

SELECTIVE RECOVERY OF PHOSPHORUS AND MANGANESE FROM STEELMAKING SLAG BY CARBOTHERMIC REDUCTION

Dong Jun SHIN¹, Xu GAO², Shigeru UEDA², Shin-ya KITAMURA²

¹ Department of Metallurgy, Graduate School of Engineering, Tohoku University

² Institute of Multidisciplinary Research of Advanced Materials, Tohoku University

shindj@mail.tagen.tohoku.ac.jp

Introduction

Recycling steelmaking slag in ironmaking processes is an efficient method to decrease the amount of generated steelmaking slag¹. However, since phosphorus and manganese can easily accumulate in hot metal under ironmaking conditions, the selective recovery of phosphorus and manganese is necessary.

Steelmaking slag contains around 4 wt% of phosphorus and 6 wt% of manganese. Both phosphorus and manganese are elements that improve properties of steel and an important source for essential nutrients in agricultural production. Therefore, many studies have been conducted regarding separating phosphorus and manganese from steelmaking slag as secondary resources. For this purpose, a selective leaching process has been proposed to recover phosphorus from steelmaking slag to produce a phosphate fertiliser². A sulphurisation-oxidation process has been suggested to recover manganese for ferro-manganese production without the contamination of phosphorus³.

Carbothermic reduction is a simple technique for the recovery of elements in the oxide state. Many studies have been conducted to investigate the mechanism of carbothermic reduction of steelmaking slag. Kazuki Morita *et al.*⁴ reported the recovery of phosphorus and iron by microwave processing, where the recovery ratio of phosphorus reached 50%. Li *et al.*⁵ proposed a waste-free steelmaking process with a regenerator based on conceptual carbothermic reduction and recycling of the slag during the steelmaking process. In addition, Ishikawa⁶ studied the reduction of the dephosphorisation slag by a regenerator process following a concept similar to that of Li *et al.*⁵ However, although these researches focused on the recovery of materials by carbothermic reduction, the selective recovery of phosphorus and manganese in steelmaking slag was not attempted.

Phosphorus and manganese have different thermodynamic characteristics. Therefore, selective reduction would be possible by controlling the reducing conditions. In this research, selective reduction of phosphorus and manganese in steelmaking slag by carbothermic reduction was investigated by adjusting experimental conditions.

Experimental

In order to prepare the CaO-SiO₂-FeO-based system with a composition similar to that of practical steelmaking slag, reagent-grade CaCO₃, SiO₂, Fe, Fe₂O₃, Ca₃(PO)₄, MnO, MgO, and Al₂O₃ were used. FeO was obtained after the reaction of Fe with Fe₂O₃ at 1673 K for 1 h, and CaO was produced by calcining CaCO₃ at 1473 K for 12 h. In preparation, the reagents were first mixed and then pre-melted at 1773 K in an Al₂O₃ crucible for 1 h in an argon gas atmosphere. Thereafter, the melted slag was quenched in water and crushed to a powder with particles smaller than 500 µm. Table 1 shows the chemical composition of the synthesised slag.

Table 1: Synthesised CaO-SiO₂-FeO system slag composition (wt%)

	FeO	CaO	SiO ₂	P ₂ O ₅	MnO	MgO	Al ₂ O ₃	Basicity (CaO/SiO ₂)
Slag A	23.36	29.87	20.07	4.06	5.61	3.43	13.60	1.49
Slag B	25.10	23.10	30.43	3.91	5.54	3.71	8.22	0.75

3 g of synthesised slag was used for each experiment after mixing them homogeneously with graphite powder. The amount of graphite was two times larger than that required for the reduction of iron oxides, manganese oxides, and phosphorus oxides, as calculated by stoichiometry. Carbothermic reduction was conducted for given durations at 1773 K in an argon gas atmosphere (the gas flow rate was controlled at 500 ml/min). Then, the samples were taken out and quenched in water. Separated slag and metal phase compositions were analysed by ICP–AES (inductively coupled plasma atomic emission spectroscopy)

Results and Discussion

Figure 1 shows the phosphorus and manganese mass balance results in metal and slag phase with different slag basicity and reduction time. The results were obtained in the following way:

1. Calculation of total slag mass: It is impossible to measure the total slag mass after carbothermic reduction, due to the strong adhesion between the slag and crucible. However, the reduction of CaO in the steelmaking slag to the metal phase during carbothermic reduction is difficult. This means that the mass of CaO in the slag after carbothermic reduction remains the same as that before reduction. Based on this logic, the total slag mass after carbothermic reduction was calculated from the CaO content in the slag measured by ICP.

$$\text{Total slag mass (g)}_{\text{after reduction}} = (\text{CaO mass (g)}_{\text{initial}} / (\text{CaO}\%)_{\text{after reduction}}) \times 100$$

