interaction between different species and  $\xi_{\text{mix}}$  takes account of the mutual interactions between different species.

### 2.2. Slag–metal equilibrium experiment in the lab

$L_S$  was measured in slag–metal equilibrium experiments, which were carried out in an electric resistance furnace with Mo–Si heating elements. A reaction tube made of Al<sub>2</sub>O<sub>3</sub> was set in the furnace and its inner diameter (ID) was 80 mm. Before heating, 200 g master steel and 40 g fluxes were added in an MgO crucible (ID: 30 mm). The fluxes were mixtures of reagent-grade CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and MgO in proportion, in which CaO was ground into powder and dehydrated in advance. MgO was added with saturated content

according to thermodynamic calculations and the slag composition used in industrial production. Then the MgO crucible was put into a graphite crucible and together they were placed at the constant-temperature zone in the furnace. Next, Ar gas flow (flow rate: 1.5 NL/min) was introduced into the reaction tube, which was top and bottom sealed.

Heating was started after Ar gas had been infilled into the reaction tube for about 120 min. The temperature of the melt was measured with a Pt/Pt-13wt%Rh thermocouple set at the bottom of the crucible and a proportional-integral-differential (PID) controller was used for temperature control with the accuracy of  $\pm 0.5$  K. When the temperature was increased to 1873 K, the melt was held at this temperature for the time needed (determined as 90 min to reach the slag-metal equilibrium in pre-equilibrium experiments) without stirring for the purpose of establishing the equilibrium, and then the crucible was picked out and quenched rapidly in water for further analysis. The contents of carbon and sulfur in the steel were analyzed by an infrared absorption method, the soluble aluminum by methods of inductively coupled plasma mass spectrometry (ICP-MS), and the silicon and manganese by inductively coupled plasma-atomic emission spectrometry (ICP-AES). CaO, MgO,  $\text{Al}_2\text{O}_3$ , and MnO in slag were analyzed by ICP-AES, FeO by a titration method, and  $\text{SiO}_2$  by a gravimetric method.

The master steel used in the experiment was prepared by using a vacuum induction furnace according to the composition of HSLA steel. Specially mentioned, the sulfur content in the steel was increased intentionally to minimize the analytical error of  $L_S$ , and the aluminum content was also increased to ensure the low oxygen potential of the reaction. The chemical composition of the master steel is shown in Table 1.

**Table 1. Chemical composition of master steel** wt%

C	Si	Mn	P	S	$\text{Al}_s$
0.083	0.18	1.31	0.008	0.013	0.07

### 2.3. Industrial tests

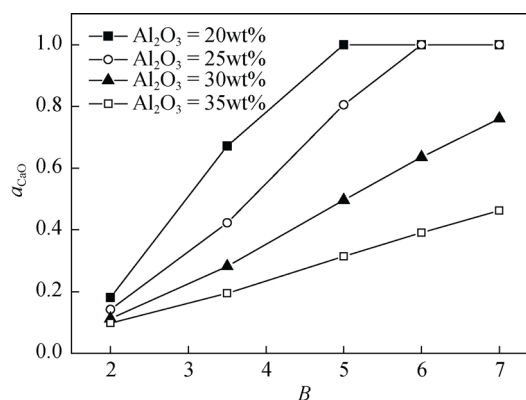
The measured  $L_S$  by the slag-metal equilibrium in the lab represented the maximum desulfurization ability under the experimental conditions. To further investigate the desulfurization ability of the new slag, industrial tests were carried out. The process routine of the industrial trial of HSLA steel was hot metal pretreatment  $\rightarrow$  basic oxygen furnace (BOF) steelmaking  $\rightarrow$  ladle furnace (LF) refining  $\rightarrow$  Ruhrstahl-Heraeus (RH) vacuum treatment  $\rightarrow$  slab continuous casting. The main technical points were as follows. (1) The

sulfur content in hot metal was removed to 0.005wt% or even lower during desulfurization pretreatment with magnesium. (2) At the end of steelmaking in a 210 t top and bottom blown vessel,  $[\text{C}] \leq 0.030\text{wt}\%$  and  $[\text{S}] = 0.005\text{wt}\% - 0.008\text{wt}\%$ . (3) After tapping, the liquid steel was refined by LF and  $[\text{S}] \leq 0.0020\text{wt}\%$  after LF refining.

