Kinetics of the reaction of SiO$_2$ and MnO reduced by C in molten copper with carbon saturated

Honghong Huang $^1$, Jianbin Chen $^{1,2}$, Wenbo Pan $^1$ and Minghui Zhao $^1$

School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, 201418, China

E-mail: 1843334784@qq.com, jianbin_chen63@126.com, 1985729474@qq.com, 1064099467@qq.com

Abstract. In order to study the effect of matrix metal species on the kinetics of the reaction of SiO$_2$ and MnO reduced by C in molten copper with carbon saturated, the experiment, in which a preliminary slag with the composition of 38%CaO-38%SiO$_2$-20%Al$_2$O$_3$-2%MnO-2%MgO that was placed in a graphite crucible and reacted with pure metallic copper at 1450°C under the atmosphere of pure CO, was carried out. The kinetics of both the reactions of SiO$_2$ and MnO in molten slag reduced by C in molten copper with carbon-saturated (2[C]$_{sat-in-Cu}$ + (SiO$_2$) =2CO(g) + [Si]$_{Cu}$ and [C]$_{sat-in-Cu}$ + (MnO) =CO(g) + [Mn]$_{Cu}$) have been studied by studying the changes of the concentration of Si and Mn in molten copper with carbon-saturated, and the reaction order and reaction rate constant of the two reactions have been obtained. The results show that: (1) The reaction of SiO$_2$ reduced by C is 0.5th order reaction while it is -0.5th order reaction for MnO; (2) The reaction rate constant of the reduction of SiO$_2$ reduced by C in molten copper with carbon-saturated is $7.50\times10^6$ mass% $0.5$ s$^{-1}$, while that of MnO reduced by C in molten copper with carbon-saturated is $5.52\times10^6$ mass% $1.5$ s$^{-1}$; (3) In this study, the reactions of SiO$_2$ and MnO reduced by C in molten copper with carbon-saturated is a slow reaction and the time for the reaction equilibrium is more than 22 hours.

1. Introduction

The reductions of oxides of manganese and silicon are very important reactions in ferrous metallurgy, also important during the process of the smelting for ferromanganese, ferrosilicon and silicon-manganese alloys.

The reductions of oxides of manganese and silicon are very important reactions in ferrous metallurgy, also important during the process of the smelting for ferromanganese, ferrosilicon and silicon-manganese alloys. There have been numerous works investigated on the thermodynamics of slag, which containing the components SiO$_2$ and MnO. These researches mainly focus on the thermodynamic activities of MnO and SiO$_2$ in the slag [1-5], also about the distribution of manganese and silicon between the molten slag and the molten metal [6-10]. In addition, researches on the kinetics of the reduction about SiO$_2$ and MnO [11-15] also have been reported. In recent years, since the researches on high strength manganese steel have become more and more popular, study on the kinetics of MnO reduction have rapidly developed [16-18]. At present, researches on the kinetics of the reactions of SiO$_2$ and MnO reduced by C mainly covered the kinetic parameters of the reduction reaction [11-14,16] (such as reaction order, activation energy), reaction mechanism and reaction steps [11,14,16]. The type of reducing agent for SiO$_2$ and MnO in molten slag could be coke [17], the saturated carbon in molten iron [11, 12], the carbon dissolved in molten iron [13,14], or the CO blown into the molten pool[15], also could be the silicon in molten Si-
Mn alloy [16]. What’s more, the effect of raw material types on the reaction kinetics was also had been studied [17,18]. The molten iron or the molten Si-Mn alloy was generally be used as molten metal.

