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The Arsenic Removal From Molten Steel

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Abstract. Arsenic removal from molten steel by the calcium iron alloy and rare earth alloy (48 % Ce, mass percentage) has been exploringly studied at 1853 K. It is found that the addition of rare earth alloy makes the arsenic removal more effective. This phenomenon may originate from the facts that the addition of Ce lowers the activity coefficient of sulfur, and the low activity of sulfur restrains the reaction of calcium iron alloy and sulfur, which promotes the arsenic removal reaction. Thus more rare earth alloy addition results in the higher arsenic removal ratio. However, due to the high cost of rare earth alloy, increasing the quantity of calcium iron alloy may be a choice to improve the arsenic removal effect in molten steel. It is found that when the weight ratio of rare earth alloy/steel is fixed at 5 %, the arsenic removal ratio increases with the calcium iron alloy amount increasing. When the weight ratio of calcium iron alloy/steel is 18 %, the arsenic removal ratio is 50 %. This result may be acceptable for the industrial purpose.

Keywords. Arsenic removal, steel, thermodynamic properties, rare earth alloy.

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1 Introduction

In 2009, the quantity of scrap steel has reached 460 millions tons, which is been considered as an important resource in the steelmaking industry. Since this recycling helps to decrease CO_2 generation and lower the cost of the production, the importance of the scrap steel is expected to increase in the future. However, this recycling leads to the accumulation of tramp elements, for example, arsenic. This has been a widely concerned problem.

Arsenic dissolved in steel leads to the surface enrichment in the hot working process. It makes the steel's thermoplastic decrease greatly and induces the steel crack easily in the stress processing [1–3]. However, it can't be removed by the conventional oxidation process. Thus a practical process for arsenic removal has attracted much attention. Several methods have been proposed and studied to solve this problem, for example adding to calcium silicon alloy, using vaccum dearsenization, and so on [1]. Among them, the process using calcium based alloys is considered to be the most possibly acceptable for the industrial purpose [1]. The principle of this method is that Ca in the alloy reacts with As in the molten iron and the generated Ca_2As_3 transfers into the basic slag. This proposition was investigated by Dong Yuanchi [4]. And a systematic thermodynamic study has been carried out for arsenic removal by using calcium based alloys in his research. However, most of these studies were focused on the carbon-saturated molten iron [5], and the research in molten steel was still lacked. Obviously, the accumulation of arsenic is more serious in scrap steel than that molten iron. Thus, a detailed study on the arsenic removal from the molten steel is needed.

In this paper, we present a pioneer research on the arsenic removal from molten steel with calcium iron. To improve the arsenic removal ratio R, the rare earth alloy was added. The aim of the paper is to clarify the influencing factors of arsenic removal in molten steel.

2 Experimental Procedure

The chemical composition of steel sample (mass percentage) is listed as following: C (0.22 %), Si (0.20 %), Mn (0.52 %), P (0.011 %), S (0.008 %). And the mass percentage of the arsenic was adjusted by the addition of the arsenic trioxide in the molten steel. In different experiments, the content of the arsenic was different, which would be described in the following text.

The arsenic removal ratio R is defined according to the following equation:

$$R = \frac{[\mathrm{As}]_i - [\mathrm{As}]_f}{[\mathrm{As}]_i}. \tag{1}$$

Where the $[\mathrm{As}]_f$ and $[\mathrm{As}]_i$ are the final and initial arsenic content in steel (mass %).

Figure 1 shows schematic diagram of the experimental apparatus (KSY-10-18 high-heat tube-type resistance furnace). The sample of steel was charged into an alumina crucible. Each sample was about 200 g. After preheating, the charged alumina crucible was lowered into the hot zone of the resistance furnace with a graphite outer crucible. High purity N_2 was introduced into the furnace at a flow rate of

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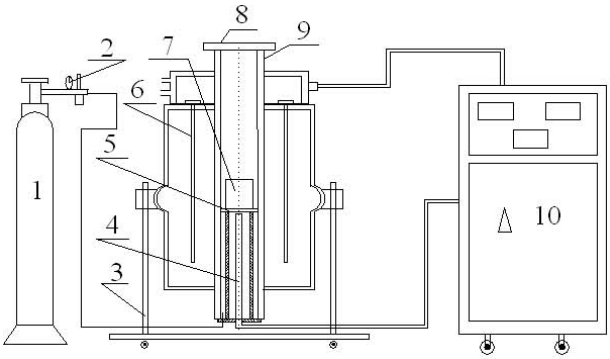

Figure 1. Schematic diagram of the experimental apparatus 1 Nitrogen cylinder, 2 Manometer, 3 Bracket, 4 Thermocouple, 5 Crucible plate, 6 Heater, 7 Crucible, 8 Furnace lid, 9 Furnace tube, 10 Temperature Controller.

