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A mathematical model for the dynamic desulfurization process of ultra-low-sulfur steel in the LF refining process

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ladle furnace; deep desulfurization; mathematical model; ultra-low-sulfur steel

Abstract – In order to obtain the dynamic variation rule of the sulfur content of liquid steel in the LF refining process, a complete mathematical model including a desulfurization kinetic model and temperature model in the deep desulfurization process is presented, based on the practical production and reaction mechanism of ultra-low-sulfur steel in a LF. The results show that the calculated values of the sulfur content in liquid steel using the model fit the experimental values well, and the relative error is less than 8%. The effects of refining slag on the desulfurization process are analyzed in this paper, which shows that slag basicity is most important at the early and middle stages of the process, while slag weight is most important at the middle and late stages. The effect of the above factors on the final sulfur content of liquid steel is further analyzed quantitatively. The simulated results provide a theoretical basis to segment control the refining process in order to achieve the maximum effect, improving efficiency, saving energy and reducing consumption.

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Due to the harmfulness of sulfur in steel and users' increasing requirements for steel quality, ultra-low-sulfur steel is increasingly popular and there are more and more studies about ultra-low-sulfur steel and the desulfurization process in a LF [1–4]. There are many studies about desulfurization models in the metallurgical process [5–8]; however, these studies tend to only focus on the effect of one or several factors on the desulfurization process, or just present a static model. There are few studies which analyze the desulfurization process by combining a thermodynamic model and kinetic model, let alone combining a temperature model, deoxidization reaction model and alloying model. Taking into account the above factors, a complete mathematical model with high precision for the dynamic desulfurization process is presented. As a result, the laws of dynamic change in sulfur content in liquid steel in the LF refining process can be acquired by mathematical modeling methods, and the effects of the initial sulfur content and refining slag on the desulfurization process are further analyzed.

1 Deep desulfurization model in a LF

1.1 Desulfurization kinetic model

The model is based on the following assumptions:

(1) Liquid steel has good mixing characteristics, and the composition of the steel is uniform, therefore a concentration gradient only exists near the phase boundary, and the mass transfer rate between the slag and metal can be treated by two-film theory.

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(2) Chemicals react very quickly under high temperature; in other words, the chemical reaction at the slag-metal interface is in local equilibrium and the deep desulfurization process is restricted by the mass transfer of [S] from liquid steel to the slag-metal interface.

Based on the above assumptions, the desulfurization rate equation can be calculated by equation (1).

$$-\frac{dC_{[S]}}{dt} = k_{[S]}\left(\frac{A}{V_m}\right)\left(C_{[S]} - \frac{C_{(S^{2-})}}{L_S}\right) \quad (1)$$

where $C_{[S]}$ is the sulfur concentration in liquid steel, t is the reaction time, $C_{(S^{2-})}$ is the sulfur concentration in slag, L_S is the equilibrium distribution coefficient of sulfur between the steel and slag, $k_{[S]}$ is the mass transfer coefficient, V_m is the liquid volume, and A is the interfacial area, that is static surface area in this paper [9–11].

The equilibrium distribution coefficient L_S is calculated [12] by equation (2).

$$\lg L_s = \lg\frac{C_{(S^{2-})}}{C_{[S]}} = -\frac{935}{T} + 1.357 + \lg f_s + \lg C_s - \lg a_{[O]} \quad (2)$$

where C_s is the sulfur capacity, calculated by the KTH model [13]. The activity interaction coefficient in the liquid steel is calculated by the Wagner equation:

$$\lg f_i = \sum\left(e_i^j\,[\%j]\right) \quad (3)$$

$a_{[O]}$ is obtained by the equilibrium between oxygen and aluminum in Al-killed steel, as follows:

$$2\,[Al] + 3\,[O] = Al_2O_3\,(s) \quad (4)$$

$$\Delta G^\theta = -244\,300 + 107.6T\,(J/mol)$$

$$\lg K_{Al}^\theta = \lg\frac{a_{Al_2O_3}}{(f_{Al}[Al])^2(f_O[O])^3} = \frac{63\,655}{T} - 20.58 \quad (5)$$

$$a_{[O]} = \sqrt[3]{\frac{a_{Al_2O_3}}{[Al]^2 \times 10^{\frac{63\,655}{T}-20.58}}}. \quad (6)$$