Regarding the reaction order of the reaction of MnO and SiO$_2$ reduced by C, Yagi and coworkers[11] studied the rate of reduction of MnO in CaO-SiO$_2$-Al$_2$O$_3$-MnO slag by carbon-saturated molten iron, and obtained that the reduction rate was proportional to the reaction driving force \((\text{mass}\% \text{ MnO}) - K \text{ [mass}\% \text{ Mn]} \)^{1.75}. Besides that, they also concluded that the apparent rate constant increased with the activity of SiO$_2$ and the temperature. Xu et al. [12] considered that the reduction reaction of MnO in molten slag using for the high-carbon ferromanganese smelting reduced by carbon-saturated molten iron was the second-order reaction. However, when carbon was added into the slag, it could be the first-order reaction. Kawai et al. [13] obtained the amount of Si which migrated to the metal from the slag was linear with time, and the apparent activation energy was about 100 kcal / mol, also the apparent rate constant increased with the exaltation of the activity of SiO$_2$ and the temperature.

When studied on the reaction mechanism of the reaction of SiO$_2$ and MnO reduced by carbon, Xu and coworkers [12] hold the opinion that the rate of reduction reaction of MnO in molten slag reduced by carbon-saturated molten iron was controlled by chemical reaction at interface. Jamieson and Coley [16] indicated that the rate of reduction reaction of MnO in MnO-SiO$_2$-CaO-Al$_2$O$_3$ slag reduced by Si in Fe-Si droplets was mixedly controlled by the mass transfer of MnO in molten slag and the mass transfer of Si in metal phase. Weldon et al. [14] thought that the reduction reaction of MnO in basic slag reduced by the carbon dissolved in molten iron was a slow reaction, and the rate-controlling step of the reaction was the chemical reaction at interface.

It can be seen that different researchers have different results on the reaction order of SiO$_2$ and MnO reduced by carbon. Similarly, the results of the study have changed under different slag system conditions. So, what effect will happen for the kinetics of reduction reaction of MnO and SiO$_2$ as the metal sources has changed?

In present study, a carbon saturated copper liquid in graphite crucible was used as the source of reducing agent C to study the kinetics of reduction of SiO$_2$ and MnO in molten slag containing 38%CaO-38%SiO$_2$-20%Al$_2$O$_3$-2%MnO-2%MgO by carbon. The kinetics of the reduction reaction of SiO$_2$ and MnO was studied by a series of reduction experiments in which slag and copper liquid were reacted at 1450 °C under CO atmosphere for different time. The reaction order and reaction rate constant were investigated.

## 2. Experimental

### 2.1. Experimental materials

A high-purity graphite crucible filled with 25g mixed-slag containing 38%CaO-38%SiO$_2$-20%Al$_2$O$_3$-2%MnO-2%MgO, 15g metal copper powder and 0.002g high-purity graphite powder was placed in the constant temperature zone of the vertical tube resistance furnace with vacuum device. Then seal the vertical tube furnace. Fig. 1 is a schematic diagram of the experimental apparatus. A SiMo-resistor furnace with mullite tube (50 mm-OD) was used in the experiments. A high-purity graphite crucible (36 mm-OD, 58 mm-height) filled with 25g mixed-slag containing 38%CaO-38%SiO$_2$-20%Al$_2$O$_3$-2%MnO-2%MgO, 15g metal copper powder and 0.002g high-purity graphite powder. The slag was prepared by 99.5% MnO, AR (analytical reagent) grade Al$_2$O$_3$, AR (analytical reagent) grade CaO, AR (analytical reagent) grade SiO$_2$, 4N grade MgO. The purity of carbon monoxide and argon were 99.995% and 99.999%, respectively. The metal was prepared using a metal copper powder reagent with a purity of 99.99%. A Pt /6% Rh-Pt /30% Rh thermocouples was used to measure the melting temperature at the bottom of the graphite crucible at the furnace bottom. A PID controller was used to control the temperature within ± 1 °C during the whole melting process.
2.2. Experimental procedure

Argon was blown into the furnace (flow rate 400 ml/min) with 0 Mpa of gage pressure and lasted for 15 min, the furnace was evacuated to reduce the gauge pressure to -0.1 Mpa and lasted for 15 min. As this step had been repeated three times, the Ar gas was inserted and lasted for 15 min. After that, the power was turned on in order to rise the temperature.