0.1 L/min, and the temperature of the furnace was maintained at 1853 K. The purpose of the nitrogen atmosphere is to avoid the oxidation of steel. When melting was done, the appropriate amount of Calcium Iron was added into the molten steel after adding aluminum. After being held for 20 minutes, the crucible was taken out to cool down in the air. This holding time was determined by some preliminary experiments to achieve a stable arsenic removal ratio. The content of arsenic was analyzed by the measurement of OPA (Original Position Analysis) technology.

3 Results and Discussion

This reaction of the arsenic removal can be written as following:

$$3[\mathrm{Ca}] + 2[\mathrm{As}] = (\mathrm{Ca_3As_2}). \tag{2}$$

In this reaction, the As in molten steel reacts with Ca to form Ca_3As_2 in the slag. According this reaction, the No. 1 experiment was designed. The $[As]_i$ is 0.08 %, and the weight ratio of calcium iron alloy/steel is 8 %. After experiment, the $[As]_f$ is equal to the $[As]_i$, which means no arsenic removal phenomenon occurs. According to thermodynamics, this is probably due to the high content of [S]. After experiment, the content of [S] is 0.003 %. It is known that the calcium can react not only with arsenic, but also with sulfide. Furthermore, since the electronegativity of S (2.5) is larger than that of As (2.0) [6], S has the priority of the reaction with Ca. Thus if the content of [S] is high, no arsenic removal reaction would occur.

To solve this problem, the rare earth alloy is added, whose Cerium content (mass Pct) is 48. This is due to the fact that according to the previous reports [7,8], the addition of Ce helps to desulfurization. So in the No. 2 experiment, besides the calcium iron alloy, whose amount is equal to the 8 % of the steel, the rare earth alloy is added. And the weight ratio of rare earth alloy/steel is 5 %. The $[As]_i$ is also 0.08 %. The result shows that after experiment, [S] is also 0.003 %, which is as same as that of No. 1 experiment. However, the $[As]_f$ is 0.018 %, and the arsenic removal ratio is 77.5 %, which is much more than that of the No. 1 experiment. This phenomenon can be explained by the following thermodynamics calculation.

From the reactions of (3) and (4), the reaction (5) can be gotten [4, 9, 10]:

$$3[\mathrm{Ca}] + 2[\mathrm{As}] = (\mathrm{Ca_3As_2})$$
$$\Delta G^{\theta} = -454730 + 63.85\,T, \tag{3}$$
$$[\mathrm{S}] + [\mathrm{Ca}] = (\mathrm{CaS})$$
$$\Delta G^{\theta} = -57586 + 14.59\,T, \tag{4}$$
$$2[\mathrm{As}] + 3[\mathrm{CaS}] = 3[\mathrm{S}] + (\mathrm{Ca_3As_2})$$
$$\Delta G^{\theta} = -281972 + 20.08\,T. \tag{5}$$

In the reaction (5), the balance is controlled by the activities of [As] and [S]. In Table 1, the chemical compositions of steel sample (mass percentage) after experiment No. 1 and No. 2 were shown. It can be seen that the distinct difference in chemical composition between them is the Ce content. This difference will affect the S activity coefficient f_S through the following equation:

$$\lg f_S = \sum e_S^i w[i] \quad i = \mathrm{C, Si, Mn, P, S, Ce.} \tag{6}$$

Where e_S^i is the activity interaction coefficient which means the effect of the element i content on the S activity coefficient, and $w[i]$ is the mass % of the element i.

From earlier reports, it is known that at 1873 K (1600 °C), the values of e_S^{Ce} is −9.1 [8]. Using the Equation (6) and the chemical compositions of steel samples after experiments in Table 1, the f_S can be calculated. The f_S in No. 1 is 1.05, and f_S in No. 2 is 0.016. This means though the content of S is equal between No. 1 and No. 2 experiments, their activity is different. The activity of S is much lower in the No. 2 experiment, so the balance of reaction (5) shifts to the right, which leads to a higher arsenic removal ratio. Thus, the arsenic removal is more effective with Ce doping.

