Reduction Kinetics of MnO in HCFeMn Slag by SiMn Melt

Jung Ho Heo, Joo Hyun Park
Department of Materials Engineering, Hanyang University
Ansan 426-791, Korea
basicity@hanyang.ac.kr

Abstract -The effect of temperature on the silicothermic reduction behavior of MnO in the 30%CaO-40%MnO-30%SiO$_2$ system, which is used to simulate high carbon ferromanganese (HCFeMn) slag, was investigated at 1773 to 1873 K. From the temperature dependence of the mass transfer coefficient of SiO$_2$, the activation energy of the silicothermic reduction process was determined to be about 220 kJ/mol, which was very close to the activation energy reported in the literature for mass transfer in the slag phase.

Keywords: Silicothermic reduction, High carbon ferromanganese (HCFeMn) slag, Mass transfer coefficient, Activation energy, Slag phase mass transfer.

1. Introduction

High carbon ferromanganese (HCFeMn) slag generally contains about 40% MnO, which is used as a raw material in the molten state to produce ultra low phosphorus FeMn (ULPFeMn) alloys by the reaction between the HCFeMn slag and silicomanganese (SiMn) alloy melt. Understanding the silicothermic reaction kinetics is very important in the production of ULPFeMn not only to increase the process efficiency but also to lower the operating cost. For the present system, viz. for the silicothermic reduction of MnO in HCFeMn slag (the so-called the Mn↔Si exchange reaction), the rate of SiO$_2$ formation and transportation (from slag-metal interface to bulk slag) is linked to that of MnO reduction and transportation (from bulk to slag-metal interface) in the slag phase.

Several authors have investigated the reduction behavior of specific oxides in molten slag by Si in liquid metals. Fundamental studies on the de-Si and oxidation kinetics of Si in liquid metal have been performed previously. The de-Si reaction was studied at different temperature ranges using a mathematical model with variation in the initial content of Si, slag composition, and amount of slag (Yamagata et al. 1990). The activation energy of the de-Si reaction was estimated to be approximately 197 kJ/mol (Bafghi et al. 2009), from which the mass transfer of SiO$_2$ in the slag phase was proposed as a rate controlling step. However, because the kinetics of the formation and transportation behavior of SiO$_2$ in the slag phase has not been systematically investigated, we examined the oxidation behavior of Si herein.

Consequently, in the present study, the effect of temperature on the silicothermic reduction of MnO (the Mn↔Si exchange reaction) by the reaction between HCFeMn slag (30%CaO-30%SiO$_2$-40%MnO) and SiMn alloy melt was investigated.

2. Experimental Procedure

The experiments were carried out using a high-frequency induction furnace, which is schematically shown in Fig. 1. The quartz reaction chamber was initially evacuated before performing the experiments using a mechanical rotary pump; it was then filled with an Ar-3%H$_2$ gas mixture. The SiMn alloy (150 g) was placed in a fused MgO refractory for induction heating with a graphite heater, which was surrounded by insulation material. The experimental temperature was 1773 to 1873 K, which was controlled within ±2 K using a B-type thermocouple and a PID controller.
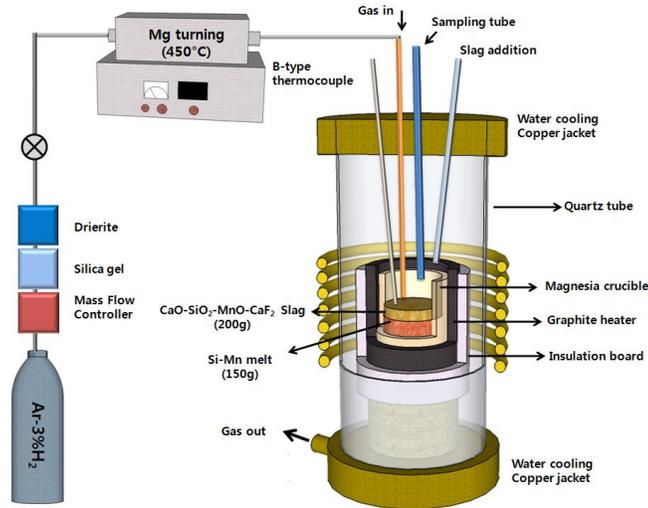
Fig. 1. Schematic diagram of the experimental apparatus.