When the zone of the constant temperature reached to 1450°C, the Ar gas was turned off and switched to CO gas (flow rate 200 ml/min) for 20 min to homogenize. After that, the time was taken as the time zero and the timekeeping was started. The temperature was kept constant throughout the whole smelting and the gas flow was stable. When the preset melting time was reached, the CO gas was turned off then switched to Ar gas, and the temperature could be dropped. As the temperature was cooled to the room temperature, the power was turned off. Then the graphite crucible were took out, in which contained the metal samples and slag samples. The slag and meltal samples should be separated without pollution.

The metal samples were sent to Shanghai Research Institute of Materials to do chemical analysis. The ICP method (inductively coupled plasma emission spectrometer) was used to chemically analyze the metal sample to obtain the Si and Mn content in the metal Cu melt sample. The slag sample was sent to the Shanghai Microspectral Analysis and Testing Center, and the content of each component in the slag sample was obtained by the XRF method of molten glass.

3. Results and Discussions

The carbon-saturated Cu liquid-molten slag-CO gas atmosphere was smelted at 1723K, 101325Pa, and the CO flow rate was 200 ml·min⁻¹. The reduction reactions of SiO₂ and MnO in molten slag by the carbon were as:

\[2[C]_{Cu} + (SiO_2) = 2CO (g) + [Si]_{Cu}\]
\[[C]_{Cu} + (MnO) = CO (g) + [Mn]_{Cu}\]

where [ ] is the component in Cu liquid and ( ) is the component in molten slag.

The variations in the content of Si and Mn in the molten Cu melt with time are shown in Table 1.
### Table 1. Variations of the concentrations of Si and Mn in molten Cu with time

| Time (h) | 0    | 5    | 10   | 15   | 20   | 22   |
|---------|------|------|------|------|------|------|
| $w_{Si}$ (mass%) | 0    | 0.008| 0.023| 0.048| 0.066| 0.13 |
| $w_{Mn}$ (mass%) | 0    | 0.38 | 0.49 | 0.64 | 0.67 | 0.82 |

#### 3.1. Reaction Rate

According to the data in Table 1, the rate of reduction reaction of SiO$_2$ and MnO can be shown in Figure 2. From the 0 moment to the 22nd hour, the reaction rate of SiO$_2$ has increased with time. However, the reaction rate of MnO experienced a sudden drop and then had a rapidly rise.

![Figure 2](image_url)

**Fig. 2.** The reaction rate of SiO$_2$ and MnO.

The reason for the sudden change of the reaction rate can be explained. In the initial stage, MnO can be easier reduced than SiO$_2$, so the driving force for MnO to be reduced was relatively large which made the reaction rate of MnO fast. As the reduction reaction proceeds on, the driving force for reduction gradually decreased with reduction reaction of MnO proceeded, therefore the reaction rate gradually decreased.

As SiO$_2$ continued to be reduced, the concentration of SiO$_2$ in the slag decreased, the alkalinity ($\text{CaO} / \text{SiO}_2$) of the slag increased, so that the activity of MnO in the slag was caused to be increased. Therefore, the reduction rate of MnO gradually increased after the fifteen-hour.

For the reaction rate of SiO$_2$, since the reduction reaction of MnO happened firstly, the reduction of SiO$_2$ was suppressed, so the reaction rate of SiO$_2$ was very slow in the initial stage. As the reduction process proceeded, the reaction rate of MnO became slow, and the reaction rate of SiO$_2$ became faster.

#### 3.2. Reaction order

When different orders of chemical reactions occur, the relationship between component concentration and time in the melt can be expressed as

$$
\frac{1}{n-1} \left( \frac{1}{w_i^{n-1}} - \frac{1}{w_{i0}^{n-1}} \right) = kt
$$

where $n$ is the reaction order, $n \neq 1$ and can be a fraction and negative; $w_i$ and $w_{i0}$ are the content of Mn and Si in molten metal at some time and at the initial time, respectively; $k_i$ is the rate constant of reduction reaction of Mn and Si; $t$ is the time.