From the upper analysis, it is deduced that the more Ce doping would result in the less f_S and higher arsenic removal ratio. To prove this conclusion, No. 3 experiments were taken and the results were shown in Figure 2. The

sample	C	Si	Mn	P	S	Ce
NO. 1	0.18	0.22	0.52	0.008	0.003	0
NO. 2	0.16	0.24	0.45	0.008	0.003	0.2

Table 1. Chemical composition of steel samples after experiments (mass percentage).

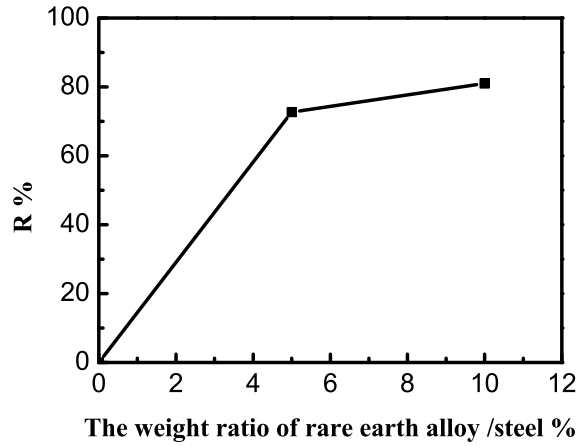

Figure 2. Relationship between the arsenic removal ratio and the weight ratio of rare earth alloy/steel (the $[As]_i$ is 0.0458 %).

$[As]_i$ is 0.0458 %. It can be seen that the R indeed increases with increasing the addition of the rare earth alloy, which is consistent with our analysis.

In fact, the As content in scrap is much lower than 0.0458 %. Furthermore, due to the high price of rare earth alloy, the 10 % (weight ratio) rare earth alloy doping is unacceptable in industry. Thus, increasing the quantity of calcium iron alloy may be the best choice. So the study on the relationship between the arsenic removal ratio and the calcium iron alloy is needed. In No. 4 experiments, the $[As]_i$ is lowed to 0.008 %, the weight ratio of rare earth alloy/steel is fixed at 5 %, and different quantities of calcium iron alloy were chosen to investigate the arsenic removal effect. The results are displayed in Figure 3. It can be seen that with the calcium iron amount increasing, the arsenic removal ratio increasing. This effect can be well explained by the reaction (3): the more calcium iron adds, the more arsenic consumes. And the arsenic removal ratio can reach 50 %. This ratio is may be acceptable for the industrial purpose.

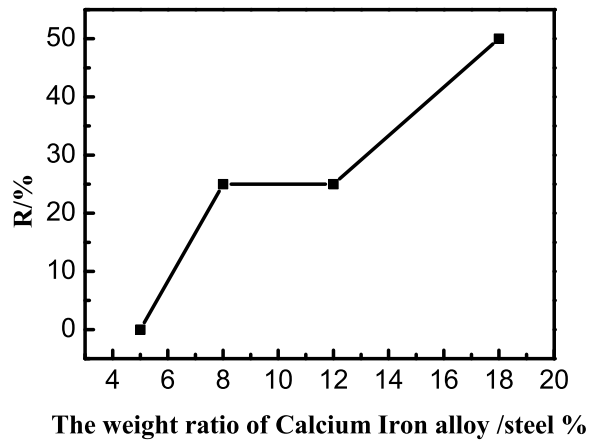

Figure 3. Relationship between the arsenic removal ratio and the weight ratio of calcium iron/steel (the $[As]_i$ is 0.008 %).

4 Conclusion

Pioneer study has been made on the arsenic removal behaviors in molten steel by the additions of the calcium iron alloy and rare earth alloy (48 % Ce, mass percentage). The results show that the addition of rare earth alloy makes the arsenic removal more effective. This phenomenon can be explained by the thermodynamics properties. The addition of Ce lowers the activity coefficient of sulfur and the low activity of sulfur would promotes the arsenic removal reaction. Thus more rare earth alloy addition results in the higher arsenic removal ratio. However, due to the high cost of rare earth alloy, the quantity of calcium iron alloy was increased to improve the arsenic removal effect in molten steel. It is found that when the weight ratio of rare earth alloy/steel is fixed at 5 %, the arsenic removal ratio increases with the increasing of calcium iron alloy. When the weight ratio of calcium iron alloy/steel is 18 %, the arsenic removal ratio is 50 %. This result may be acceptable for the industrial purpose.

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