

EFFECT OF CaF_2 ON THE REDUCTION RATE OF MnO in $\text{CaO-SiO}_2\text{-MnO}$ SLAG BY SiMn MELT¹Jung Ho Heo, ²Sung Dae Jeon, ²Sang Chul Shim, ³Joo Hyun Park¹School of Materials Science and Engineering, University of Ulsan, Ulsan 680-749, Korea²Technology Development Center, PosHimetal, Gwangyang 545-826, Korea³Department of Materials Engineering, Hanyang University
Ansan 426-791, Korea, e-mail: basicity@hanyang.ac.kr**ABSTRACT**

We investigated the effect of CaF_2 in slag and Si content in SiMn alloy on the reaction kinetics between $\text{CaO-SiO}_2\text{-MnO-CaF}_2$ slag and SiMn alloy melt. The content of MnO consistently decreased by the reaction between slag and 30%Si-Mn alloy melt, resulting in an increase of SiO_2 content in slag phase. From kinetic analysis, the mass transfer coefficient of MnO and SiO_2 (k_{MnO} and k_{SiO_2}) was obtained as a function of CaF_2 content at 1773 K. Both k_{MnO} and k_{SiO_2} increased until 5% CaF_2 , followed by a decrease at higher (>5%) CaF_2 content. In the composition of slag of which CaF_2 content was greater than 5%, the solid phase, e.g. cuspidine, was precipitated during reduction reaction, resulting in an increase of apparent viscosity of slag phase. Moreover, it was observed that the mass transfer coefficient of Si, k_{Si} in 30%Si-Mn alloy melt was 3.5 times greater than that in 10%Si-Mn alloy melt due to higher activity of Si in 30%Si-Mn melt. Thus, the MnO reduction was controlled by the metal phase mass transfer when the Si content was lower than 30%, whereas it was generally controlled by slag phase mass transfer.

KEYWORDS: $\text{CaO-SiO}_2\text{-MnO-CaF}_2$ slag, SiMn alloy, MnO reduction kinetics, mass transfer coefficient, cuspidine, viscosity.

1. INTRODUCTION

Understanding the reduction behavior of slag containing MnO has been an essential issue from economical point of view in production of manganese ferroalloys. High carbon ferromanganese (HCFeMn) slag generally contains about 40% MnO , which is used as a raw material in molten state to produce low phosphorus FeMn alloy by the reaction between the slag and silicomanganese (SiMn) alloy melt. Specifically, it is the most important to understand the reduction kinetics of MnO in slag by Si in SiMn melt during plant operation not only to increase the production efficiency but also to lower the operating cost.

Shinozaki et al. [1] investigated the rate of transfer of Mn from slag to liquid iron by measuring the change of Mn content in liquid iron reacting with the $\text{CaO-SiO}_2\text{-MnO-MgO-FeO}$ slag ($\text{MnO}=17\sim36\%$) with various basicity ($(\text{CaO}+\text{MgO})/\text{SiO}_2=0.6\sim1.2$) under Ar atmosphere at 1873 K. They assumed that the reduction rate of MnO by liquid iron was controlled by mass transfer of Mn, O, MnO and FeO in boundary layers. Daines and Pehlke examined the kinetics of MnO reduction in the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-MnO}$ slag ($\text{MnO}<5\%$) by Si and C dissolved in liquid iron at 1792 to 1873 K by applying diffusion model [2, 3]. They suggested that a diffusion of Mn in metal phase was the rate-controlling step in case of the reduction by Si, while the reaction was controlled by the interfacial chemical reaction in case of the reduction by C.

Tarby and Philbrook studied the reduction of MnO in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MnO}$ slag ($\text{MnO}<5\%$) by carbon saturated iron at 1713 to 1848 K [4]. They concluded that the reduction of

MnO occurred in two stages; in the first stage, the stirring caused by CO evolution resulted in forced convection in the slag (apparent reaction order=1.5~2.9) and in the second stage, as the boiling action subsided, the flow conditions became those defined by natural convection (reaction order=0.9~1.4). The reaction was interpreted to be controlled by slag phase mass transfer and differences in reaction rate were attributed to differences in the activity of MnO in the various slags.