## 3. Results and discussion

### 3.1. Calculated $a_{\text{CaO}}$ and effects of slag composition

The main desulfurization reaction in secondary refining is  $3\text{CaO} + 3[\text{S}] + 2[\text{Al}] = 3\text{CaS} + \text{Al}_2\text{O}_3$ , so the activity of CaO and  $\text{Al}_2\text{O}_3$  in slag has a great influence on the desulfurization ability. Fig. 1 shows the effect of slag basicity and  $\text{Al}_2\text{O}_3$  content in the CaO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -MgO system on  $a_{\text{CaO}}$ . The value of  $a_{\text{CaO}}$  increases gradually up to 1 with the rise of slag basicity. The lower the  $\text{Al}_2\text{O}_3$  content, the higher the value of  $a_{\text{CaO}}$  is when slag basicity keeps constant. For example,  $a_{\text{CaO}}$  is 1.000, 0.805, 0.496, and 0.314, respectively, when the  $\text{Al}_2\text{O}_3$  content is 20wt%, 25wt%, 30wt%, and 35wt% with a slag basicity of 5.0. Moreover, the lower the  $\text{Al}_2\text{O}_3$  content, the more significantly  $a_{\text{CaO}}$  changes with basicity. For instance, when the slag basicity increases from 2.0 to 5.0,  $a_{\text{CaO}}$  increases from 0.181 to 1.000 and the increment is 0.819 with 20wt%  $\text{Al}_2\text{O}_3$ , whereas  $a_{\text{CaO}}$  increases from 0.098 to 0.314 and the increment is 0.216 with 35wt%  $\text{Al}_2\text{O}_3$ . The effect of  $\text{Al}_2\text{O}_3$  content on  $a_{\text{CaO}}$  becomes stronger with further increase of slag basicity. For example, when the basicity is 2,  $a_{\text{CaO}}$  is 0.181, 0.142, 0.112, and 0.098, respectively, with 20wt%, 25wt%, 30wt%, and 35wt%  $\text{Al}_2\text{O}_3$ ; while when the basicity is 5.0,  $a_{\text{CaO}}$  is 1.000, 0.805, 0.496, and 0.314 accordingly and the difference is greater. The  $a_{\text{CaO}}$  of slag with 20wt%  $\text{Al}_2\text{O}_3$  is 1.000 when the basicity is 5.0; the  $a_{\text{CaO}}$  of slag with 25wt%  $\text{Al}_2\text{O}_3$  is 1.000 when the basicity is 6.0. For slag with 30wt% or more  $\text{Al}_2\text{O}_3$ , the basicity should be higher than 7.0 if  $a_{\text{CaO}}$  is unity.



**Fig. 1. Effect of slag composition on  $a_{\text{CaO}}$ .**

In summary, a minimum basicity exists to realize the saturation of CaO in slag ( $a_{\text{CaO}} = 1$ ) with the  $\text{Al}_2\text{O}_3$  content keeping constant. When the slag basicity is higher than the critical value, the CaO content is supersaturated. A decrease of  $\text{Al}_2\text{O}_3$  content in slag is beneficial to the increase of  $a_{\text{CaO}}$ , which means that it is helpful to desulfurization. Slags with 3.5 basicity, 20wt%  $\text{Al}_2\text{O}_3$  and 5.0 basicity, 20wt% and 25wt%  $\text{Al}_2\text{O}_3$  have relatively higher  $a_{\text{CaO}}$ , with the values of 0.672, 1.000, and 0.805, respectively, which may mean that they have strong desulfurization ability.

