Sulfur Control in Ultra-Low Sulfur Steel Refined by Ladle Furnace-Vacuum Degassing

Yang Jing-bo[1, 2], Yang Shu-feng[1], Gao Xiang-zhou[1], Li Jing-she[1]

1. School of Metallurgical and Ecological Engineering, University of Science and Technology, Beijing, 100083, China

2. Hebei Iron and Steel Group, Tangshan Iron and Steel Group Co., Ltd, Tangshan, 063016, China

Abstract
Sulfur is deleterious in most kinds of steel Many factors influence the sulfur content in steel. We have investigated how ladle furnace (LF) slag deoxidizers, LF dynamic conditions and Ca-treatment after Ruhrstahl-Heraeus treatment affect desulfurization. The (FeO+MnO) content can be controlled below 0.5% after the addition of more than 300 kg aluminum particles and sulfur in the steel is reduced from 30 to 6 ppm. When the bottom gas flowrate is 500 NL/min, sulfur in the steel can be reduced to 6 ppm after 10 min. Too high or too low an argon flowrate reduces the desulfurization efficiency. Vacuum degassing followed by Ca-treatment has no effect on desulfurization, but Ca input helps maintain a low sulfur content.
Keywords: *Ultra-low sulfur steel; desulfurization; ladle furnace-vacuum degassing refining; Ca-treatment*

Introduction

Sulfur is deleterious in most kinds of steel. It not only causes hot brittleness and impacts ductility, toughness and weldability, but can also form MnS inclusions, which become extended and elongated in the rolling process and lead to an increase in mechanical anisotropy. To achieve good resistance to the corrosion by hydrogen sulfide, the sulfur content in steel must be controlled below 0.0020%. Refining by desulfurization of clean steel has become the focus of many studies. High basicity refining of slag and calcium treatment can be used to control the sulfur content and reduce MnS inclusions.

1. Experimental methods

Ultra-low sulfur steel is produced by the basic oxygen furnace-ladle furnace (LF)-Ruhrstahl-Heraeus-Ca-treatment-continuous casting method. The effect of (FeO+MnO) content in the LF slag, the kinetic conditions for LF refining and vacuum degassing (VD) with late calcium treatment on desulfurization were studied. Five industrial trials were carried out to determine the effect of (FeO+MnO) content in the LF slag on sulfur content. In the LF unit process, 100, 200, 250, 300 and 320 kg of aluminum particles were added into the furnace. Twenty five steel samples and 25 slag samples were taken before refining which lasted 10, 20, 30 and 45 min. After determining the optimal amount of aluminum particles required, a further five trials were carried out. Fifteen steel samples and 15 slag samples were taken at the LF refining slag stage with argon inflow at the bottom of the furnace for 5 and 10 min. The optimum input of aluminum and argon flow in the LF process was determined using these trials. Fourteen steel samples from seven steel trials were taken before and after VD. The elemental content in the steel samples and chemical composition of the slag samples were analyzed.
The basicity of the LF slag is high and up to 9.9 on average during production. The average mass ratio of CaO/Al_2O_3 is 2.0. The composition of molten steel produced by the converter is shown

 © Metallurgical and Mining Industry, 2013/3

in Table 1. The composition of the LF slag produced by LF refining is shown in Table 2.

Table Molten steel composition (%)

Elements in steel	C	Si	Mn	P	S	Als
Content / %	0.18	0.26	0.54	<0.17	0.0025–0.0035	0.020–0.350

Table 2 LF slag composition (%)

Composition	CaO	SiO_2	MgO	TFe	Al_2O_3	MnO	P_2O_5	S	R
Maximum	57.293	10.285	10.169	4.024	36.252	0.267	0.068	0.300	23.056
Minimum	46.347	2.209	4.831	0.379	24.034	0.010	0.012	0.198	5.176
Average	52.583	6.076	7.247	0.782	28.863	0.041	0.019	0.250	9.899

2. Results and Discussion

2.1 Effect of (FeO+MnO) content in LF slag on desulfurization

The oxygen content in the slag depends on the (FeO+MnO) content in the slag and(FeO+MnO) content also has an important influence on the distribution ratio of sulfur between the slag and steel in secondary refining. Because the slag can be oxidized easily, its potential for desulfurization is limited and increases the desulfurization time. The relationship between (FeO+MnO) content and distribution ratio of sulfur (Ls) in the initial slag is shown in Fig. 1. The ability of the slag to be oxidized has an obvious influence on the desulfurization efficiency of molten steel. The lower the (FeO+MnO) content in the initial slag, the higher the Ls. To limit desulfurization, the (FeO+MnO) content in the initial slag should be below 1%.