The activity of Al_2O_3 is calculated [14,15] by equation (7).

$$\lg a_{Al_2O_3} = \frac{\{-0.275\,(\%\,CaO) + 0.167\,(\%MgO)\}}{(\%\,SiO_2)} + 0.033\,(\%\,Al_2O_3) - 1.560 \quad (7)$$

$k_{[S]}$ is calculated by equations (8) and (9).

$$k_{[S]} = \frac{D_{[S]}}{\delta_m} \quad (8)$$

$$D_{[S]} = 4.33 \times 10^{-8}\exp\left(\frac{-4282}{T}\right) \quad (9)$$

where $D_{[S]}$ is the sulfur diffusion coefficient in liquid steel and δ_m is the boundary layer thickness in liquid steel, 1×10^{-4}/m [16].

1.2 The temperature model in the LF refining process

The desulfurization model contains the variable temperature, and the temperature will vary in a certain range in the refining process (1560–1640 °C), so it is necessary to establish a temperature model of the LF refining process at the same time, in order to simulate the desulfurization process as accurately as possible.

The temperature of liquid steel in a LF is calculated by equation (10).

$$T_c = T_p + \frac{Q_{total}}{G_{steel}C_{steel} + G_{slag}C_{slag}} \quad (10)$$

where T_p is the liquid steel temperature at the initial moment, T_c is the liquid steel temperature Δt seconds later, C_{steel} is the specific heat of liquid steel, C_{slag} is the specific heat of slag, G_{steel} is the steel weight, G_{slag} is the slag weight and Q_{total} is the total heat variation obtained Δt seconds later.

According to the principle of conservation of energy, the heat model of the system is built:

$$Q_{total} = Q_{arc} \pm Q_{alloy} - Q_{ld} - Q_{lx} - Q_{slag} - Q_{Ar} - Q_{smoke} \quad (11)$$

where Q_{arc} is heat produced by the electrode, Q_{alloy} is heat produced by the alloy, Q_{lx} is refractory heat storage, Q_{slag} is the slag thermal effect, Q_{Ar} is heat taken away by argon and Q_{smoke} is heat taken away by smoke. Q_{ld} is the heat loss of the furnace lining, which is a non-steady-state heat transfer process. To calculate this, heat loss from the ladle wall and heat loss from the bottom of the ladle are calculated separately.

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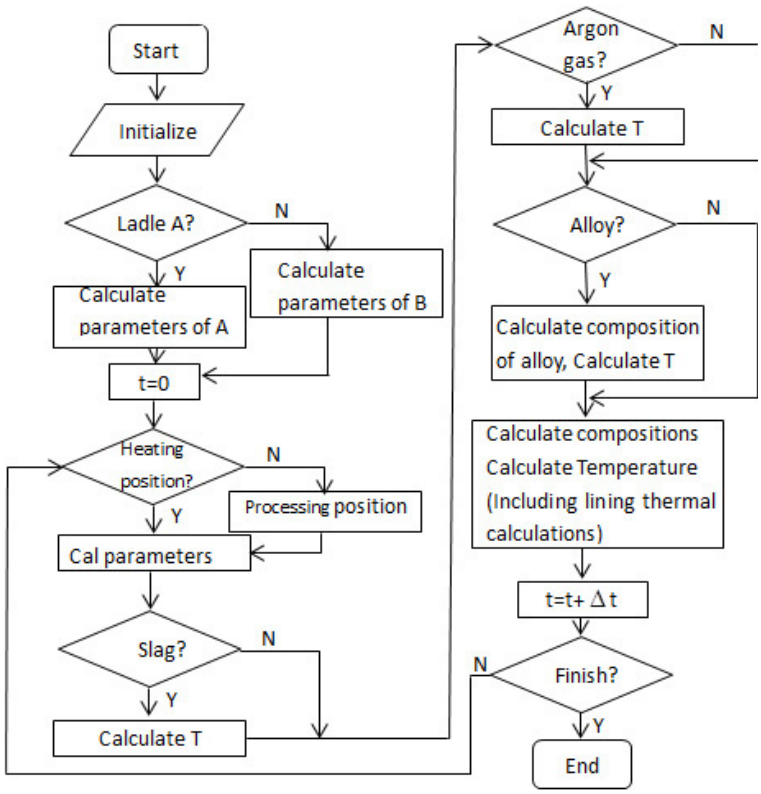


