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PHOSPHORUS(P) MIGRATION BEHAVIOR IN THE PROCESS OF CONVERTER SLAG GASIFICATION DEPHOSPHORIZATION

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The high P content in steel slag limits its recycling during the smelting process, and the P can be effectively removed from the steel slag by gasification dephosphorization. In this experiments, the effects of temperature, basicity, and FeO for gasification dephosphorization rate are studied through thermodynamic calculations. The Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) analysis that microscopic morphology of slag before and after reduction. In addition, a model is established to describe the phosphorus migration behavior of gasification dephosphorization process.

Keywords: steel, converter, phosphorus, gasification dephosphorization rate, X-ray research

INTRODUCTION

A large number of value-added steel slag will be discharged every year in China, but the utilization rate of converter slag less than 30% [1,2], due to the existence of C_2S phase which can enrich the harmful P element and limit its recycling [3]. In recent years, the method of gasification dephosphorization of converter slag is rapidly developed in China, P can be effectively removed from the steel slag by gasification vaporization. After such this operation, the slag can be more easier reused in the next furnace, which has attracted more and more attention [4-9].

The phosphorus dephosphorization process is a novel method, which it easier to remove the P from the slag. The above scholars had done a lot of basic research on gasification dephosphorization, but the phosphorus migration behavior during gasification dephosphorization has not been studied yet. In this paper, the favorable conditions of gasification dephosphorization and the migration behavior of phosphorus are studied on the experimental data.

EXPERIMENTAL MATERIALS AND PROCESSES

The steel slag composition used in the test is shown in Table 1. Before the experiments, the steel slag and carbon were crushed to less than 200 mesh with electromagnetic crusher, which weighed 100 g of slag and 2 unit of carbon to be mixed. The minimum amount of carbon required to reduce all of the FeO, MnO and P_2O_5 in the slag to a simple substance was defined as 1 unit. In all experiments, the amount of coke was 10,26 g.

The coke powder composition is shown in the Table 2.

Table 1 **The composition of steel slage used in the experiments/wt.%**

FeO	CaO	SiO_2	MgO	MnO
15,82	42,85	12,55	7,15	3,35
P_2O_5				
3,08				

Table 2 **The composition of coke powder used in the experiments/wt.%**

C	CaO	SiO_2	MgO	P_2O_5
86,55	1,37	6,42	0,33	0,36
S				
0,98				

The main equipment of the experiment was vertical resistance furnace,The equipment shown in in Figure 1. During the experiment, the furnace was raised with 5 °C per minute under the protection of N_2(0,4 m^3/h) until the required experimental temperature was reached 1 813 K, all the furnace holding time was set to 1h.

For the convenience of research, the gasification dephosphorization rate of slag was characterized with the mass fraction of P_2O_5 in the slag before and after the reaction, such as formula (1).

$$\eta = \frac{\%^1 P_2O_5 - \%^2 P_2O_5}{\%^1 P_2O_5} \quad (1)$$

Where $\%^1P_2O_5$ indicates that P_2O_5 content is existed in the slag before the test, $\%^2P_2O_5$ indicates that P_2O_5 content is existed in the gasification dephosphorization slag.

EXPERIMENTAL RESULTS AND ANAIYSIS

The effect of temperature on gasification dephosphorized rate

The change of gasification dephosphorization rate with temperature is shown in Figure 2. Figure 2 shows

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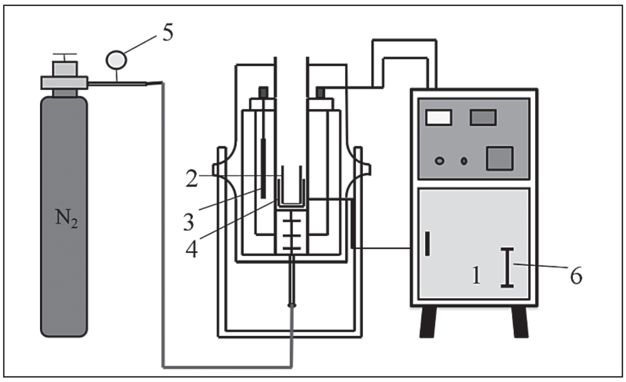