A chemical analysis was conducted on the slag samples taken after LF refining with different aluminum particle input masses. Results from the analysis of (FeO+MnO) content are shown in Table 3. If the initial (FeO+MnO) content is below 0.5%, the desulfurization rate increases. The addition of a certain amount of deoxidizer in the LF refining process can reduce the FeO content in the slag. In this study, aluminum was selected as the deoxidizer.

Results from the experiments investigating the change of sulfur content in molten steel from different aluminum particle input masses are shown in Fig. 2. To effect desulfurization and to achieve sufficient reaction between the deoxidizer and oxide, aluminum particles were added into the slag on average three times. As shown in Fig. 2, with the addition of 300 kg of aluminum particles, the sulfur content in the molten steel after refining for 45 min was reduced from the original 29 to 7.9 ppm and from 30 to 6 ppm with the addition of 320 kg.

Table 3 (FeO+MnO) composition in LF slags with different Al input masses (%)

Al input / kg	100	200	250	300	320
(FeO+MnO) / %	1.01	0.77	0.52	0.39	0.46

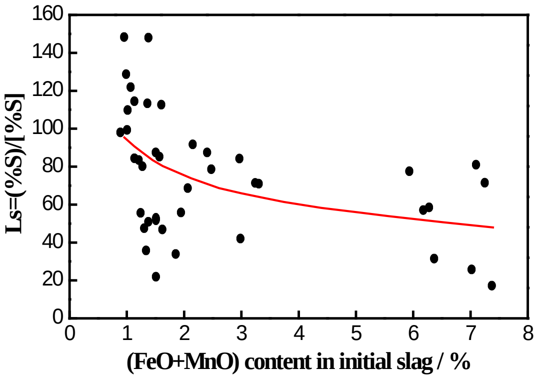

Figure 1 Relationship between sulfur ratio and (FeO+MnO) content in initial slag

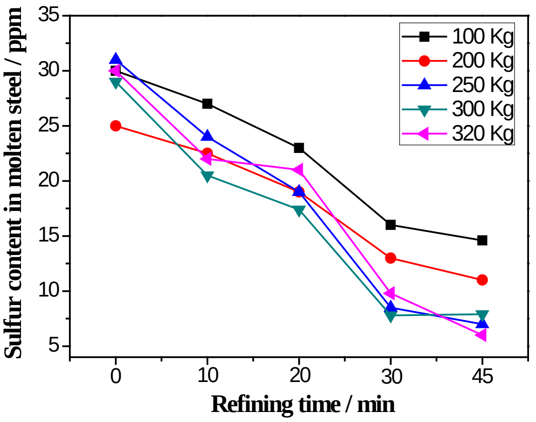

Figure 2 Relationship between sulfur in molten steel and aluminum particle input in slag

2.2 Effect of dynamic conditions on desulfurization

Fig. 2 also shows that the sulfur content in the molten steel is reduced rapidly over 30 min from the beginning of LF refining. The sulfur content in the molten steel is reduced slowly between 30 to 45 min. When the sulfur content in molten steel is reduced to a certain concentration, the diffusion of [S] in the molten steel is a restrictive step in the desulfurization reaction. The kinetic conditions for desulfurization need to be improved to obtain further desulfurization.

To study the effect of the dynamic conditions on desulfurization, some steel samples were taken after LF refining slag melting, and argon inflow at the bottom of the furnace for 5 and 10 min to determine the sulfur content in molten steel. Aluminum particles (320 kg) were added in the LF refining process. To study the effect of argon flow on desulfurization during gas stirring, the sulfur content in molten steel was analyzed at different argon flowrates, as shown in Fig. 3.