Even though several studies have been carried out by considering the effect of slag composition, temperature and the flux additives on the MnO reduction kinetics to obtain the higher MnO reduction rate, they mainly focus on the reaction between MnO-containing slags and iron melt because manganese plays critical role in steelmaking process. Therefore, in the present study, the effect of CaF₂ on the reduction behavior of MnO in the CaO-SiO₂-MnO-CaF₂ slags (CaF₂=0~15%) by the interfacial reaction between slag and SiMn alloy melts was investigated in view of the application in the high purity FeMn alloy production.

2. EXPERIMENTAL

In the present study, the experiments were carried out using a high-frequency induction furnace. The quartz reaction chamber was initially evacuated using a mechanical rotary pump, and then was filled with the Ar-3%H₂ gas mixture, which was controlled by a mass flow controller. The SiMn alloy was placed in a fused magnesia (99.9% purity) crucible (OD; 60 mm, ID; 50 mm, HT; 120 mm) combined with a graphite heater, which was surrounded by insulation material. Impurities in the Ar-3%H₂ gas mixture were removed by passing the gas through Drierite[®], Mg(ClO₄)₂, silica gel, and soda lime and Mg turnings at 723 K.

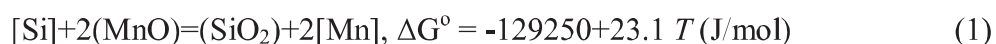
The experimental temperature was 1773 K, which was controlled within ± 2 K using a B-type thermocouple and a PID controller. After temperature stabilization was confirmed, the premelted slag mixture (CaO/SiO₂=1.0, MnO=40%, CaF₂=0~15%), which had been prepared in a resistance furnace, was quickly added through a quartz tube on the surface of SiMn melt under an inert atmosphere. The slag samples were taken using a stainless steel rod coupled with Mo wire by dipping the rod into the slag layer at defined time intervals (0, 3, 5, 10, 30 and 60 minute), followed by quickly quenching by flushing with highly purified Ar gas.

Additionally, the equilibrium experiments were separately carried out using a super-kanthal electric furnace with a MoSi₂ heating element in order to confirm the equilibrium concentration of slag and metal phase. After performing the experiments, the composition of metal and slag samples were determined using ICP-AES and XRF. The slag samples were further analyzed using XRD in order to confirm the precipitated solid phase during experiments.

3. RESULTS AND DISCUSSION

3.1. Influence of CaF₂ in the CaO-SiO₂-MnO-CaF₂ Slag on the Reduction Rate of MnO

Reduction reaction of MnO at the slag-metal interface is believed to take place by the following equation [5].



The reduction of MnO in conjunction with the oxidation of Si as function of reaction time by addition of CaF₂ at 1773 K are shown in figure 1, which shows consistent decrease in the content of MnO and an increase in SiO₂ content with reaction time. The solid lines in figure 1 represent the calculated results based on the kinetic analysis discussed in this study. It is interesting that the content of MnO in molten slag rapidly decreased within initial 5~10 minutes of the reaction,

irrespective of CaF_2 content in molten slag. Therefore, in the present study, the effect of CaF_2 on the initial reaction rate was considered assuming that chemical equilibrium at slag-metal interface is assured due to induction stirring at high temperatures, viz. mass transfer in metal or slag phase can be a rate determining step.

