

SEPARATION OF PHOSPHORUS AND MANGANESE FROM STEELMAKING SLAG BY SELECTIVE REDUCTION

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Introduction

The integrated steelmaking process generates blast furnace slag and steelmaking slag as by-products, where most of the blast furnace slag is valuably reused for cement production, whereas the steelmaking slag is used as a material for road base and civil engineering work.¹ Meanwhile, steelmaking slag contains a high percentage of MnO and P₂O₅, and in Japan, the amounts of these elements in steelmaking slag are close to those of manganese imported as ferro-alloy or manganese ore and phosphorus as phosphate rock.^{2,3} Mn is a key alloying element for various steel products, and P is an essential nutrient in agricultural production. Therefore, their stable supply is an important national issue and steelmaking slag is considered as a secondary resource for these elements.

Carbothermic and smelting reduction are simply applicable for recovering Fe, Mn, and P from steelmaking slag.⁴ However, in general, Fe, Mn, and P in steelmaking slag are reduced simultaneously, and a Fe-P-Mn-C alloy is formed. To utilise Mn and P as a secondary resource, these elements must be recovered separately.

The authors have proposed the selective reduction method of Mn and P from steelmaking slag by controlling the slag basicity and temperature. Previously, the thermodynamic calculation of the theoretical background and the results of some simple experiments have been shown.⁵ In this paper, the influence of melting behaviour of slag on the selective reduction was clarified.

Experimental Method

Slag was made by the melting of reagents at 1673 K followed by quenching in water. The 3 g of crushed slag was mixed homogeneously with graphite powder which was used as a reductant. The amount of graphite powder was set as 200% of the amount required for reducing all of the FeO, MnO, and P₂O₅ in slag. The mixture of slag and graphite powder loaded in the crucible was charged into the heated furnace, and this moment was set as the start of the experiment. To reach the target temperature,

generally, it took 7 to 9 minutes. After the experiment for given time, the sample with the crucible was unloaded from the furnace and quenched in water immediately. The sample was separated into slag and metal, and the compositions of each phase were analysed by ICP–AES. The mass of the slag was calculated by CaO balance and the mass of the metal was determined by the change in FeO content in the slag. The slag composition is shown in Table 1. By the previous experiments, the selective reduction of P, suppressing the reduction of Mn, was achieved by using the acid slag. Therefore, the basicity was set as 0.5.

Table 1: Slag composition for the experiment

	FeO	CaO	SiO ₂	P ₂ O ₅	MnO	MgO	Al ₂ O ₃
Slag G	25.91	16.75	33.43	3.90	6.22	3.44	10.31
Slag H	23.70	16.29	31.46	4.12	5.92	3.16	15.36
Slag I	23.56	14.58	28.99	4.20	5.87	3.15	19.64
Slag J	23.64	13.25	26.31	3.88	5.97	2.78	24.17

Results and Discussion

The change in the compositions of slag and metal with reduction time showed the fast reduction of FeO and P₂O₅ in each case. However, the reduction rate of MnO was changed with the slag composition. In addition, since an Al₂O₃ crucible was used, the Al₂O₃ content increased gradually. The mass balances of Mn and P is shown in Figure 1.

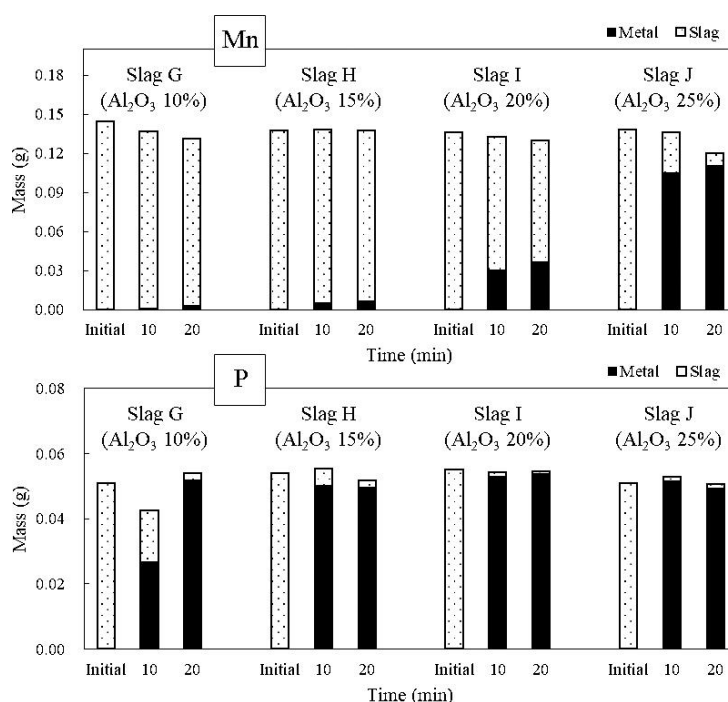


Figure 1: Mass balance of Mn and P for each experiment

The result shows that an increase in the initial content of Al_2O_3 enhances the reduction of MnO . In the cases of Slag I and J, considerable amount of MnO reduced during the early period of the reduction. To clarify the mechanism of Mn reduction in the initial stage, the experiment with shorter time was conducted for Slag G and I.