After temperature stabilization was confirmed, the master slag (200 g), which was prepared by melting reagent grade CaO, SiO_2, MnO and CaF_2, was quickly added through a quartz tube on the surface of the molten SiMn alloy under an inert atmosphere. Slag samples were taken by dipping a stainless steel rod into the slag layer at certain time intervals and quenched by flushing with highly purified Ar gas. After finishing all experiments, the compositions of the metal and slag samples were determined using ICP-AES and XRF spectroscopy. Moreover, the precipitated solid compounds in the slag phase during the slag-metal reactions were confirmed using XRD analysis.

3. Results and Discussion

The effect of temperature on the concentration change of SiO_2 in the 30CaO-30SiO$_2$-40MnO (wt%) slag system at different temperatures from 1773 to 1873 K is shown in Fig. 2. The SiO_2 content rapidly increases with increasing temperature to 300 seconds, after which it remains nearly constant. Since the free energy of the reaction [1] is significantly low, local equilibrium can be achieved at the slag-metal interface under present experimental temperature range. Therefore, a film theory can be employed for kinetic analysis.

$$[Si] + 2(MnO) = (SiO_2) + 2[Mn], \quad \Delta G^o = -129,200 + 23.1\,T \text{ (J/mol)} \tag{1}$$
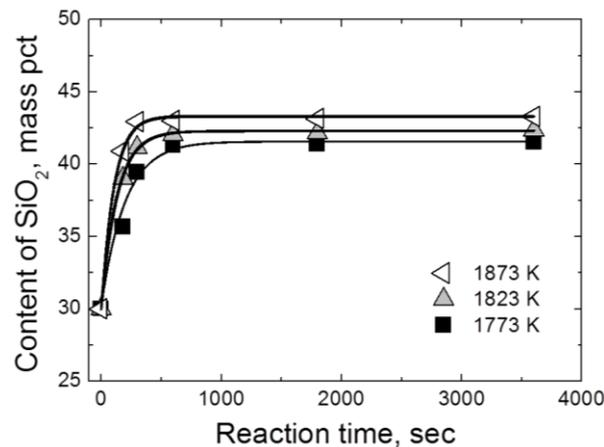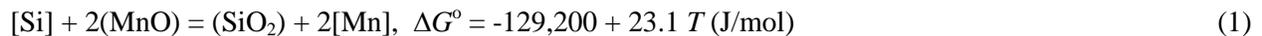
Fig. 2. Content of SiO_2 in slag phase as a function of reaction time at different temperatures from 1773 K to 1873 K.

On the other hand, since induction furnace was employed in the present study, the diffusion of SiO_2 in the slag phase can be reasonably assumed to be the rate determining rather than the diffusion of Si in the metal phase. The net flux of SiO_2 in the molten slag can be written as follows (Deo and Boom, 1993).

$$J_{SiO_2} = k_{SiO_2} \cdot [(C^i_{SiO_2})_s - (C^b_{SiO_2})_s] \tag{2}$$

where J_{SiO_2}, k_{SiO_2}, $(C^i_{SiO_2})_s$, and $(C^b_{SiO_2})_s$ are the net flux of SiO_2 [mol·m^{-2}·s^{-1}], the mass transfer coefficient of SiO_2 [m·s^{-1}], and the molar concentration of SiO_2 at the interface and in the bulk slag phase [mol·m^{-3}], respectively. Assuming local equilibrium at the slag-metal interface, the concentration of SiO_2 at the interface is equal to the equilibrium concentration of SiO_2. Thus, the distribution ratio of Si between slag and metal (L_{Si}) can be defined as follows.

$$L_{Si} = \frac{(C^i_{SiO_2})_s}{[C^i_{Si}]_m} = \frac{(C^{eq}_{SiO_2})_s}{[C^{eq}_{Si}]_m} \tag{3}$$

By combining Eqs. (2) and (3), Eq. (4) can be deduced.

$$J_{SiO_2} = \frac{d(C^b_{SiO_2})_s}{dt} \cdot \frac{V_s}{A} = k_{SiO_2} \cdot \left(L_{Si}[C^i_{Si}]_m - (C^b_{SiO_2})_s \right) \tag{4}$$