Fig. 1. Program principle of the desulfurization model of a LF.

Heat loss of the ladle wall: the ladle wall one-dimensional unsteady heat transfer equation is expressed as:

$$\frac{1}{a}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}. \tag{12}$$

Boundary conditions:

$$r = r_1,\ T = T_{\mathrm{st}};\ r = r_2,\ -\lambda\frac{\partial T}{\partial x}|_{r=r_2} = h(T - T_a). \tag{13}$$

Initial conditions ($t = 0$):

$$\frac{T - T_{\mathrm{ls},0}}{T_{\mathrm{st},0} - T_{\mathrm{ls},0}} = -\frac{\ln\frac{r_2}{r}}{\ln\frac{r_2}{r_1}}. \tag{14}$$

The heat transfer differential equations above can be solved by using the explicit difference method. The temperature distribution of the ladle wall can be obtained, so the heat loss of unit time can be calculated further. The heat loss from the ladle bottom can be calculated by the method described above.

2 Validation of the deep desulfurization model

The steel temperature change and steel composition change can be calculated continuously during the LF refining process in the model, by reading the amount of slag, the amount of argon gas flow, electrode heated stalls and the amount of alloy real-time in the refining process. The program principle of the desulfurization model is shown in Figure 1.

The experimental results and calculated results are compared in order to verify the accuracy of the model. Parameters, which are based on ultra-low-sulfur steel (only Al-killed steel is considered), and production records, such as temperature (Fig. 2), ladle type (Table 1), slag analysis (Table 2), steel analysis (Table 3), argon flow (Fig. 3) and heating power (Fig. 4), are used to complete the validation. The calculated values and experimental values of the sulfur content in liquid steel fit well (Fig. 5), and the relative error is less than 8%, so the model was proved accurate. The measured values and calculated

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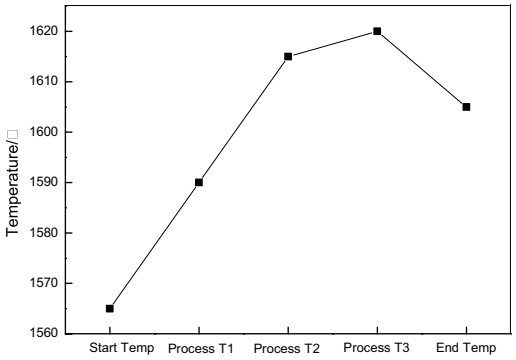


Fig. 2. Temperature change curve of the verification experiment in the LF refining process.

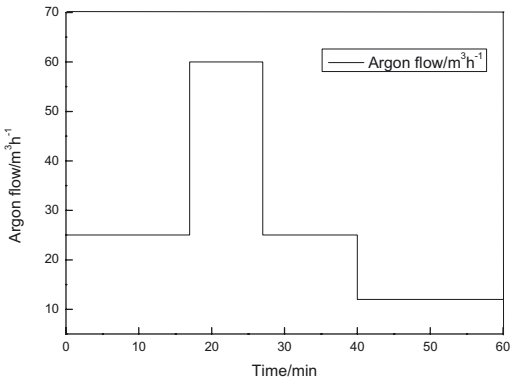


Fig. 3. Diagrammatic sketch of Argon flow.