When $n=1$, the integral form of the rate equation can be expressed as

$$
\ln w_i - \ln w_{i0} = kt
$$

When $n=2$, the rate equation is

$$
\frac{1}{w_i} - \frac{1}{w_{i0}} = kt
$$

When $n=-1$, the rate equation is

$$
\frac{1}{w_i^{n-1}} - \frac{1}{w_{i0}^{n-1}} = kt
$$
Each linear regression analysis has been carried out from the relationship determined by Eqns. (3) and (4) for the data of SiO2 reduced by C, when n = -0.5, 0, 0.5, 1 and 1.5. For MnO, n = -1.5, -1, -1.5, 0 and 0.5.

Table 2. Coefficient of determination $R^2$ and corresponding slope and intercept of linear regression when taking different reaction order for the reaction of SiO2 reduced by C.

| Reaction order | -1 | -0.5 | 0 | 0.5 | 1 | 1.5 |
|----------------|----|------|---|-----|---|-----|
| t/h            | $1/|w_{[Si]}|^2$ | $1/|w_{[Si]}|^{1.5}$ | $w_{[Si]}$ | $1/|w_{[Si]}|^{0.5}$ | In$w_{[Si]}$ | $1/|w_{[Si]}|^{1.5}$ |
| 0              | 3.1623×10^-8 | 3.1623×10^-5 | 0.001 | 0.0316 | -6.908 | 31.6228 |
| 5              | 5.7243×10^-6 | 7.1554×10^-4 | 0.008 | 0.0894 | -4.828 | 11.1803 |
| 10             | 8.0227×10^-5 | 0.0035 | 0.023 | 0.1516 | -3.772 | 6.5938 |
| 15             | 5.0478×10^-4 | 0.0105 | 0.048 | 0.2191 | -3.037 | 4.5643 |
| 20             | 0.0011 | 0.0170 | 0.066 | 0.2569 | -2.718 | 3.8925 |
| 22             | 0.0061 | 0.0469 | 0.13 | 0.3605 | -2.040 | 2.7735 |

R$^2$(COD) | 0.4808 | 0.66567 | **0.81429** | **0.9563** | **0.9272** | **0.7153** |
Intercept | -0.0010 | -0.00713 | -0.0143 | 0.0224 | 0.1972 | -1.0766 |
Slope | 1.9243×10^-4 | 0.0017 | 0.0050 | 0.0135 | -6.2507 | 23.0242 |

Table 3. Coefficient of determination $R^2$ and corresponding slope and intercept of linear regression when taking different reaction order for the reaction of MnO reduced by C.

| Reaction order | -1.5 | -1 | -0.5 | 0 | 0.5 | 1 |
|----------------|-----|----|------|---|-----|---|
| t/h            | $1/|w_{[Mn]}|^{1.5}$ | $1/|w_{[Mn]}|^2$ | $1/|w_{[Mn]}|^{1.5}$ | $w_{[Mn]}$ | $1/|w_{[Mn]}|^{0.5}$ | In$w_{[Mn]}$ |
| 0              | 3.1623×10^-8 | 1×10^-6 | 3.1623×10^-5 | 0.001 | 0.0316 | -6.9078 |
| 5              | 0.0890 | 0.1444 | 0.2342 | 0.38 | 0.6164 | -0.9676 |
| 10             | 0.1682 | 0.2401 | 0.343 | 0.49 | 0.7 | -0.71336 |
| 15             | 0.3277 | 0.4096 | 0.512 | 0.64 | 0.8 | -0.4463 |
| 20             | 0.36744 | 0.4489 | 0.5484 | 0.67 | 0.8185 | -0.4005 |
| 22             | 0.6089 | 0.6724 | 0.7425 | 0.82 | 0.9055 | -0.1985 |

R$^2$(COD) | **0.9109** | **0.9470** | **0.9587** | **0.9124** | **0.7634** | 0.5669 |
Intercept | -0.0334 | -0.0068 | 0.0392 | 0.1166 | 0.2591 | -4.3483 |
Slope | 0.0245 | 0.0272 | 0.0298 | 0.0320 | 0.0322 | 0.2286 |

