

Silicothermic reduction behaviour of MnO in MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags

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Abstract – MnO-rich slags are produced not only in a submerged arc furnace (SAF) but also in the manganese oxygen refining (MOR) process for production of manganese ferro-alloys. In the present study, two types of MnO-rich slags are classified, namely MnO-CaO-SiO₂ and MnO-BaO-SiO₂ slags. Because they contain high amounts of MnO (approximately 40%), they are used to produce silicomanganese (SiMn) alloy by the chemical reaction between MnO-rich slags and Si-rich metals. Therefore, understanding the silicothermic reduction (Si↔Mn exchange reaction) behaviour is an important factor to increase production efficiency during plant operation. Nevertheless, the silicothermic reduction of MnO in the slag has not been investigated fully in view of reaction kinetics, as well as Mn recovery. Therefore, we thoroughly investigated the effect of CaF₂ content (0 to 15 wt%) in slag on the silicothermic reduction behaviour of MnO in the MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags. From the results, the silicothermic reduction behaviour of MnO, in terms of reaction kinetics and Mn recovery, is strongly affected by the physicochemical properties of slag, such as viscosity.

Keywords: silicothermic reduction, MnO slag, Mn recovery, reaction kinetics, viscosity

INTRODUCTION

Two types of MnO-rich slags are classified to MnO-CaO-SiO₂ and MnO-BaO-SiO₂ systems, produced by the submerged arc furnace and manganese oxygen refining process for production of manganese ferro-alloys. Because these slags contain high amounts of MnO (approximately 40%), they are used to produce silicomanganese (SiMn) alloy by the chemical reaction between MnO-rich slags and Si-rich metals. Therefore, to achieve a high yield of manganese from the slag, understanding the silicothermic reduction reaction is a key issue.

The silicothermic reduction behaviour of MnO is strongly affected by the physicochemical properties of slag, such as viscosity. The relationship between silicothermic reduction and the physicochemical properties of slag is very important to quantitatively evaluate the reaction kinetics as well as Mn recovery. Therefore, we have thoroughly investigated the effect of CaF₂ addition on the silicothermic reduction behaviour of MnO (and Mn recovery) in the MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags, by considering the physicochemical properties of such slags.

EXPERIMENTS

Two types of experiments were performed independently in the present study; one is for observing the silicothermic reduction reaction using a high-frequency induction furnace, the other is for measuring slag viscosity using a rotating cylinder viscometer.

In the experiments for silicothermic reduction, we employed a slag-metal reaction technique between (20–50% Si) SiMn (or Fe–80% Si) alloys (100–150 g) and MnO-SiO₂-

MO-CaF₂ (M=Ca or Ba) slags (200 g) at 1773 to 1873 K (1500–1600°C) under a purified Ar-H₂ gas atmosphere. Metal and slag samples were taken, using a quartz suction tube and stainless steel rod, respectively, at certain time intervals, and rapidly quenched.

In the experiments for the viscosity measurement, the rotating cylinder method was used under a purified Ar atmosphere in a super Kanthal electric furnace. The experimental temperature ranges from 1373 to 1873 K (1100–1600°C). The compositions of slags are listed in Table I. High-MnO (*i.e.*, 40% MnO) slags represent the initial condition of the reduction process, whereas low-MnO (*i.e.*, 10% MnO) slags represent the later stage of the process.

Table I: Slag compositions for viscosity measurement (wt%)