Table 1. Working conditions of Ladle A (120t).

Position	Argon m^3/h	Temperature decreases °C/min
Cover	55–60	–1.2990
	20–40	–1.0290
No cover	10–20	–1.0091

Table 2. Chemical composition (in mass pct) of refining slag.

CaO	SiO_2	Al_2O_3	MgO	CaF_2	FeO	MnO
47.5	9.0	25.8	8.7	7.3	0.9	0.57

Table 3. Chemical composition (in mass pct) of liquid steel before refining treatment.

C	Si	Mn	P	Als	S
0.025	0.08	1.62	0.0084	0.065	0.0051

values in the final sulfur content are compared as well (Fig. 6). The calculated values are less than the experimental values as a whole, but the relative error is kept within 8%, so the accuracy of the model is validated further.

3 Results and discussion

In this study, the early stage is defined as 0–15 min of the refining process, the middle stage is defined as 15–30 min, and the late stage is defined as 30 min–end refining, in order to facilitate the following discussion. The effects of refining slag basicity on the desulfurization process are analyzed (W_{sl}/W_{st} is 1.5%, other parameters are the same as the verification experiment) using the validated mathematical model (Figs. 7–8). As can be seen from Figure 7, at the early and middle

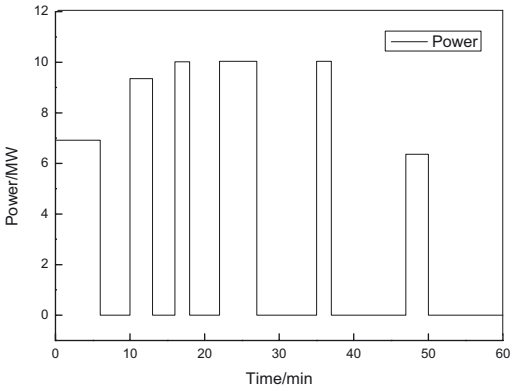


Fig. 4. Diagrammatic sketch of heating power.

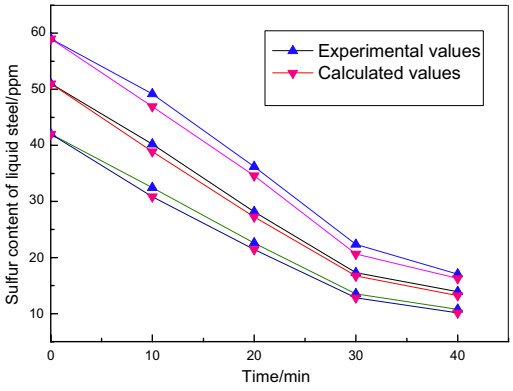


Fig. 5. Comparison between calculated values and measured values in the refining process.

stages of the desulfurization process, the difference in the sulfur content of the liquid steel increases with the increase in slag basicity; at the late stage, the difference continues to increase, but the rate decreases dramatically. There is a slope change at 17 min in Figure 7 due to the argon flow increase from 25

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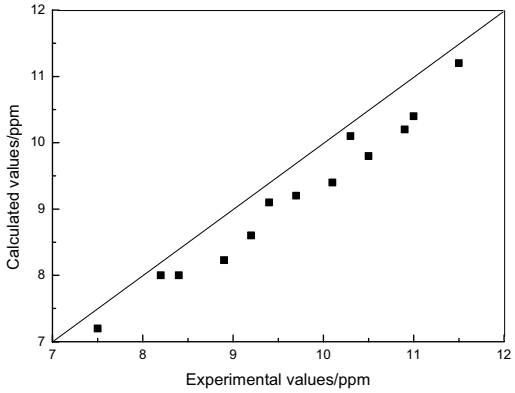


Fig. 6. Comparison between calculated values and measured values in the final sulfur content.