In the trials, temperatures were chosen at which the sulfur content in the molten steel differs little before argon stirring. Argon flowrates of 400, 500, 600, 700 and 800 NL/min were selected. The sulfur content in the molten steel is reduced rapidly in the 5 min before argon stirring and is reduced more significantly during heating when the initial sulfur content is high. After stirring for some time and with an argon flow for 5 and 10 min, the sulfur content in the molten steel is reduced slowly and decreases to approximately 2 ppm. The results shown in Fig. 3 indicate that when the argon flow is 400 NL/min, the sulfur content in the molten steel is reduced the least. The results shown in Table 4 indicate that when the argon flow is 500 NL/min, the sulfur content in the molten steel is reduced by 62.50% from 16 to 6 ppm. When the argon flowrate increases, higher quantities of large bubbles will be produced. An increased argon flow facilitates the formation of a bare slag surface in molten steel, which leads to uptake by the molten steel and reduces the desulfurization efficiency. A large flow rate can cause the turbulence of molten steel, slag entrapment, severe erosion of the ladle lining and an increase in the quantity and size of inclusions. Too high or too low an argon flowrate negatively affects the desulfurization of molten steel under dynamic conditions. In this study, the optimum argon flowrate is 500 NL/min as the sulfur content in the molten steel can be reduced from 16 to 6 ppm.

Table 4 Relationship between argon flowrate and desulfurization efficiency

Argon inflow at furnace bottom / NL/min	400	500	600	700	800
Reduction in sulfur content / %	30.71	62.50	50.00	52.94	14.06

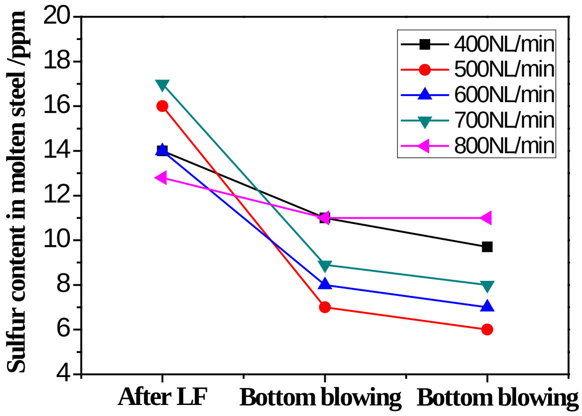

Figure 3 Relationship between sulfur in molten steel and argon flow

2.3 Relationship between calcium treatment and sulfur content

After the ultra-low sulfur steel has been treated by VD, the molten steel is fed with silicon-calcium wire to the calcium treatment stage. At this point, the temperature of the molten steel is approximately 1580°C. The [Ca]-[S] reaction calculated at 1580°C is given below.

There is a balance between the [Ca] and [S] in the molten steel:

$$[Ca]+[S]=CaS\ (s) \qquad (1)$$

$$\lg(a_S \cdot a_{Ca} / a_{CaS}) = -28300/T + 10.11 \qquad (2)$$

$$a_S \cdot a_{Ca} = 10^{(-28300/T+10.11)} \cdot a_{CaS}. \qquad (3)$$

When $a_{CaS} = 1$, $\quad a_S \cdot a_{Ca} = 10^{(-28300/T+10.11)}$. (4)

The activity interaction coefficient in literature was used to calculate the activity coefficient of the [Ca] solution in steel.

$$\lg f_{Ca} = e_{Ca}^{O}[\%O] + e_{Ca}^{Al}[\%Al] + e_{Ca}^{C}[\%C] + e_{Ca}^{Mn}[\%Mn] + e_{Ca}^{P}[\%P] + e_{Ca}^{S}[\%S] \qquad (5)$$

$e_{Ca}^{O} = -445$, $e_{Ca}^{Al} = -0.072$, $e_{Ca}^{C} = -0.32$,

$e_{Ca}^{Mn} = -0.10$, $e_{Ca}^{P} = -4.0$, $e_{Ca}^{S} = -1.33$

$$\log f_S = e_S^S[\%S] + e_S^{Al}[\%Al] + e_S^{C}[\%C] + e_S^{Mn}[\%Mn] \qquad (6)$$

$e_S^S = -0.153 + 233/T$, $e_S^{Al} = 0.035$,

$e_S^C = 0.11$, $e_S^{Mn} = -0.026$,

where, $e_S^{Al} = 0.035$ and $e_S^{C} = 0.11$. When the temperature is 1873 K, $e_S^{Mn} = -0.026$. Because the value changes little at the steelmaking temperature, it is assumed to be constant.

The [Ca]-[S] balance ($a_{CaS} = 1$) is shown in Fig. 4 at 1580°C.