### 3.2. Calculated $C_S$ of different slags

The calculated  $a_{\text{CaO}}$  indicates that slag with 3.5 basicity and 20wt%  $\text{Al}_2\text{O}_3$ , and 5.0 basicity and 20wt% or 25wt%  $\text{Al}_2\text{O}_3$  may have strong desulfurization ability. For further verification, the  $C_S$  of slag was calculated with the Young's model [5] and the KTH model [7]. Two groups of refining slags were chosen. Group one included slag N1 ( $B$  3.5 and  $\text{Al}_2\text{O}_3$  20wt%), slag N2 ( $B$  5.0 and  $\text{Al}_2\text{O}_3$  20wt%), and slag N3 ( $B$  5.0 and  $\text{Al}_2\text{O}_3$  25 wt%), which had relative lower basicity and  $\text{Al}_2\text{O}_3$  content. Group two included slag N4 ( $B$  7.0 and  $\text{Al}_2\text{O}_3$  30wt%) and slag N5 ( $B$  7.0 and  $\text{Al}_2\text{O}_3$  25wt%) with relative higher basicity and  $\text{Al}_2\text{O}_3$  content, which were conventional desulfurization slag. As the content of the slag components was used in both models for  $C_S$  calculations, the mass percentage of MgO was set in this work. The calculated conditions were as follows:  $T = 1873$  K, a CaO– $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ –MgO system, and 6wt% MgO, according to thermodynamic calculations and refining slag used in industrial production.

The  $C_S$  values of the five slags are shown in Fig. 2. The calculated  $C_S$  values are different by the Young's model and the KTH model, but change in the same trend with the five slags. The  $C_S$  of slags N1, N3, and N4 differs slightly, with the values (obtained by the Young's model) of 0.0069, 0.0079, and 0.0075, respectively. The  $C_S$  of slags N2 and N5 is relatively higher, with the values of 0.0119 and 0.0115. Results show that the  $C_S$  values of group one are similar to those of group two, indicating that slag with relatively lower basicity and  $\text{Al}_2\text{O}_3$  content may have as strong desulfurization ability as conventional desulfurization slag.

### 3.3. Measured $L_S$ by the slag–metal equilibrium in the lab

To verify the thermodynamic calculations, slag–metal equilibrium experiments were carried out in the lab to measure  $L_S$  between the slag and HSLA steel.

Three slags were chosen in the experiment. They were slag N3 ( $B$  5.0 and  $\text{Al}_2\text{O}_3$  25wt%) and slag N1 ( $B$  3.5 and

$\text{Al}_2\text{O}_3$  20wt%), which had relatively lower basicity and  $\text{Al}_2\text{O}_3$  content, and slag N6 ( $B$  7.0 and  $\text{Al}_2\text{O}_3$  23wt%), which had the same parameters as practical refining slag used in some plants and very similar composition to slag N5 ( $B$  7.0 and  $\text{Al}_2\text{O}_3$  25wt%). To investigate the desulfurization ability of the above three slags, the reduced atmosphere in the reaction tube was strictly controlled during the experiment. For this purpose, highly pure argon (purity: 99.999 wt%) was introduced for about 120 min to replace the air in the tube as much as possible before heating and was infilled during the experiment to keep the oxygen potential as low as possible.

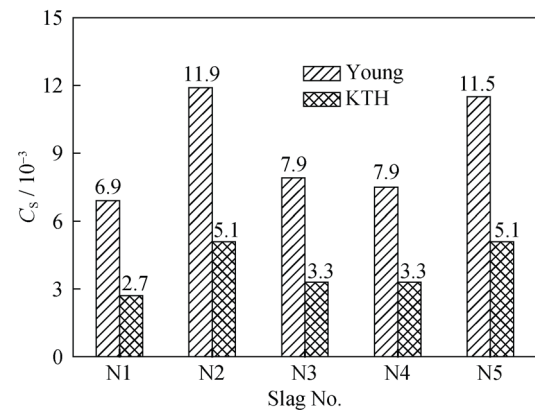


Fig. 2. Calculated  $C_S$  of the five slags.