| MnO | BaO | CaO | SiO ₂ | MgO | CaF ₂ | MnO | BaO | CaO | SiO ₂ | MgO | CaF ₂ |
|-----|------|------|------------------|-----|------------------|-----|------|------|------------------|-----|------------------|
| 40 | 27.5 | 0.0 | 27.5 | 5.0 | 0.0 | 10 | 42.5 | 0.0 | 42.5 | 5.0 | 0.0 |
| 40 | 25.0 | 0.0 | 25.0 | 5.0 | 5.0 | 10 | 40.0 | 0.0 | 40.0 | 5.0 | 5.0 |
| 40 | 22.5 | 0.0 | 22.5 | 5.0 | 10.0 | 10 | 37.5 | 0.0 | 37.5 | 5.0 | 10.0 |
| 40 | 20.0 | 0.0 | 20.0 | 5.0 | 15.0 | 10 | 35.0 | 0.0 | 35.0 | 5.0 | 15.0 |
| 40 | 0.0 | 30.0 | 30.0 | 0.0 | 0.0 | 10 | 0.0 | 30.0 | 60.0 | 0.0 | 0.0 |
| 40 | 0.0 | 27.5 | 27.5 | 0.0 | 5.0 | 10 | 0.0 | 28.3 | 56.7 | 0.0 | 5.0 |
| 40 | 0.0 | 25.0 | 25.0 | 0.0 | 10.0 | 10 | 0.0 | 26.7 | 53.3 | 0.0 | 10.0 |
| 40 | 0.0 | 22.5 | 22.5 | 0.0 | 15.0 | 10 | 0.0 | 25.5 | 50.0 | 0.0 | 15.0 |

After finishing all experiments, the compositions of metal and slag samples were determined using ICP-AES and XRF, respectively, and the precipitation of solid compounds in the slag was confirmed by XRD. Moreover, quantitative analysis of Raman spectra was carried out for structural understanding. The more detailed descriptions of equipment, experimental procedures, and preparation, as well as analysis of samples are available in our previous articles (Heo *et al.*, 2015; Park *et al.*, 2008; Ko & Park, 2012).

RESULTS AND DISCUSSION

Effect of CaF₂ on Mn recovery and silicothermic reduction kinetics

The equilibrium compositions of metal and slag after the silicothermic reduction are shown in Table II.

Table II: Equilibrium slag compositions after silicothermic reduction (wt%)

| Reaction system | Initial CaF ₂ | Fe | Mn | Si | MnO | BaO | CaO | SiO ₂ | MgO | CaF ₂ |
|--------------------------------------|--------------------------|------|------|------|-----|------|------|------------------|------|------------------|
| MCSF ¹⁾ + 30Si-Mn | 0 | 12.7 | 62.4 | 13.0 | 7.5 | 0 | 29.1 | 42.9 | 20.5 | 0 |
| | 5 | 12.2 | 62.4 | 12.4 | 5.1 | 0 | 26.2 | 42.4 | 21.8 | 4.5 |
| | 10 | 13.9 | 63.0 | 12.5 | 5.7 | 0 | 18.2 | 41.7 | 20.3 | 14.1 |
| | 15 | 13.7 | 68.7 | 13.0 | 4.1 | 0 | 11.3 | 40.6 | 23.0 | 21.0 |
| MBSMgF ²⁾ + 80Si-Fe | 0 | 15.1 | 34.9 | 50.0 | 0.5 | 66.6 | 0 | 23.1 | 8.3 | 0 |
| | 5 | 17.4 | 45.5 | 37.1 | 1.4 | 61.9 | 0 | 21.2 | 9.3 | 5.9 |
| | 10 | 16.9 | 47.0 | 36.1 | 0.4 | 55.3 | 0 | 21.3 | 11.6 | 11.3 |
| | 15 | 18.1 | 45.5 | 36.5 | 0.5 | 50.6 | 0 | 20.3 | 12.2 | 15.8 |

¹⁾ 40%MnO-CaO-SiO₂-CaF₂ (C/S=1.0)

²⁾ 40%MnO-BaO-SiO₂-5%MgO-CaF₂ (B/S=1.0)

The effect of CaF₂ content (0 to 15 wt%) in MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags on the Mn recovery is shown in Figure 1. Mn recovery is defined as the ratio of the amount of Mn transferred to metal ingot to the initial amount of Mn in the slag phase before reduction. Mn recovery rapidly increases to about 90% yield at 5% CaF₂

addition, followed by not so different values with some scatter irrespective of CaF_2 content.