The linear correlation coefficient of each regression straight line can also be obtained. Table 2 shows the linear regression results of the relationship between the concentration and time for the reduction reactions of SiO2 reduced by C in a carbon-saturated molten copper when the reaction order is (-0.5 ~ 1.5th) , according to Eqns. (3) and (4). Tables 3 shows the linear regression results of the relationship between the concentration and time for the reduction reactions of MnO reduced by C in a carbon-saturated molten copper when the reaction order is (-1.5 ~ 0.5th). In the tables, the value in bold italic font indicates the maximum coefficient of determination $R^2$ value.

It can be known from Table 2 and 3 that the maximum correlation coefficient $R^2$ in the linear regression of the two reactions appears at the 0.5th-order reaction and -0.5th-order reaction, respectively. From a mathematical perspective, as long as the correlation coefficient value is greater than the correlation coefficient with critical value of the significance level $\alpha = 0.05$ ($R^2>0.658$), it can be explained that the functional relationship between the two variable value obey the linear regression relationship. In Table 2 and Table 3, the coefficients of determination $R^2$ for the C-reduced SiO2 at the 0 ~ 1.5th order reactions are greater than the square of the corresponding critical value, and the same applies to the C-reduced MnO reaction at the -0.5 ~ 0.5th order reactions. It can therefore be seen that the C-reduced SiO2 reaction can be expressed as 0th order, 0.5th order, 1th order and 1.5th order reaction. And the C-reduced MnO reaction can be expressed as -1.5th order, -1th order, -0.5th order, 0th order and 0.5th order.
However, according to mathematical principles, the corresponding reaction order is the most reasonable when the correlation coefficient is closest to 1. Therefore, based on the above discussion, it is considered that the reaction of SiO\(_2\) reduced by C is 0.5th order reaction and -0.5th order reaction for MnO.

### 3.3. Rate constant of reactions

For the 0.5th-order reaction, when the C in a carbon-saturated molten Cu reduces SiO\(_2\), the relationship between the Si concentration in the copper melt and time is

\[
\frac{1}{0.5-1} \left( \frac{1}{w_{[\text{Si}]}^{0.5-1}} - \frac{1}{w_{[\text{Si}]}^{0.5-1}} \right) = k_{\text{Si}}t
\]

From Eqn.(5), the rate constant of the reaction of SiO\(_2\) reduced by C can be expressed as \(k_{\text{Si}}=0.0270\) mass\%\(^{0.5}\).h\(^{-1}\)=7.50\(\times\)10\(^{-6}\) mass\%\(^{0.5}\).s\(^{-1}\).

Similarly, the rate constant of the reaction of MnO reduced by C can be expressed as \(k_{\text{Mn}}= 0.0199\) mass\%\(^{1.5}\).h\(^{-1}\)=5.52\(\times\)10\(^{-6}\) mass\%\(^{1.5}\).s\(^{-1}\).

### 4. Rate equation of reduction reaction of SiO\(_2\) and MnO

#### 4.1. Reaction mechanism

The reaction studied in this investigation involves three phases: slag, metal, and gas. It may include both the mass transfer process in molten metal and molten slag, the chemical reaction at interface and the mass transfer process in gas phase. Considering the reaction (1) and (2), the overall reaction involves the following steps:

1. Transport of reactants SiO\(_2\) and MnO from the molten slag to the slag-metal interface or the slag-crucible interface.
2. Interfacial chemical reaction at the slag-metal interface.
3. Transport of products, CO, from interface to the bulk of gaseous phase. And the transport of Si and Mn from the slag-metal interface or the metal-crucible interface to the molten coper.