To investigate the effect of oxidability in the reaction system on desulfurization, a contrast experiment was conducted in which slag N1 was used. The experiment procedure was the same as described earlier except that regular argon (purity: 99.5 wt%) was infilled both before heating and during the experiment. As a result, the oxygen potential was higher in the contrast experiment than in the previous regular experiments.

In addition, to minimize the influence of analytical error on  $L_S$ , the reagent FeS was added into the fluxes before heating to enhance the sulfur content of the reaction system. The chemical composition of the slags before the experiments is shown in Table 2.

Table 2. Chemical composition of slags before experiments

Experiment No.	$B$	$\text{Al}_2\text{O}_3$ / wt%	MgO / wt%	FeS / g	Slag / g	Atmosphere
1	5.0	25	6	0.074	40	Highly pure Ar
2	3.5	20	6	0.592	40	Highly pure Ar
3	7.0	23	5	1.887	40	Highly pure Ar
4	3.5	20	6	0.592	40	Regular Ar

The chemical composition of the steel and slag samples after equilibrium is shown in Tables 3 and 4, respectively. Fig. 3 shows the measured  $L_S$  between slag and steel. In ex-

periment No. 1, the sulfur content in the master steel was 0.013wt% and FeS reagent was added before heating; after equilibrium, the sulfur content in steel reduced greatly to 0.0004wt% and the measured  $L_S$  was 275. Thus, slag N3 used in experiment No.1 had strong desulfurization ability. However, it is worth mentioning that the sulfur content in steel after equilibrium was still very low. To reduce the analytical error as much as possible, the amount of FeS reagent added before heating was further increased in the following heats.

**Table 3. Chemical composition of steel samples after experiments**

Experiment No.	C	Si	Mn	P	S	Als
1	0.084	0.18	1.28	0.009	0.0004	0.065
2	0.084	0.18	1.29	0.009	0.0020	0.065
3	0.086	0.19	1.27	0.008	0.0030	0.067
4	0.083	0.20	1.25	0.009	0.036	0.003

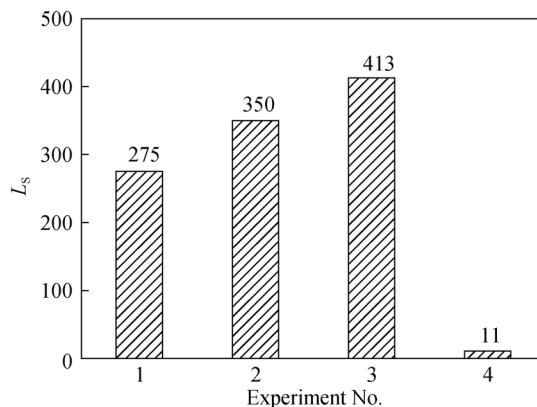
**Table 4. Chemical composition of slag samples after experiments**

Experiment No.	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MnO	FeO	S	B
1	52.95	8.12	24.92	10.77	0.18	0.3	0.11	4.92
2	51.16	9.14	19.80	15.32	0.24	0.3	0.70	3.34
3	55.82	8.15	23.32	8.32	0.21	0.1	1.24	6.71
4	51.66	8.14	21.55	14.89	0.66	0.6	0.39	3.47

From Tables 1–4 and Fig. 3, the sulfur content in the master steel was 0.013wt% and FeS reagent was added before heating to increase the sulfur content in the reaction system. When the slag–metal equilibrium was reached, the sulfur content in the steel samples of experiment Nos. 1, 2, and 3 were effectively removed to 0.0004wt%, 0.002wt%, and 0.003wt%, respectively; the  $L_S$  values were 275, 350, and 413, accordingly. The results indicated that slags N3, N1, and N6 had strong desulfurization ability although the ability of slags N3 and N1 was not as good as that of slag N6, which is commonly used in industrial production.