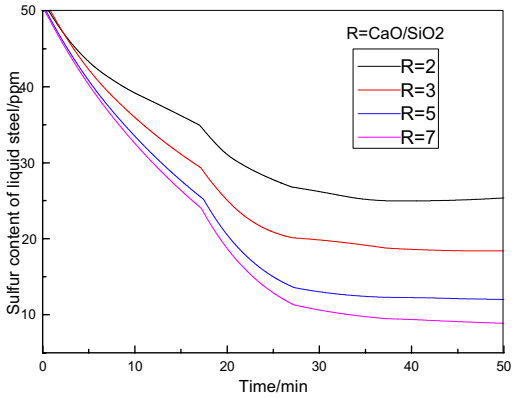


Fig. 7. The effect of basicity on desulfurization process.

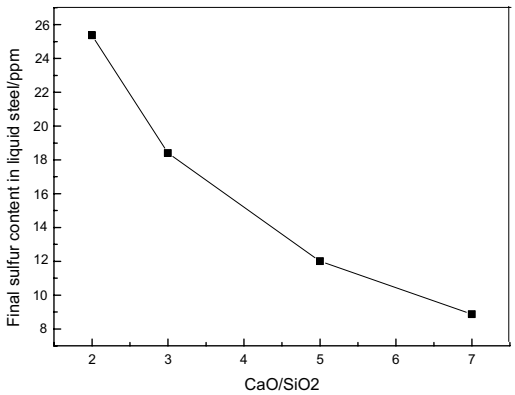


Fig. 8. The effect of basicity on the final sulfur content in liquid steel.

to 60 (m^3/h). As shown in Figure 8, with an increase in slag basicity (R = CaO/SiO2), the effect of increasing basicity on the sulfur content in the steel decreases. The final sulfur content decreases by 7 ppm when R increases from 2 to 3; the final sulfur content decreases by 6.4 ppm when *R* increases from 3 to 5; and the final sulfur content decreases by 3.2 ppm when *R* increases from 5 to 7.

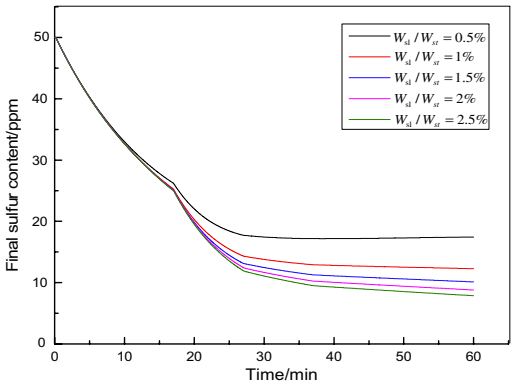


Fig. 9. The effect of slag weight on the desulfurization process.

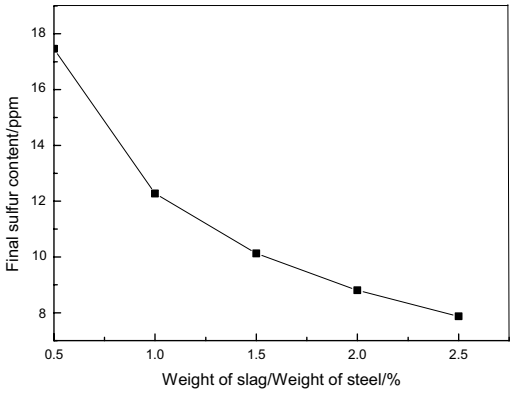


Fig. 10. The effect of slag weight on the final sulfur content.