Weldon et al. [14] thought that the rate of the reduction reaction of MnO in basic slag reduced by the carbon dissolved in molten iron was controlled by the interfacial chemical reaction rate. In this study, the equilibrium time for the reduction process of Si and Mn was more than 22 hours, so it is also can be considered as a slow reaction, and also can be concluded that the interface chemical reaction should be a rate-limiting step. Xu et al. [12] also hold the same view. Jamieson and Coley [16] believed that the reduction rate of MnO in MnO–SiO\(_2\)–CaO–Al\(_2\)O\(_3\) slag reduced by Si in Fe-Si droplets was controlled by the mass transfer of MnO in the slag and the mass transfer of Si in the metal phase. Since the slag and metal were almost stock-still during the experiment, the mass transfer of SiO\(_2\) and MnO from the slag phase to the slag-metal interface or the slag-crucible interface were also considered as a rate-limiting step. As the rate of mass transfer for products Si and Mn in the metal-side boundary layer was fast, it will not become a rate-limiting step. What’s more, since CO was always blown into the system at a flow rate of 200 ml / min, it is considered that the desorption of CO generated by the reaction and its diffusion in the gas-phase boundary layer will not become a rate-limiting step. Therefore, present investigation consider that the reduction of SiO\(_2\) and MnO in the molten slag by carbon is mixed control mechanism by the mass transfer of SiO\(_2\) and MnO in the slag and the chemical reaction at the interface of the slag-metal or the slag-crucible interface.

#### 4.2. Rate equation of reduction reactions

**4.2.1. Rate equation of reduction reaction of SiO\(_2\).** As discussed in 3.2, the reduction reaction of SiO\(_2\) (Eqn.(1)) is the 0.5th order reaction and the reaction process is mixed controlled by the mass transfer of SiO\(_2\) in the slag and the chemical reaction at the interface of the slag-metal or the slag-crucible interface. However, the rate equation will be unable to be derived because of the difficulty solving of the equation when based on the mechanism in which the reaction is the 0.5th order reaction. In
addition to the 0.5th-order reaction, the first-order reaction was also reasonable. So, for the -1st order reaction, the interface reaction rate can be expressed as

$$v_{R_{Si}} = k_{w_{Si}} w_{Si}^* - k_{p_{CO}} w_{Si}^*$$

Where $v_{R_{Si}}$ is the rate of the interface chemical reaction; $k_{w}$ and $k_{p}$ are the rate constant of the positive reaction and the reverse reaction for the reaction of SiO$_2$ reduced by C (Eqn.(1)). The superscript "*" indicates the value at the interface. As the carbon came from the carbon-saturated copper liquid, the standard state of activity is taken as the carbon-saturated molten copper. And the activity standard state for the carbon in the crucible is taken as the solid carbon (graphite). So the activity of carbon at the interface is $a_C = 1$. Due to the blowing of pure CO, $p_{CO}$ is 1 in the atmosphere. Therefore, there is

$$v_{R_{Si}} = k_{w_{Si}} w_{Si}^* - k_{p_{CO}} w_{Si}^* = k_{w} \left( w_{Si}^* - \frac{k_{p}}{k_{w}} w_{Si}^* \right) = k_{w} \left( w_{Si}^* - \frac{w_{Si}^*}{K_{Si}} \right)$$

Where, $K_{Si}$ is the equilibrium constant for the reaction (Eqn.(7)).

The rate of the mass transfer for oxide SiO$_2$ in the boundary layer on the slag side can be expressed as

$$v_{R_{Si}} = \beta_{SiO2} \left( w_{SiO2} - w_{SiO2}^* \right)$$

Where, $\beta_{SiO2}$ is the coefficient of mass transfer. When the reaction reaches steady state, it can be expressed as follows,

$$v_{R_{Si}} = v_{fsi}$$

Thus, Eqns.(7) and (8) are combined to eliminate the interface concentration. Moreover, since the faster mass transfer in the boundary layer on the metal side, the interface concentration of Si generated at the interface is equal to the bulk-phase concentration in molten metal. Hence, the reaction rate is

$$v = \frac{w_{SiO2} - w_{Si}}{K + \frac{1}{k_{w} + \beta_{SiO2}}}$$

This is the kinetic equation for the reaction of SiO$_2$ reduced by C in carbon saturated copper liquid and or on the surface of the crucible.