Final formula can be deduced from the weight and volume of slag and metal, and the molecular weight of each species. Thus, the following equation is obtained after integration:

$$\ln \left[\frac{(\text{pct SiO}_2)_{eq} - (\text{pct SiO}_2)_t}{(\text{pct SiO}_2)_{eq} - (\text{pct SiO}_2)_o} \right] = k_{SiO_2} \cdot \frac{A}{V_s} \cdot \frac{(\text{pct SiO}_2)_o}{(\text{pct SiO}_2)_o - (\text{pct SiO}_2)_{eq}} \cdot t \tag{5}$$

where t, A, V_s, $(pct SiO_2)_o$, $(pct SiO_2)_{eq}$ and $(pct SiO_2)_t$ are the reaction time [s], interfacial reaction area between the slag and metal [m^2] (calculated as the inner cross sectional area of the crucible), the volume of the slag [m^3], the initial mass pct of SiO_2, the equilibrium mass pct of SiO_2, and the mass pct of SiO_2 at the reaction time t, respectively. The quantity V_s was calculated using the density equation of the CaO-SiO$_2$-MnO slag, which was proposed by Lee et al. (2012) assuming that small amounts of CaF$_2$ do not significantly affect the density of slag. Based on Eq. (5), the value of k_{SiO_2} was obtained from the kinetic plot for the slag-metal reaction at different temperatures.

It is very important to quantitatively determine the activation energy of the process, which is critical to assigning a reaction mechanism. The activation energy can be obtained from the Arrhenius equation, which is expressed as follows.

$$k_{SiO_2} = k_o \cdot \exp\left(-\frac{E}{RT}\right) \tag{6}$$

where k_o, E, R, and T are the pre-exponential constant, the activation energy, the universal gas constant, and the absolute temperature, respectively. The mass transfer coefficient of SiO_2, $\ln k_{SiO_2}$, is

expressed as a function of reciprocal temperature as given in Eq. (7) and is shown in Fig. 3.

$$\ln k_{SiO_2} = -\frac{26,210}{T} + 5.11 \quad (r^2 = 0.99) \tag{7}$$
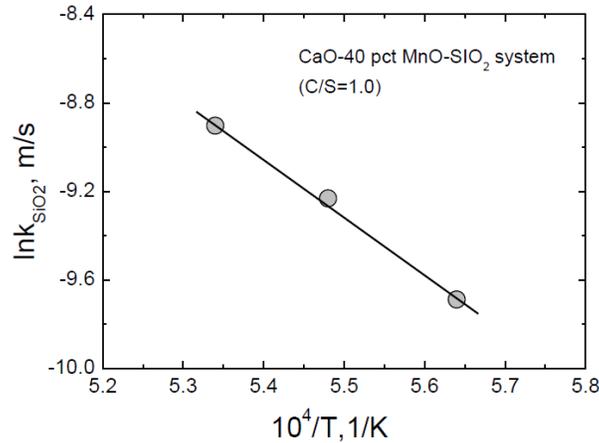
Fig. 3. An Arrhenius plot of the mass transfer coefficient of SiO_2 (k_{SiO2}).

From the slope of the line in the Arrhenius plot, the activation energy was found to be about 220 kJ/mol. Bafghi et al.(2009) studied the oxidation kinetics of Si from molten brass by the ZnO-Na_2O-B_2O_3-Na_2CO_3 slag. They concluded that the slag-metal reaction was predominantly controlled by the mass transfer of SiO_2 and/or ZnO in the slag phase based on a kinetic analysis. The activation energy they obtained was about 197 kJ/mol, which is very similar to the present value. According to Robinson Jr. and Pehlke (1974), the activation energies for mass transfer in the metal phase and in the slag phase range from about 20 to 70 kJ/mol and from about 270 to 420 kJ/mol, respectively. Consequently, it can be concluded that the silicothermic reduction of MnO in the HCFeMn slag by the Si in SiMn alloy was controlled by the mass transfer of SiO_2 in the slag phase.

4. Conclusions

In the present study, the effect of temperature on the silicothermic reduction behavior of MnO in the HCFeMn slag was investigated. The temperature dependence of the mass transfer coefficient of SiO_2, k_{SiO_2}, was found to be:

$$\ln k_{SiO_2} = -\frac{26,210}{T} + 5.11 \quad (r^2 = 0.99).$$

The activation energy was deduced to be about 220 kJ/mol, which was very close to the activation energy for the mass transfer in slag phase.

References

Bafghi, M.S., Asghari, A.R., Zakeri, A., & Seyedein, S.H. (2009). Metall. *Mater. Trans. B,* 40B, 749-754.
Deo, B., & Boom, R. (1993). Fundamentals of Steelmaking Metallurgy. Prentice Hall, New York, NY.
Lee, J., Hoai, L.T., Choe, J.K., & Park, J.H. (2012). *ISIJ Int.,* 52, 2145-2148.
Robinson, J.W., & Pehlke, R.D. (1974). Metall. *Trans.,* 5, 1041-1051.
Yamagata, C., Kajiwara, Y., Suyama, S., & Miyake, T. (1990). *ISIJ Int.,* 30, 740-747.