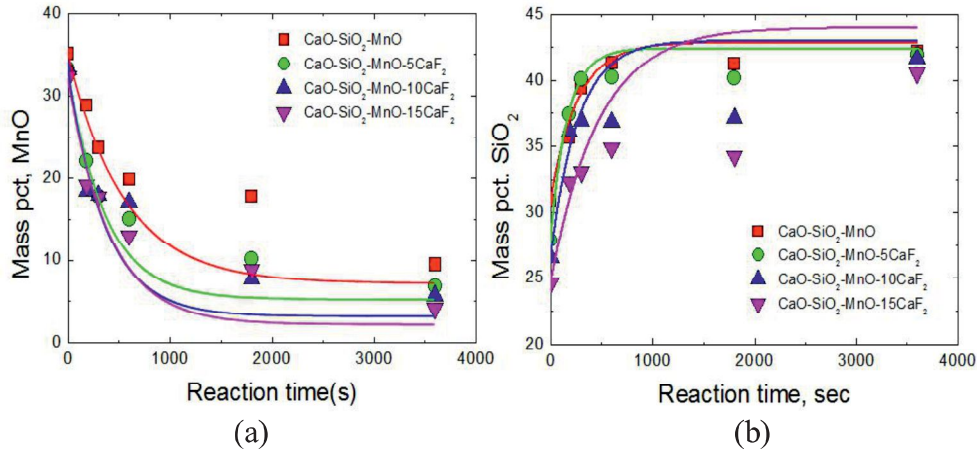


Figure 1: Change of MnO (a) and SiO_2 (b) contents in the $\text{CaO-SiO}_2\text{-MnO-CaF}_2$ slag by the reaction between slag and SiMn melt as a function of reaction time at 1773 K

The kinetic analysis of MnO reduction in molten slag can be written as follows.

$$-\ln \left[\frac{(\% \text{MnO})_t - (\% \text{MnO})_{eq}}{(\% \text{MnO})_o - (\% \text{MnO})_{eq}} \right] = k_{\text{MnO}} \cdot \frac{A}{V_s} \frac{(\% \text{MnO})_o}{(\% \text{MnO})_{eq}} t \quad (2)$$

where t , A , V_s , $(\% \text{MnO})_o$, $(\% \text{MnO})_{eq}$ and $(\% \text{MnO})_t$ are reaction time (sec), reaction area between slag and metal (m^2), which is calculated from inner cross sectional area of the crucible, the volume of slag (m^3), initial content and equilibrium content of MnO, and MnO content at reaction time t , respectively. Based on equation [2], the kinetic plots for MnO and SiO_2 in slag phase at 1773 K are shown in figure 2.

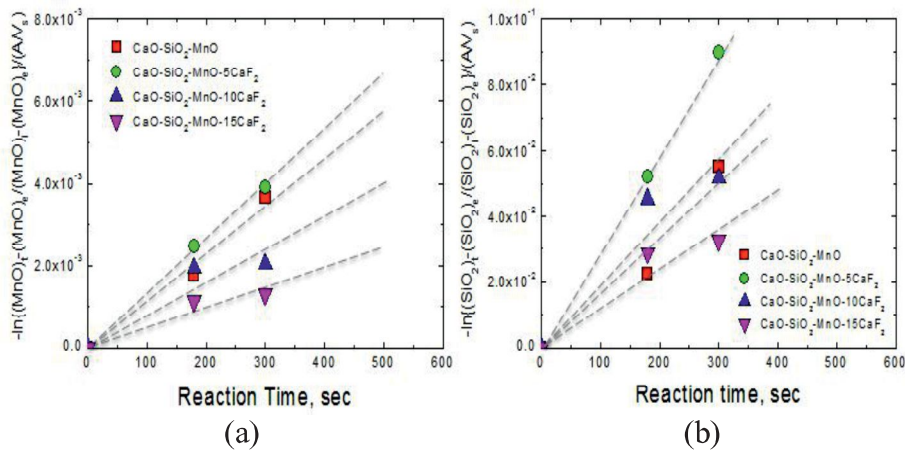


Figure 2: Kinetic plots for MnO (a) and SiO_2 (b) in molten slag reacted with SiMn melt as a function of reaction time at 1773 K

The mass transfer coefficient of MnO and SiO₂ are deduced from the slope of the lines using linear regression analysis. Mass transfer coefficient of MnO (k_{MnO}) and SiO₂ (k_{SiO_2}) were significantly affected by addition of CaF₂ in the slag as shown in figure 3. Both k_{MnO} and k_{SiO_2} increases until 5%CaF₂, after which they decrease as the CaF₂ content increases in the slag. It is noteworthy that k_{SiO_2} is about one order higher than k_{MnO} in the slags, indicating that the mass transfer of MnO in molten slag from bulk to interface is relatively slower than that of SiO₂ from interface to bulk slag in the boundary layer. Therefore, the mass transfer of MnO in slag phase can be a rate controlling step at fixed initial metal composition, i.e. 30%Si-Mn alloy.