### 4.2.2. Rate equation of reduction reaction of MnO

As discussed in 3.2, the reduction reaction of MnO (Eqn.(2)) is the -0.5th order reaction and the reaction process is mixed controlled by the mass transfer of MnO in the slag and the chemical reaction at the interface of the slag-metal or the slag-crucible interface. However, the rate equation will be unable to be derived because of the difficulty solving of the equation when based on the mechanism in which the reaction is the -0.5th order reaction. In addition to the 0.5th-order reaction, the -1st order reaction was also reasonable. So, for the -1st order reaction, the interface reaction rate can be expressed as

$$v_{R_{Mn}} = k_{w} \left( w_{MnO}^* a_{C}^* \right)^{-1} - k_{p} \left( p_{CO} w_{Mn}^* \right)^{-1}$$

where $v_{R_{Mn}}$ is the rate of the interface chemical reaction; $k_{w}$ and $k_{p}$ are the rate constant of the positive interfacial reaction and the reverse interfacial reaction for the reaction of MnO reduced by C (Eqn.(13)). Therefore, there is

$$v_{R_{Mn}} = k_{w} \left( w_{MnO}^* a_{C}^* \right)^{-1} - k_{p} \left( p_{CO} w_{Mn}^* \right)^{-1} = k_{w} \left( w_{MnO}^* \right)^{-1} \left( \frac{k_{p}}{k_{w}} \left( w_{Mn}^* \right)^{-1} \right) = k_{w} \left( w_{MnO}^* \right)^{-1} \left( \frac{w_{Mn}^*}{K_{Mn}} \right)^{-1}$$

Where, $K_{Mn}$ is the equilibrium constant for the reaction (Eqn.(12)).

The rate of the mass transfer for oxide MnO in the boundary layer on the slag side can be expressed as

$$v_{fsi} = \beta_{MnO} \left( w_{MnO}^* - w_{MnO}^* \right)$$

Where, $\beta_{MnO}$ is the coefficient of mass transfer. When the reaction reaches steady state, it can be expressed as follows,
Thus, Eqns.(12) and (13) are combined to eliminate the interface concentration. Moreover, since the faster mass transfer in the boundary layer on the metal side, the interface concentration of Mn generated at the interface is equal to the bulk-phase concentration in molten metal. Hence, the reaction rate is

\[
v = \beta \left( h_{\text{MnO}} - \frac{1}{2 \beta w_{\text{Mn}}} K \left[ k - \sqrt{\beta^2 w_{\text{Mn}}^2 K^2 w_{\text{MnO}}^2 - 4 \beta w_{\text{Mn}}^2 K^2 k + K^2} \right] \right)
\]

This is the kinetic equation for the reaction of MnO in the slag reduced by C in carbon saturated copper liquid and or on the surface of the crucible.

5. Conclusions
(1) The reaction of SiO\textsubscript{2} reduced by C in molten copper with carbon-saturated is the 0.5th-order reaction, while the reaction of MnO reduced by C in molten copper with carbon-saturated is the -0.5th-order reaction.

(2) The reaction rate constant of the reduction of SiO\textsubscript{2} by C in molten copper with carbon-saturated is 7.50×10\textsuperscript{-6} mass\%\textsuperscript{0.5}·s\textsuperscript{-1}, while that of MnO by C in molten copper with carbon-saturated is 5.52×10\textsuperscript{-6} mass\%\textsuperscript{-1.5}·s\textsuperscript{-1}.

(3) The reactions of SiO\textsubscript{2} and MnO reduced by C in molten copper with carbon-saturated is a slow reaction and the time for the reaction equilibrium is more than 22 hours.

Acknowledgments
The authors express their gratitude to the funding support by National Natural Science Foundation of China (No. 51874198).