In the contrast experiment, the [Al] in steel after equilibrium decreased greatly to a content of 0.003wt% and the contents of FeO and MnO in the slag sample were much higher than in the regular experiments, which showed that the oxygen potential was higher in the contrast experiment than in the regular experiments. The sulfur content of the steel sample was 0.036wt%, which was much higher than that of the master steel, with an increase of 0.023wt%, and the  $L_S$  in the contrast experiment was 11. This meant that the refining slag not only could not cause desulfurization, but

also could cause sulfur pickup in steel because of the high sulfur content in the slag if the reduced atmosphere in the reaction system was not well controlled. Therefore, the oxygen potential in the reaction system must be as low as possible to cause high-efficiency desulfurization.



**Fig. 3. Measured  $L_S$  of four heats after the equilibrium is reached.**

### 3.4. Industrial tests

Slag–metal equilibrium experiments in the lab show that slags N3 and N1 have strong desulfurization ability. To further verify the desulfurization ability of slag with a relatively lower basicity, industrial tests were done including eight heats. In the tests, the target basicity of the slag used in LF refining was set at 4.5, and the target Al<sub>2</sub>O<sub>3</sub> content was 20wt%. The key parameters and practices during LF refining were as follows: treatment time, 45–50 min; bottom blowing flow rate, 600–800 L/min; and methods were implemented to keep the reduced atmosphere in the LF, including optimizing the method of dust removal, balancing between bottom blowing and dust removal, and argon sealing around the furnace roof.

The chemical composition of the steel and slag samples after LF refining in the tests is shown in Tables 5 and 6, respectively. The slag basicity at the end of LF refining of the eight heats ranged from 4.35 to 4.54 and the Al<sub>2</sub>O<sub>3</sub> content was from 20.80wt% to 22.00wt%, which related well with the set refined slag targets. It should be noted that the oxygen potential was controlled very low with the (T.Fe + MnO) in slag of 0.46wt%–0.58wt%.

The sulfur content in the samples obtained in the industrial trials after LF refining varied from 0.0006wt% to 0.0018wt%, which met the requirement of HSLA steel. The measured  $L_S$  was from 113 to 297 with an average of 218, which indicated that refining slag with the basicity of about 4.5 and the Al<sub>2</sub>O<sub>3</sub> content of about 20wt% had strong desulfurization ability.

**Table 5. Chemical composition of steel samples after LF refining** wt%

Heats	C	Si	Mn	P	S	Als
1	0.052	0.25	1.76	0.008	0.0007	0.032
2	0.054	0.24	1.84	0.007	0.0010	0.030
3	0.052	0.25	1.79	0.008	0.0008	0.036
4	0.051	0.24	1.78	0.009	0.0018	0.030
5	0.054	0.25	1.76	0.010	0.0006	0.036
6	0.053	0.23	1.78	0.012	0.0010	0.037
7	0.048	0.25	1.77	0.010	0.0009	0.039
8	0.053	0.24	1.77	0.009	0.0007	0.034