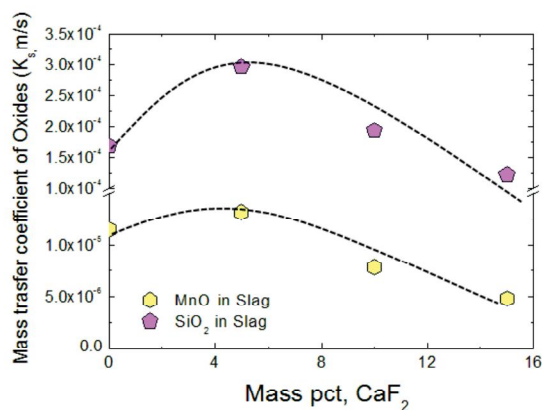


Figure 3: Mass transfer coefficient of MnO and SiO₂ in the CaO-SiO₂-MnO-CaF₂ slags by the reaction between slag and 30%Si-Mn alloy melt as a function of CaF₂ content at 1773 K

The above result shown in figure 3 is somewhat different from our original expectation that the reaction kinetics would be promoted by addition of CaF₂, which is not in the case in the present experiments. It should be considered that the precipitation of solid compounds in slag phase during slag-metal reaction can strongly increase the apparent viscosity of slag phase [6, 7]. The solid compounds were identified by XRD analysis of slag samples as shown in figure 4.

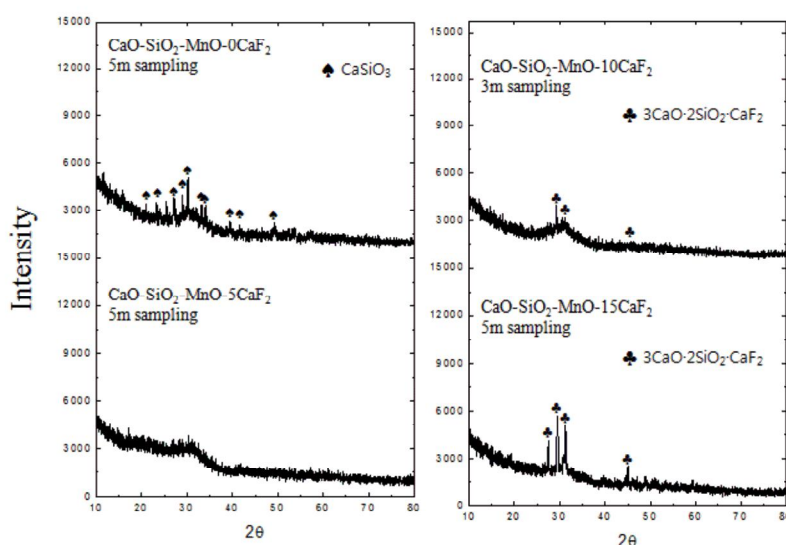


Figure 4: XRD analysis of slag samples in an initial stage of the reaction at different CaF₂ contents

In the CaF_2 -free slag system, the wollastonite (CaSiO_3) compound was precipitated after 5 min, whereas no solid compound was formed in the 5% CaF_2 system. However, the cuspidine ($3\text{CaO}_2 \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$) compound was appeared in the higher ($\geq 10\%$) CaF_2 systems [8]. Therefore, it is qualitatively expected that precipitation of cuspidine increases the apparent viscosity of slag, resulting in a retardation of slag-metal reaction kinetics at $\text{CaF}_2 \geq 10\%$. [6]

3.2. Influence of Silicon Content in SiMn Alloy Melts on the Reduction Rate of MnO

The variation of Si content in the SiMn melts as a function of reaction time for high Si (30%) and low Si (10%) systems reacted with the CaO-SiO_2 -40%MnO (C/S=1.0) slag at 1773 K is shown in figure 5. There are consistent decreases of Si content in the SiMn melts with reaction time.