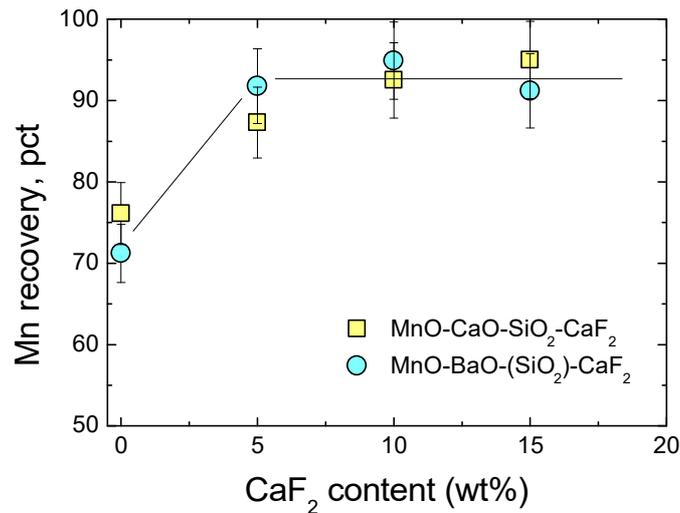


Figure 1: Effect of CaF_2 content (0 to 15 wt%) in $\text{MnO-SiO}_2\text{-MO-CaF}_2$ ($M=\text{Ca}$ or Ba) slags on Mn recovery

From Table II, it is noticeable that the final content of MnO in the slag was generally lower than about 5%, excluding specific conditions. Therefore, it is suggested that there was not a very significant difference in MnO activity with varying CaF_2 content, in the present experiments.

Changes in the content of SiO_2 in the slag phase are shown in Figure 2 as a function of reaction time at different CaF_2 contents. The solid lines in Figure 2 represent the calculated results based on kinetic analysis. The SiO_2 content changed drastically within 300–400 seconds, and followed nearly constant in the present system.

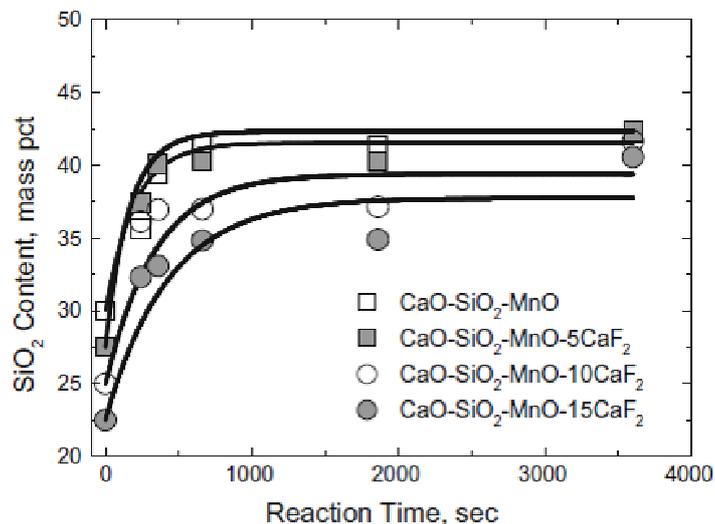


Figure 2: Change in the content of SiO_2 as a function of reaction time at different CaF_2 contents

To consider the reaction kinetics, the diffusion of SiO_2 in the slag phase can reasonably be assumed to be the rate determining step, rather than others. From a consideration of kinetics, the activation energy was found to be about 218 kJ/mol, which is similar to the literature values (Bafghi *et al.*, 2009; Robinson & Pehlke, 1974). Therefore, it can be concluded that the silicothermic reduction of MnO in the high-MnO slag by the Si in the SiMn alloy was controlled by the mass transfer of SiO_2 in the slag.

The mass transfer coefficient of SiO_2 (k_{SiO_2}) that was deduced from a fundamental flux equation is shown in Figure 3 as a function of CaF_2 content at 1773 K (1500°C). Assuming local equilibrium at the slag-metal interface, the content of SiO_2 at the interface is equal to the equilibrium content of SiO_2 . The volume of slag was calculated using a density equation for the slag. It is interesting that k_{SiO_2} increases until 5% CaF_2 , after which it decreases with an increasing content of CaF_2 . Thus, a more systematic investigation of the relationship between CaF_2 content and thermophysical properties of the slag is required.