**Table 6. Chemical composition of slag samples after LF refining** wt%

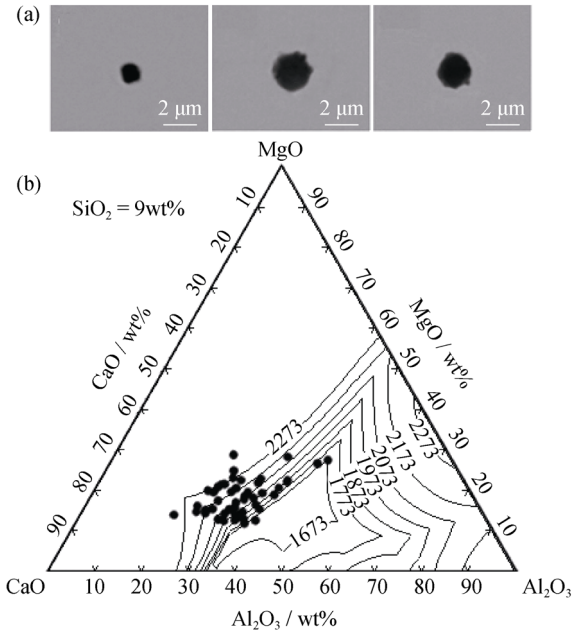
Heats	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	T.Fe + MnO	S	B
1	55.20	7.78	21.27	12.16	0.58	0.178	4.54
2	55.09	7.75	21.18	12.49	0.51	0.184	4.41
3	55.01	7.67	20.80	12.48	0.52	0.197	4.41
4	53.96	8.06	22.00	12.24	0.46	0.203	4.41
5	55.01	7.72	21.35	12.19	0.57	0.178	4.51
6	54.03	8.08	21.97	12.41	0.47	0.182	4.35
7	54.99	7.72	21.23	12.19	0.52	0.179	4.51
8	55.09	7.81	21.20	12.33	0.54	0.186	4.47

Inclusions in steel samples of eight heats after LF refining were analyzed. About six points on the cross-sectioned plane of each steel sample were randomly chosen to detect inclusions by using a scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS), for a total of 50 inclusions, to get statistical information about the inclusions including morphology, size, and chemical composition. Most inclusions were the CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system, and the SiO<sub>2</sub> content in the inclusions was relatively stable. The typical morphology and composition distribution of inclusions in the phase diagram at the end of LF refining are shown in Fig. 4, and the liquid regions of different temperatures in Kelvin calculated by the thermodynamic software FactSage are also plotted in the diagram. The composition of most inclusions is located in the relatively higher melting region ( $\geq 1773$  K), indicating that inclusions with relatively higher melting temperature can be formed in HSLA steel refined by slag with relative lower basicity and Al<sub>2</sub>O<sub>3</sub> content.

### 4. Conclusions

Thermodynamic calculations and experiments in the lab

have been done to investigate the desulfurization ability of refining slag with a relatively lower basicity, which was also tested by industrial experiments in a steel plant. Based on the analysis and results, the following conclusions can be drawn.



**Fig. 4. Typical morphology (a) and composition distribution (b) of inclusions at the end of LF refining.**

(1) An MgO-saturated CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–MgO system with the basicity of about 3.5–5.0 and the Al<sub>2</sub>O<sub>3</sub> content of about 20wt%–25wt% has high  $a_{CaO}$  and  $C_S$ , and the new slag has similar  $C_S$  to the conventional desulfurization slag.

(2) In the lab, the measured  $L_S$  between HSLA steel and slag with the basicity of about 3.5 and the Al<sub>2</sub>O<sub>3</sub> content of about 20wt% and between HSLA steel and slag with the basicity of about 5.0 and the Al<sub>2</sub>O<sub>3</sub> content of about 25wt% was 350 and 275, respectively.

(3) Refining slag with the basicity of about 4.5 and the Al<sub>2</sub>O<sub>3</sub> content of about 20wt% was used in industrial tests. At the end of LF refining, the sulfur content in the trial steels was lower than 0.002wt%, the measured  $L_S$  was from 113 to 297, and most inclusions were the CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system with a relative higher melting temperature ( $\geq 1773$  K).

(4) CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–MgO system slag with the basicity of about 3.5–5.0 and the Al<sub>2</sub>O<sub>3</sub> content of about 20wt% has strong desulfurization ability which meets the requirement of HSLA steel. The key for high-efficiency desulfurization is to keep oxygen potential in the reaction system as low as possible.

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