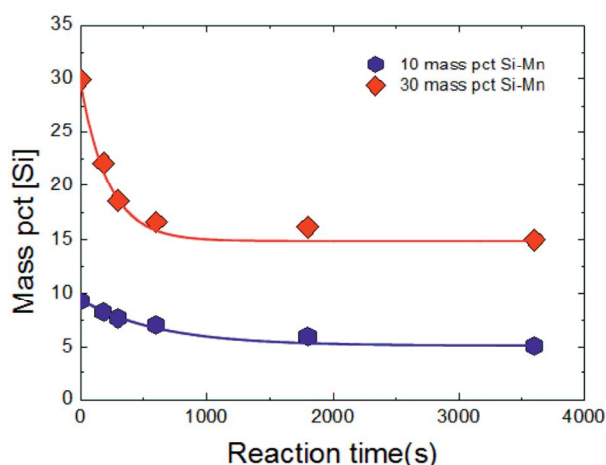


Figure 5: Change of Si content in 10 and 30%Si-Mn melts as a function of reaction time at 1773 K

Silicon content is more sharply decreased in the 30%Si-Mn melt than in the 10%Si-Mn melt. Thermodynamic driving force of forward reaction [1] was expected to increase at higher Si-containing melts due to higher Si activity, which is in good agreement with the measured results. Thus, the mass transfer in metal phase was assumed to be a rate controlling step in the low Si melts as follows.

$$-\ln \left[\frac{[\%Si]_o - [\%Si]_{eq}}{[\%Si]_o - [\%Si]_{eq}} \right] = k_{Si} \cdot \frac{A}{V_m} \frac{[\%Si]_o}{[\%Si]_o - [\%Si]_e} t \quad (3)$$

where $[\%Si]_t$, $[\%Si]_o$, $[\%Si]_{eq}$, A , and V_m are the content of Si at reaction time t , initial and equilibrium content of Si, reaction area between slag and metal (m^2) and the volume of metal (m^3), respectively. From equation [3], the kinetic plot of the initial oxidation of Si as function of reaction time at 1773 K is shown in figure 6. The slope of the line in the 30%Si-Mn alloy melt is steeper than that in the 10%Si-Mn melt, indicating that the mass transfer coefficient of Si in the former is higher than in the latter system, as shown in figure 7.

It was confirmed that k_{Si} of 30%Si-Mn alloy is about by a factor of three higher than 10%Si-Mn alloy due to higher forward driving force of reaction [1] in the former system.

The activity coefficient of Si ($\ln \gamma_{Si}$) in SiMn alloy melts as a function of reaction time was calculated using a commercial thermochemical computing package, FactSageTM 6.3, and the results calculated by thermodynamic data measured by Lee and Paek et al. are also compared in figure 8

[9,10]. The activity coefficient of Si, $\ln \gamma_{Si}$ in the 30 %Si-Mn melt is significantly higher than that in the 10 %Si-Mn melt through the entire reaction time and it rapidly decreases within initial 10 minute. Thus, the MnO reduction in slag phase by Si in SiMn melts was interpreted to be controlled by mass transfer of Si in metal phase boundary layer when the Si content is lower than 30 %.