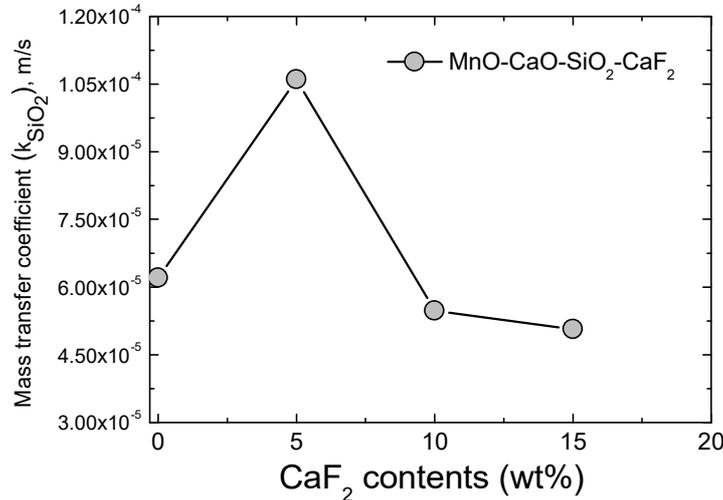


Figure 3: Mass transfer coefficient of SiO_2 (k_{SiO_2}) as a function of CaF_2 content at 1773 K

We found that the solid compounds precipitated in the slag during the slag-metal reactions strongly affected the apparent viscosity of the slag. Precipitated solid phases in the slag samples in $\text{MnO-SiO}_2\text{-MO-CaF}_2$ ($\text{M}=\text{Ca}$ or Ba) slags were identified using XRD, with the results shown in Figure 4.

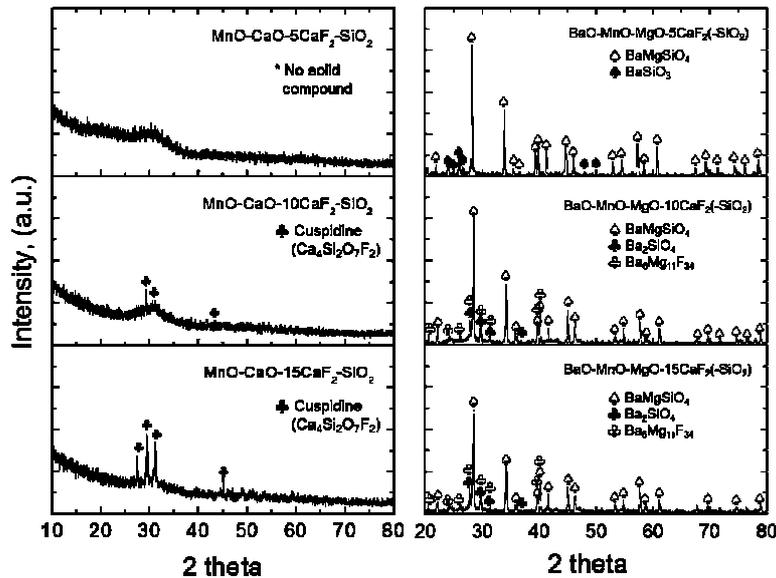


Figure 4: X-ray diffraction pattern at different CaF_2 contents in $\text{MnO-SiO}_2\text{-MO-CaF}_2$ ($\text{M}=\text{Ca}$ or Ba) slags

In the $\text{MnO-SiO}_2\text{-CaO-CaF}_2$ slags, no solid compound was formed in the 5% CaF_2 -containing system, whereas a cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) appeared in the higher (> 5%) CaF_2 systems. In the $\text{MnO-SiO}_2\text{-BaO-CaF}_2$ slags, a BaSiO_3 phase was detected in the 5% CaF_2 slag system, whereas Ba_2SiO_4 and $\text{Ba}_6\text{Mg}_{11}\text{F}_{34}$ compounds were formed in 10 to

15% CaF₂ slag systems. The precipitation of solid compounds, such as Ca₄Si₂O₇F₂ and Ba₂SiO₄, strongly increased the apparent viscosity of the slag and was thus unfavourable for maintaining enough liquid fraction in the slags. Therefore, the addition of CaF₂ should be carefully determined, because the precipitation of solid compounds increases the viscosity of slags.