References
[1] Ohta H, Suito H. Activities of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} and activity coefficients of FeO and MnO in CaO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-MgO slags. Metallurgical and Materials Transactions B, 1998, 29(1): 119-129.
[2] Kang Y J, Du S C, Morita K. Activities of SiO\textsubscript{2} in some CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} (-10% MgO) melts with low SiO\textsubscript{2} contents at 1873 K. ISIJ International, 2007, 47(6): 805-810.
[3] Wang Z C, Su Y, Tong S H. Activity of SiO\textsubscript{2} in \{(1-x) B\textsubscript{2}O\textsubscript{3} + xSiO\textsubscript{2}\} determined by (slag + metal) equilibrium at the temperature 1723 K, using (0.25 Cu + 0.75 Sn) as metal solvent. The Journal of Chemical Thermodynamics, 1996, 28(10): 1109-1113.
[4] Cengizler H, Eric R H. Activity of MnO in MnO-CaO-MgO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} slags at 1500°C. Steel Research International, 2006, 77(11): 793-802.
[5] Yan B J, Chen X X, Jun T. Activity of MnO in MnO-CaO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-MgO molten slags. Metallurgical & Materials Transactions B, 2017, 48(2): 1100-1107.
[6] Choi J Y, Kim D J, Lee H G. Reaction kinetics of desulfurization of molten pig iron using CaO-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-Na\textsubscript{2}O slag systems. ISIJ International, 2001, 41(3): 216-224.
[7] Haruhiko F, Shigeaki M. Equilibrium between FeO-MnO-SiO\textsubscript{2} slags and molten iron. Tetsu to Hagane, 1970, 56(7): 830-851.
[8] Yasuji K, Katsumi M. Equilibrium and kinetics of slag-metal reactions. Transactions of the Iron and Steel Institute of Japan, 1973, 13(5): 303-317.
[9] El-Faramawy H, Fathy A, Elwais E, et al. Manganese distribution between FeO-MnO-SiO\textsubscript{2}-CaO-MgO-Al\textsubscript{2}O\textsubscript{3} Slags and Molten Iron. Steel Research International, 2003, 74(4): 195-200.
[10] Tsomondo M B C, Simbi D J. Kinetics of chromite ore reduction from MgO-CaO-SiO\textsubscript{2}-FeO-Cr\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} slag system by carbon dissolved in high carbon ferrochromium alloy bath. Ironmaking & steelmaking, 2002, 29(1): 22-28.
[11] Yagi T, Ono Y. On the rate of reduction of MnO from molten slag by carbon-saturated iron. ISIJ International, 1970, 10(1): 36-37.
[12] Xu K D, Jiang G C, Ding W Z, et al. The kinetics of the reduction of MnO in molten slag with carbon saturated liquid iron. ISIJ International, 1993, 33 (1): 104-108.
[13] Kawai Y, Mori K, Iguchi M, et al. Study on the Rate of Silica Reduction by Carbon from Slag to Metal. Tetsu To Hagane-journal of The Iron and Steel Institute of Japan, 1967, 53(7): 761-763.

[14] Weldon L D, Robert D P. Kinetics of manganese oxide reduction from basic slags by carbon dissolved in liquid iron. Metallurgical Transactions, 1971, 2(4): 1203-1211.

[15] Barati M, Chen E, Coley K. A comparison of the kinetics of the CO-CO₂ reaction with steelmaking and copper making slags. VII International Conference on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy, 2004, 393-398.

[16] Jamieson B J, Coley K S. Kinetics of silicothermic reduction of manganese oxide for advanced high-strength steel production. Metallurgical and Materials Transactions B, 2017, 48(3): 1613-1624.

[17] Vincent C, Merete T. Kinetics of slag reduction in silicomanganese production. Metallurgical and Materials Transactions, 2020, 51(3): 953-962.

[18] Kim P P, Tangstad M. Kinetic investigations of SiMn slags from different Mn sources. Metallurgical and Materials Transactions B-process Metallurgy and Materials Processing Science, 2018, 49(3): 1185-1196.