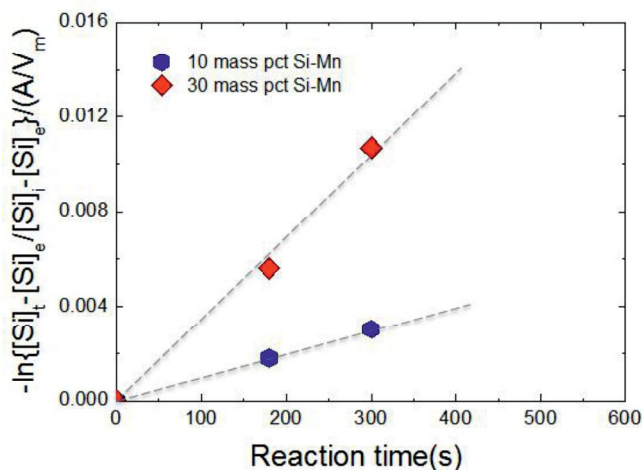


Figure 6: Kinetic plots for Si oxidation in SiMn melt as a function of reaction time at 1773 K

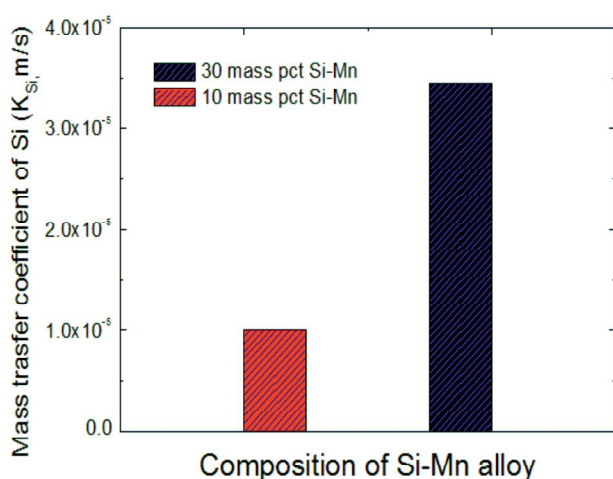


Figure 7: Mass transfer coefficient of Si in the 10 and 30%Si-Mn alloy melts, respectively

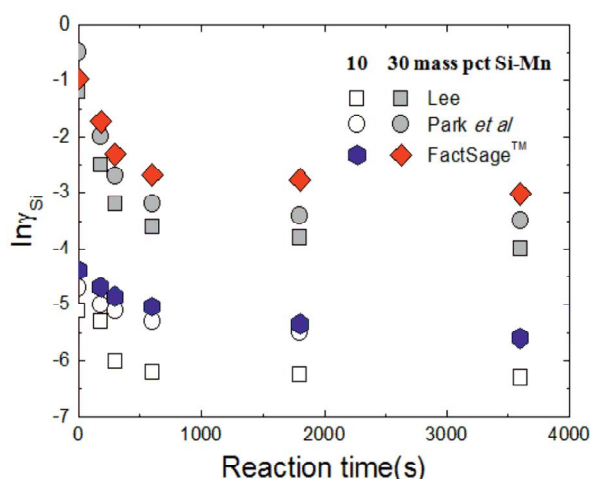


Figure 8: Changes in the activity coefficient of Si in the 10 and 30%Si-Mn melts as a function of reaction time

4. CONCLUSIONS

The effect of CaF_2 on the reduction behavior of MnO in the $\text{CaO-SiO}_2\text{-MnO-CaF}_2$ slag by the reaction between slag and SiMn melts was investigated at 1773 K in view of mass transfer of interested element from slag to interface and metal to interface based on a film theory. The experimental results are summarized as follows.

1. The content of MnO in molten slag rapidly decreased within initial 10 minutes of the reaction irrespective of CaF_2 content in molten slag.
2. Mass transfer coefficient of MnO and SiO_2 (k_{MnO} and k_{SiO_2}) as function of CaF_2 content

was deduced at 1773 K. Both k_{MnO} and k_{SiO_2} increased until 5 % CaF_2 due to an increase of fluidity of slag and decreased at $CaF_2 > 5$ %. This result originated from the fact that cuspidine compound was precipitated in the slag phase with CaF_2 content greater than 5 %. The cuspidine suspensions potentially increased the apparent viscosity of the slags.

3. Mass transfer coefficient of Si in the 30 %Si-Mn melt was about by a factor of three higher than that in the 10 %Si-Mn melt due to higher driving force of MnO reduction reaction, viz. higher activity of Si, in the former system.

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