1. Control cabinet 2. Corundum crucible
3. Silicon molybdenum heating element 4. Graphite crucible
5. Pressure gauge 6. Rotameter

Figure 1 Equipment schematic diagram

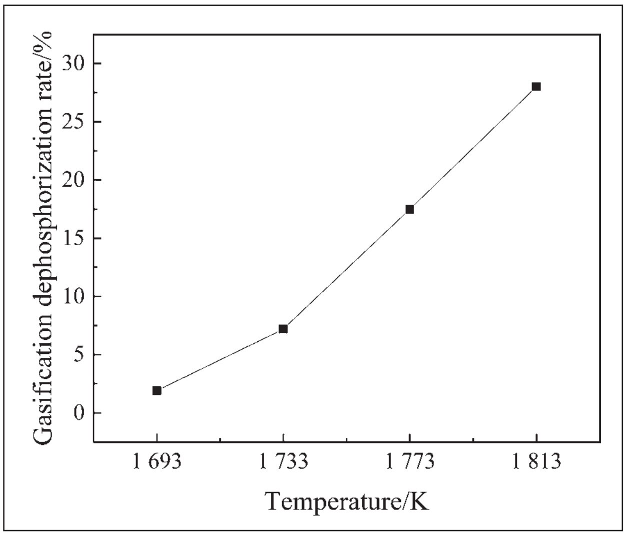

Figure 2 Effect of temperature on the gasification dephosphorization rate

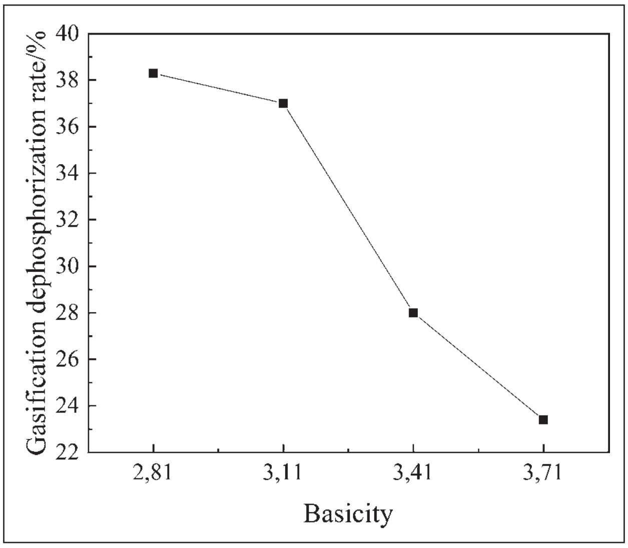

Figure 3 Effect of binary basicity on the gasification dephosphorization rate

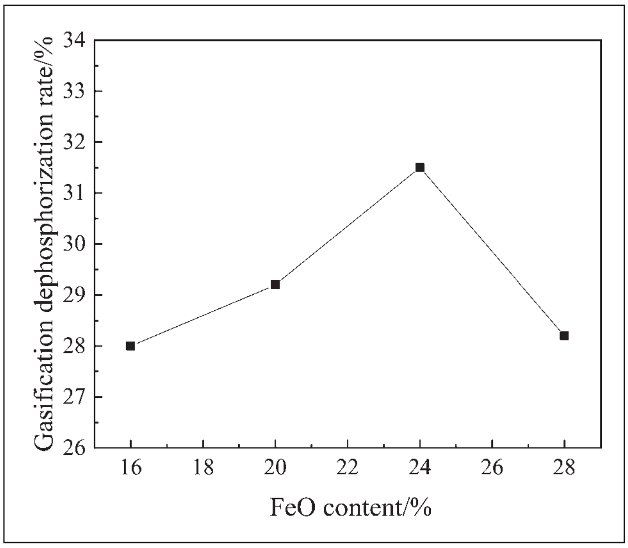

Figure 4 Effect of FeO content on the gasification dephosphorization rate

that the gasification dephosphorization rate increases with the increase of temperature. When the reaction temperatures in the range of 1 693-1 813 K, it is obviously that the gasification dephosphorization rate is as high as 27,9 % at 1 813 K. From the thermodynamic of view, because the reaction between carbon and P_2O_5 is endothermic, high temperature is beneficial to the forward reaction. From the kinetic of view, high temperature will reduce the viscosity of slag and improve the flow ability of the slag. Therefore, increasing temperature is more conducive to the gasification dephosphorization reaction.