- Calculation of the total metal mass: Since gasification of phosphorus and manganese is expected during carbothermic reduction, measuring the reduced total metal mass is impossible. However, since gasification of iron does not happen in these conditions, the sum of the iron mass in metal and slag phases should be constant. Therefore, the reduced iron mass and total metal mass were calculated. The mass of phosphorus and that of manganese in the metal phase were calculated from the ICP results and total metal mass.

$$\text{Total metal mass (g)} = \text{Iron mass (g)}_{\text{reduced}} / [\text{Fe}\%]_{\text{after reduction}} \times 100$$

$$\text{P, Mn mass (g)}_{\text{in Metal}} = \text{Total metal mass (g)} \times [\text{P, Mn}\%]_{\text{after reduction}} / 100$$

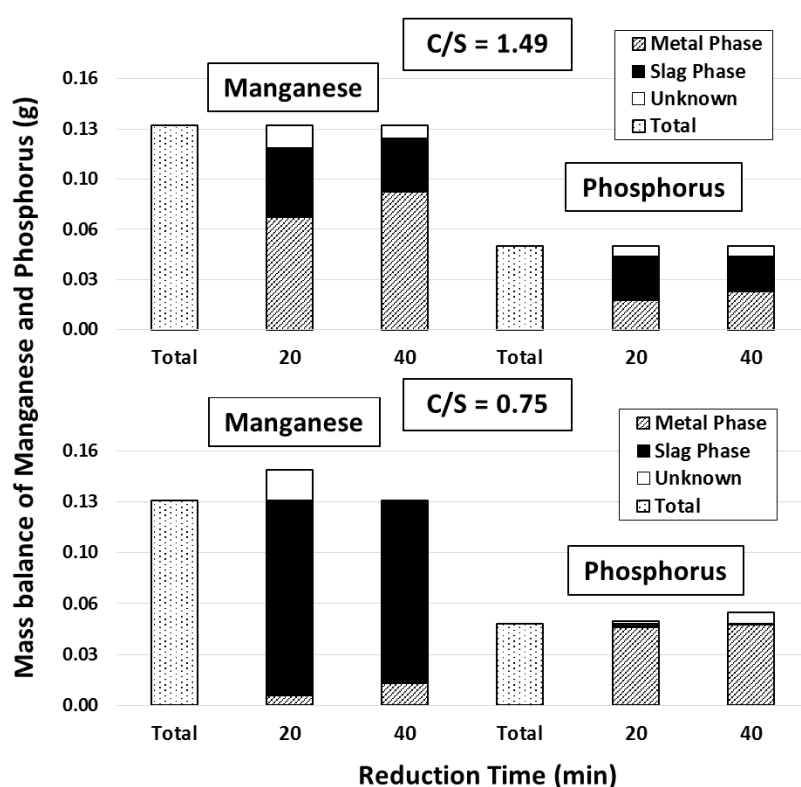


Figure 1: Mass balance of manganese and phosphorus in metals and slags

The unknown mass in Figure 1 represents the difference between the total mass measured after the experiment and the initial mass. This difference is considered to be caused by the gasification of phosphorus and manganese. When the slag basicity was 1.49, both phosphorus and manganese were gradually reduced to the metal phase with increasing time. However, when the slag basicity was 0.75, most of the phosphorus was reduced to the metal phase after 20 min, and only a small amount of manganese was reduced. Thus, by decreasing the slag basicity, the rate of reduction of phosphorus could be enhanced but that of manganese was suppressed. In other words, selective reduction of phosphorus could be achieved.

Conclusions

In the present study, selective carbothermic reduction for the separation of phosphorus and manganese in steelmaking slag was investigated. The obtained results show that decreasing the slag basicity enhanced the rate of phosphorus reduction, whereas that of manganese reduction was suppressed. By decreasing the slag basicity to 0.75, selective reduction of phosphorus to the metal phase was achieved after 20 min of carbothermic reduction.

References

1. R. Dippenaar, "Industrial uses of slag (the use and re-use of iron and steelmaking slags)", *Ironmak Steelmak*, **32** (1) 35-46 (2005).
2. C-M. Du *et al.*, "Effects of Acid and Na₂SiO₃ Modification on the Dissolution Behavior of 2CaO·SiO₂·3CaO·P₂O₅ Solid Solution in Aqueous Solutions", *ISIJ Int*, **56** (8) 1436-1444 (2016).
3. S-J. Kim *et al.*, "Novel recycling process of Mn by sulfurization of molten slag from a by-product of steelmaking process", *High Temp Mat Pr-Isr*, **30** (4-5) 425-434 (2011).
4. K. Morita *et al.*, "Resurrection of the iron and phosphorus resource in steel-making slag", *J Mater Cycles Waste*, **4** (2) 93-101 (2002).
5. H. J. Li, H. Suito and M. Tokuda, "Thermodynamic analysis of slag recycling using a slag regenerator", *ISIJ Int*, **35** (9) 1079-1088 (1995).
6. M. Ishikawa, "Reduction behaviors of hot metal dephosphorization slag in a slag regenerator", *ISIJ Int*, **46** (4) 530-538 (2006).