Figure 2a shows the cross-sections of Slag G after 3 min of reduction. In this case, slag was melted within 1 min and as the reduction time was elongated, the diameter of the reduced metal particle was increased, and these particles were observed mainly on top of the molten slag. The cross section of Slag I after 3 min is shown in Figure 2b. Different from Slag G, the slag was not completely melted, and pores with graphite powder were observed inside the slag. Small reduced metal particles were observed near the surface of pores where the molten slag was directly contacted with the graphite powders. Figure 3a shows the composition change of Slag G analysed by EPMA. The content of FeO decreased rapidly and that of P_2O_5 gradually decreased; but the content of MnO was almost constant. This result indicated that the Fe and P were selectively reduced. The changes in the composition of the liquid phase in Slag I are shown in Figure 3b. At 1 min, most of the FeO and P_2O_5 were reduced, and the MnO content started to decrease after 1 min. Considering the melting behaviour of the slag, shown in Figure 2, when the melting process of slag took time, not only the reduction of Fe and P but also that of Mn occurred due to the increase in the interfacial area between solid or molten slag and graphite. Based on the phase diagram, the melting point of slag increases by the increase in the initial Al_2O_3 content.

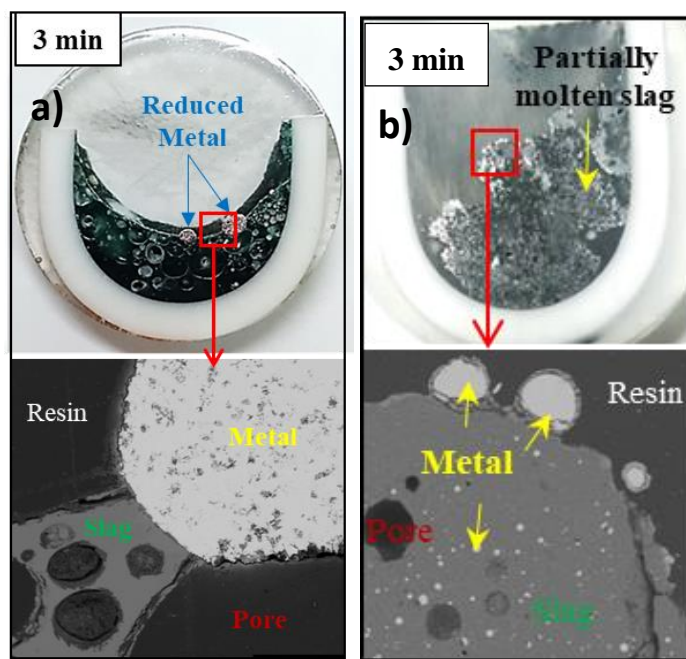


Figure 2: Cross-section of slag at 3 minutes; a) Slag G, b) Slag I

For the slag of high melting point, a solid and liquid coexisting slag with high viscosity would be formed at the early stage of heating. In this situation, graphite powders trapped inside the slag enhance the reduction of Mn. By the thermodynamic analysis, the reaction of solid oxide containing high MnO with the trapped graphite was deduced. Therefore, for the selective reduction of P suppressing the reduction of Mn, rapid formation of liquid slag is important.

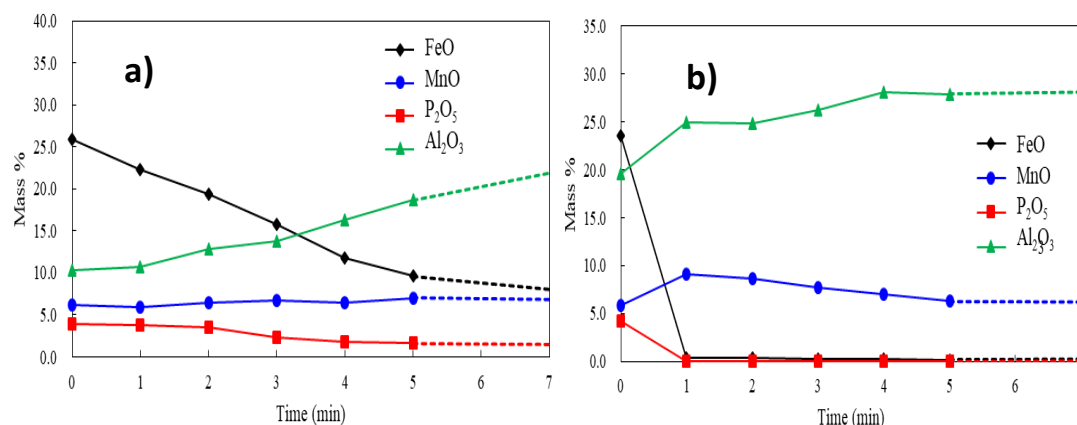


Figure 3: The composition change of slag with time; a) Slag G, b) Slag I

Conclusions

The influence of the melting behaviour of the slag on the selective reduction of P and Mn was investigated by the change in the initial content of Al₂O₃. The results showed that the slag with high melting point enhances the reduction of MnO by the entrapped graphite powders in highly viscous slag. Therefore, for the selective reduction of P, quick formation of liquid slag is important.

References

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