The effect of binary basicity on gasification dephosphorization rate

At 1 813 K, the variation of gasification dephosphorization rate with basicity is shown in Figure 3. Figure 3 shows that phosphorus vaporization rate decreases with the increase in slag basicity. When R = 2,81, the phosphorus vaporization rate reaches the highest, which is 38,3 %. The CaO content increases with the increase in slag basicity, and SiO_2 and CaO in slag will form high-melting compounds. Under certain temperature, the high-melting compounds are difficult to melt, which leads to the poor fluidity of slag and hinders the reduction of P_2O_5 by carbon. Therefore, low basicity is beneficial to the gasification dephosphorization of converter slag.

The effect of FeO content on gasification dephosphorizing rate

Figure 4 shows that the effect of FeO content on phosphorus vaporization rate under the condition of different FeO content. The phosphorus vaporization rate increases first and then decreases with the increase in FeO content. When it is 24 %, the gasification dephosphorization rate is 31,5 %, which reaches the highest. When it is 28 %, the gasification dephosphorization rate is only 28,2 %. With the increase of FeO content, the fluidity of slag can be improved and the reaction of carbon reduction of P_2O_5 can be promoted. But FeO content is excessive, carbon will react with a large amount of FeO, which will cause the temperature in some areas to drop and inhibit gasification dephosphorization.

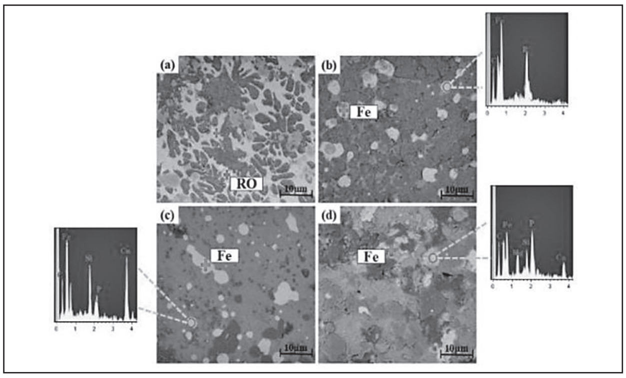

Figure 5 SEM-EDS analysis of slag samples

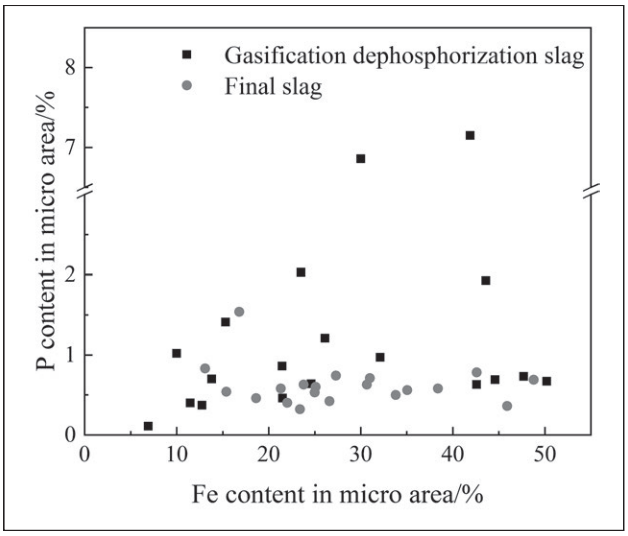

Figure 6 P and Fe in RO phase of final slag and Fe phase of phosphorus vaporization slag