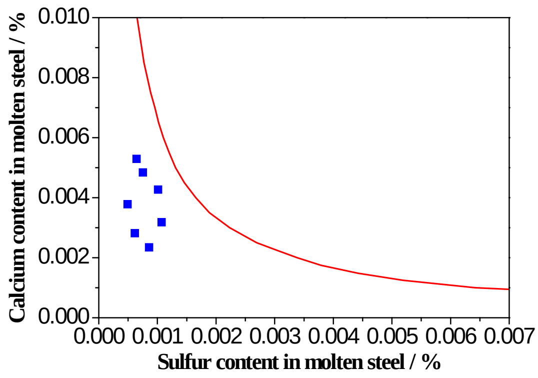

Figure 4 [Ca]-[S] balance at 1580°C (a_{CaS}=1)

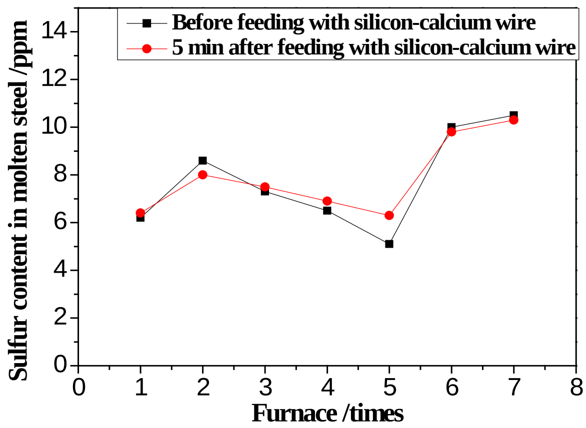

Figure 5 Sulfur content in molten steel after Ca-treatment

The seven points in Fig. 4 show the sulfur contents before feeding with silicon-calcium wire and the calcium content after feeding calcium with the molten steel in a different furnace. These points are located below the [Ca]-[S] equilibrium line at 1580°C. This indicates that calcium has no desulfurization ability. Fig. 5 shows the sulfur content in molten steel after Ca-treatment and feeding with silicon-calcium wire. The sulfur content in the molten steel is essentially invariant and all are below 10 ppm except for the sample from the seventh trial. Feeding calcium with the molten steel helps retain the calcium content in the steel, inhibits resulfurization and keeps the sulfur content low.

Conclusions

The ability of the slag to be oxidized has an obvious influence on the desulfurization efficiency of molten steel. The lower the (FeO+MnO) content in the initial slag, the higher the Ls. To obtain desulfurization, the (FeO+MnO) content in the initial slag should be below 1%.

When the argon inflow at the bottom of the furnace is 500 NL/min, the sulfur content in the steel is reduced to 6 ppm after 10 min. Too high or too low an argon flowrate will reduce the desulfurization efficiency.

The [Ca] content in the molten steel is under the [Ca]-[S] equilibrium line when the steelmaking temperature is 1580°C. Under these conditions, calcium has no desulfurization ability. Addition of calcium into the molten steel is useful for inhibiting resulfurization and helps maintain the sulfur content at a low level.

Acknowledgments

The authors are grateful for support from the National Science Foundation China (grant no.51304016)

References

1. LiuXingbo,Dong Jianxin and Xie Xishan.Influence of impurity elements-phosphorusand sulfur in special steel[J].Special Steel,1998,19(3):1-5.

2. Susaki K, Maeda M, Sano N. Influence of additives on sulfide capacity of $CaO-SiO_2-CaF_2$ slags[J]. Metallurgical and materials transactions B .1990, 21(6):1081-1084.

3. JANG Zhou-hua, ZHANG He-yan, ZhAN Dong-Ping. Determination of process parameters for refining of ultra-low sulfur steels in ladle furnace[J]. Journal of Northeastern University ,2002, 23(10) : 953-955.

4. LiuLiu.Technology of metallurgy for ultra-low sulphur steel[J].Special Steel, 2000, 21(5) : 293-295.

5. LI Bo, ZHU Rong, GUO Han-jie,etal. An experimental research into desulphurization in the process of refining ultra-low sulphur steel.[J].Jiangxi Metallurgy,2003 , 23 (6) : 98-102.

6. NI Pei-liang,WANG Yu-chun,SHI Zhen-ming. Practice of sulfur content control during the smelting of low-sulfur steel in laiwu steel[J], Journal of iron and steel,2010,45 (3) :49-54.

7. Howard M, Pielet, Debanshu Bhattacharya. Thermodynamics of Nozzle Blockage in Continuous Casting of Calcium-Containing Steels[J]. Metallurgical Transaction, 1984,15(3) : 547-562

8. Song Bo,Han Qiyong,Wang Fuming,etal.Thermodynamic calculation on modification of Al_2O_3 inclusions by feeding CaSi alloy in liquid steel[J]. Special Steel, 1999, 20(5):20-22.