Effect of CaF₂ content on viscosity of MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags

The influence of viscosity on reduction kinetics is very important to the understanding of mass transfer of species in slag-metal reactions. Because viscosity is strongly affected by the precipitation of solid compounds in the slag phase, it is essential to evaluate solid precipitates, to support kinetic analysis. The viscosities of 10% MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags at temperatures from 1673 to 1873 K (1400–1600°C) are shown in Figure 5 as a function of CaF₂ content. Slag viscosity drastically decreases with CaF₂ addition, resulting in an increase of Mn recovery, as shown in Figure 1.

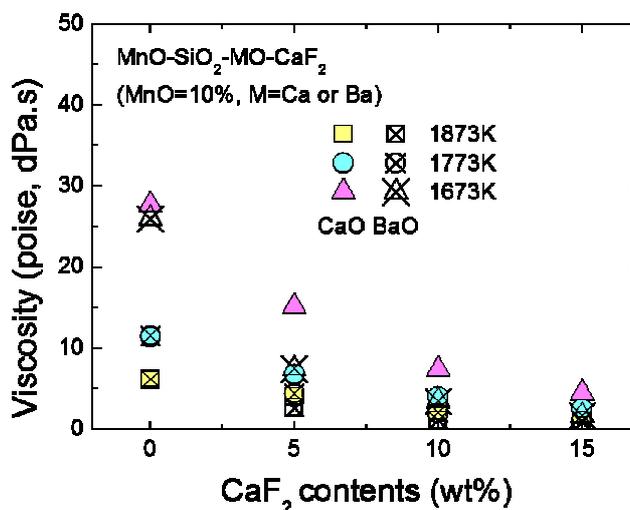


Figure 5: Viscosities of 10%MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags as a function of CaF₂ content

The viscosities of 40% MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags at temperatures from 1673 to 1873 K (1400–1600°C) are shown as a function of CaF₂ content in Figure 6. Slag viscosity slightly decreases with CaF₂ addition at 1773 to 1873 K (1500–1600°C). However, an abrupt increase in viscosity is observed due to the precipitation of a solid phase when CaF₂ is greater than 10% at 1673 K (1400°C), which causes a decrease in mass transfer coefficient of SiO₂, as shown in Figure 3.

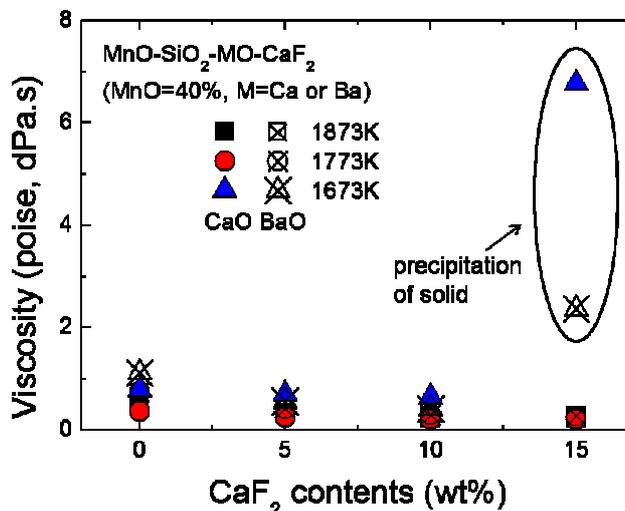


Figure 6: Viscosities of 40% MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags as a function of CaF₂ content

Because the Mn recovery from MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags is strongly dependent on the fluidity of the slags, it is important to control the viscosity of the slags during the silicothermic reduction process. Moreover, excess addition of CaF₂ to the MnO-rich slags is not effective to enhance the Mn recovery of the slags.

CONCLUSIONS

In the present study, the effect of CaF₂ addition on the silicothermic reduction behaviour of MnO in MnO-rich slags was investigated by a slag-metal reaction technique. Furthermore, the viscosity of MnO-SiO₂-MO-CaF₂ (M=Ca or Ba) slags was measured by employing the rotating cylinder method. We found that the silicothermic reduction behaviour of MnO is strongly affected by the viscosity of the slags.

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Current research interests are:

- > Thermochemistry of metallurgical slags
 - > Pyrometallurgical reaction kinetics
 - > Viscosity-Structure relationship
 - > Refractory-Slag-Metal multiphase reaction equilibria
 - > Process modelling with computational thermodynamics
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