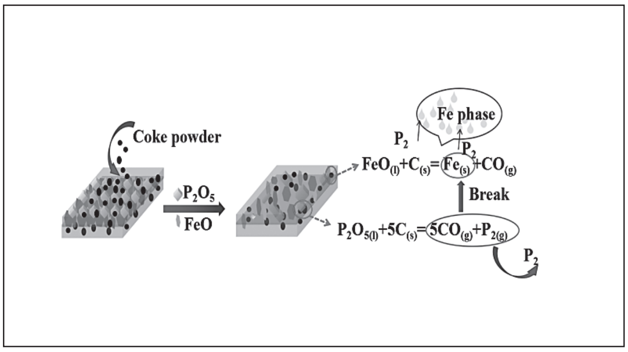

Figure 7 The behavior of P migration during gasification dephosphorization

The tendency of the above data points indicates tha the furnace temperature and FeO should be moderately increased to keep the basicity of the slag low to raise the rate of gasification dephosphorization. Especially the temperature has a particularly significant effect on gasification dephosphorization.

The results from Scanning electron microscopy

The detection from SEM-EDS indicates that the mineral phases before and after the reduction of converter slag have changed significantly, which are shown in Figure 8. The mineral phases of the reduced slag are evenly distributed without special rules, but some black micro-zones contain unmelted carbon. The white phase in Figure 5(a) is mostly RO phase, which the RO phase small-diameter granular or strip. After reduction, the RO phase becomes a bright white large-diameter granular and dispersed distribution in Figure 5(b), 5(c) and 5(d). Due to the high temperature at 1 813 K, the white phase of Fe appears in Figure 8(b) and so on. The FeO in the RO phase is reduced by carbon.

Phosphorus migration behavior of gasification dephosphorization process

There is a large amount of P element in the Fe phase of phosphorus vaporization slag by SEM-EDS. Due to the migration behavior of P during Phosphorus vaporization cannot be captured at high temperature, In order to determine the migration law of P, the 20 micro-zones of the RO phase in the final slag and the Fe phase in the gasification dephosphorization slag are analyzed respectively, as shown in Figure 6.

The tendency of the data points in Figure 6 indicates that the content of P in RO phase micro-zones of final slag is in the range of 0,4 - 0,8 %, and the Fe content is in the range of 10 - 50 %. the content of P in RO phase increases first and then decreases with the increase in Fe content and that the Fe and P contents have an slightly linear relationship. However, the P content in the Fe phase micro-regions of the phosphorus vaporization slag is unevenly distributed, which is 0,15 - 7,5 %, while the Fe content is in the range of 0 - 60 %. On the whole, the Fe and P content are not obviously linear relationship in the Fe phase micro-zones, When the content of Fe is less than about 30 %, the content of P in phosphorus vaporization slag increases with the increase in Fe content. When Fe content is greater than 30 %, the P content in the gasification dephosphorization slag decreases with the increasing trend of Fe content, but there are still high P content.

The P content in the Fe phase of gasification dephosphorization slag is generally higher than RO phase of final slag. Indicating that part of P_2 gas of the reduction product is volatilized out of the furnace, and the other part will be adsorbed by Fe phase. The migration behavior of phosphorus gasification is shown in Figure 7. According to the occurrence of P in Fe phase, the absorptive ability to P of Fe phase increased as Fe content increased and the P content in Fe phase will increase. Therefore, keeping Fe content to an appropriately high level in final slag can facilitate the gasification dephosphorization reaction. The activity coefficients of P_2O_5 will be improved under the presence of FeO. It is helpful to the reduction by carbon, which is consistent with the above thermodynamic calculations.

CONCLUSION

The single-factor experiments proves that the moderate increase in temperature and FeO is beneficial to phosphorus dephosphorization rate; the phosphorus dephosphorization rate decreases as slag basicity increased. And the phosphorus dephosphorization rate will first increase and then decrease as the FeO content in the slag increases.

During phosphorus dephosphorization, Small-diameter granular or strip RO phase is changed into granular-shaped Fe phase. The part of the P_2 gas generated is discharged out of the furnace, and part of it will be absorbed by the Fe phase.

Acknowledgments

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Note: The responsible translator for English language is S. CUI -Tangshan Normal University, China