The effect of the slag weight on the desulfurization process is analyzed (slag basicity is 5) by the model (Figs. 9–10). As can be seen from Figure 9, in contrast to the effect of basicity, slag weight has almost no effect on the early desulfurization stage, but it has an impact on the middle and late stages. It can be seen from Figure 10 that the effect of increased slag weight on the sulfur content in steel decreases when slag weight increases. When W_{sl}/W_{st} varies from 0.5% to 1%, the final sulfur content is reduced by 1 ppm with W_{sl}/W_{st} increase of 0.1%, while when W_{sl}/W_{st} varies from 2% to 2.5%, it is 0.19 ppm.

Based on the above analysis, these results show that the impact of slag basicity on the desulfurization process is most important at the early and middle stages, while

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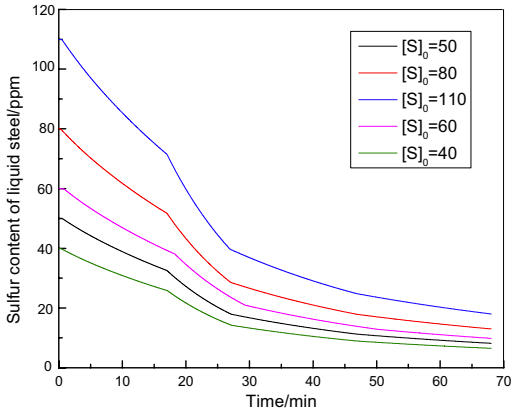


Fig. 11. The effect of the initial sulfur content in liquid steel on the desulfurization process.

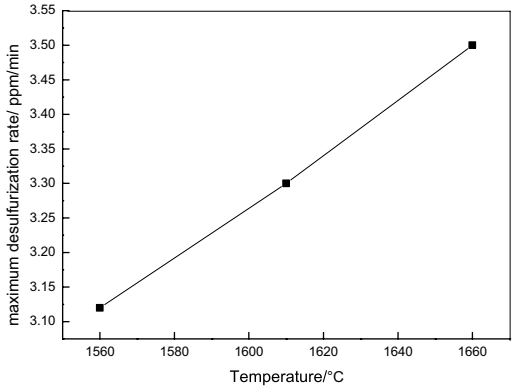


Fig. 13. The effect of temperature on the maximum desulfurization rate.

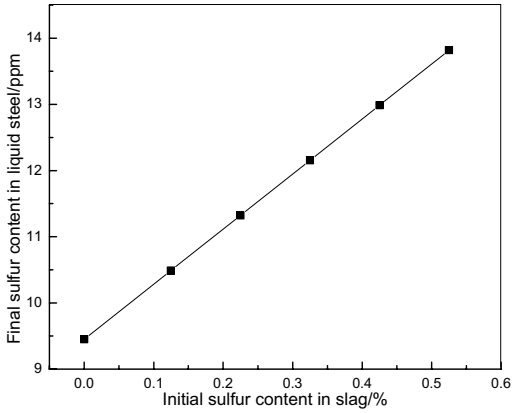


Fig. 12. The effect of the initial sulfur content in slag on the final sulfur content in liquid steel.

the impact of the slag weight is noticeable at the middle and late stages. Thus, the method that controls the basicity and slag weight in the refining process by segment is presented theoretically. That is to say, a small amount of slag weight with high basicity is controlled at the early and middle stages and then slag weight increases without considering basicity so that a large amount of slag weight is controlled at the late stage. By this method, the desulfurization effect can achieve its maximum, and therefore improve efficiency and reduce consumption.

The effect of the initial sulfur content in liquid steel and in slag on the desulfurization process is analyzed (slag basicity is 5, W_s/W_{st} is 1.5%) as well by the model (Figs. 11–12). According to Figure 11, when the initial sulfur content in liquid steel is 40 ppm, 50 ppm, 60 ppm, 80 ppm and 110 ppm, the final sulfur content is 6.49 ppm, 8.19 ppm, 9.88 ppm, 12.9 ppm and 17.7 ppm, respectively. Namely, the final sulfur content increases 1.6–1.7 ppm when the initial sulfur content in steel increases 10 ppm on average. According to Figure 12, the initial sulfur content in slag has little impact on the desulfurization process. The final sulfur content increases 0.83 ppm with the initial sulfur content in slag increasing 1000 ppm on average.

The maximum desulfurization rate, which is the maximum $-\frac{dC_{[S]}}{dt}$ in the desulfurization process, at 1560 °C, 1610 °C and 1660 °C is calculated (slag basicity is 5, W_{sl}/W_{st} is 1.5%, argon flow is 35 (m^3/h)) (Fig. 13) by the model, respectively. As shown in Figure 13, the maximum desulfurization rate is 3.5 ppm/min at 1660 °C, while it is only 3.12 ppm/min at 1560 °C and 3.3 ppm/min at 1610 °C. The maximum desulfurization rate increases by about 0.038 when the refining temperature increases by 10 °C.

4 Conclusions

A complete mathematical model of the deep desulfurization process in a LF is presented in this paper. The model proved that the calculated values of the sulfur content in liquid steel fit the experimental values well, and that the relative error is maintained at less than 8%. The effects of slag basicity and slag weight on the desulfurization process were analyzed using the model. The effects of the initial sulfur content in liquid steel and in

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slag on the desulfurization process were analyzed as well. The results are summarized as follows.

(1) Slag basicity has a great influence on the desulfurization process at the early and middle desulfurization stages, while it has little effect at the late stage, relatively.
(2) Slag weight has almost no effect on the early desulfurization stage, while it has a continuous impact on the middle and late stages.
(3) An idea that controls the basicity and slag weight by segment in the refining process is presented, based on the results above.
(4) The initial sulfur content in steel, rather than in slag, has a greater influence on the desulfurization process. The final sulfur content in steel increases by 1.6–1.7 ppm when the initial sulfur content in steel increases by 10 ppm, while it increases by 0.83 ppm on average when the initial sulfur content in slag increases by 1000 ppm.

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References

[1] T. Schambron, A.W. Phillips, D.M. O'Brien et al., *ISIJ Int.* **49** (2009) 284
[2] M.C. Zhao, T. Hanamura, H. Qiu et al., *ISIJ Int.* **45** (2005) 116
[3] P.V. Riboud, C. Gatellier, *Ironmaking Steelmaking* **12** (1985) 79–86
[4] D. Merson, S. Dement'ev, A. Ioffe et al., *ISIJ Int.* **51** (2011) 1682
[5] X.M. Yang, J.S. Jiao, R.C. Ding et al., *ISIJ Int.* **49** (2009) 1828
[6] S.Q. Li, G.H. Xiong, S.Q. Li et al., *J Univ. Sci. Technol. Beijing* **26** (2004) 244
[7] C.B. Shi, X.M. Yang , J.S. Jiao et al., *ISIJ Int.* **50** (2010) 1362
[8] Z.S. Zou, Y.S. Zou, L.B. Zhang et al., *ISIJ Int.* **41** (2001) S66
[9] J.M. Coudure, G.A. Irons, *ISIJ Int.* **34** (1994) 155
[10] Shigeo Asai, Iwao Muchi. *ISIJ* **55** (1969) 122
[11] G.C. Jiang, K.D. Xu , Z.C. Guo et al., *Acta Metallurgica Sinica* **26** (1990) 33
[12] Gornerup M. *Studies of Slag Metallurgy in Stainless Steelmaking* [Dissertation]. Stockholm: Department of Metallurgy, Royal Institute of Technology (1997)
[13] M.M. Nzotta, D. Sichen, *ISIJ Int*. **38** (1998) 1170
[14] H. Ohta, H. Suito, *Metall Trans. B* **28** (1998) 119
[15] M.A.T. Andersson, P.G. Jonsson, M.M. Nzotta, *ISIJ Int.* **39** (1999) 1140
[16] J.Y. Zhang, Metallurgical physical chemistry, The Metallurgical Industry Press, Beijing, 2009, p. 232 (in Chinese)

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