Kinetics of Silicon Transfer from Pulverized Coal Injected into Blast Furnace under Intensive Coal Injection

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With the progress of shifting to operation of intensive coal injection, Si in molten metal tends to increase, and this phenomenon cannot be explained by a conventional estimation model which does not distinguish between coke and pulverized coal on contribution to Si in molten metal. With respect to SiO gasification reactions from SiO₂ in pulverized coal, basic experiments were carried out on SiO(g) generation from pulverized coal char packed in a crucible under flow of reducing gas, and reaction rate was deduced with SiO₂ concentration in pulverized coal ash and slag composition taken into account. Furthermore, with respect to Si transfer in blast furnace, the SiO(g) generation rate derived from pulverized coal under intensive coal injection was evaluated and effects of pulverized coal on Si in molten metal were investigated. Consequently the molten metal Si variation associated with changes of pulverized coal brand in an actual furnace is become to be estimated.

KEY WORDS: blast furnace; molten metal composition; silicon; pulverized coal injection; pulverized coal char.

1. Introduction

With respect to reactions of Si transfer to molten metal which is one of the indices indicating phenomena at the lower part of blast furnace, multifaceted studies have been carried out including thermodynamic1) and kinetic studies2) as well as operation analysis3) based on these. It is an accepted theory that gas-metal reactions via SiO gas greatly contribute to Si transfer in blast furnace, and kinetic studies have advanced with the research made by Tsuchiya.2) And the rate equations of SiO(g) generation from SiO₂ in coke ash were reported by Yamagata,4) and based on these rate equations, Sugiyama5) clarified two-dimensional Si transfer phenomena in blast furnace by kinetic simulations.

However, as shifting to operation with intensive coal injection progresses, Si in molten metal tends to increase, and this phenomenon cannot be explained by a conventional estimation model which does not distinguish between coke and pulverized coal on contribution to Si in molten metal. With respect to SiO gasification reactions from SiO₂ in pulverized coal, basic experiments were carried out on SiO(g) generation from pulverized coal char packed in a crucible under flow of reducing gas, and reaction rate was deduced with SiO₂ concentration in pulverized coal ash and slag composition taken into account. Furthermore, with respect to Si transfer in blast furnace, the SiO(g) generation rate derived from pulverized coal under intensive coal injection was evaluated and effects of pulverized coal on Si in molten metal were investigated. Consequently the molten metal Si variation associated with changes of pulverized coal brand in an actual furnace is become to be estimated.

KEY WORDS: blast furnace; molten metal composition; silicon; pulverized coal injection; pulverized coal char.

2. Experimental Investigation of Si Transfer from Injected Pulverized Coal

Figure 1 shows a transfer route of Si into molten metal. And the input amount of Si for molten metal under the coal rate of 200 kg/thm are shown in the left figure. For the SiO generating reaction rate, cases when SiO₂ source is SiO₂ in coke and SiO₂ in slag are reported by Yamagata,4) and Ebizawa et al.9) respectively, suggesting that the SiO generation rate from SiO₂ in coke is about 10 times greater than that from SiO₂ in slag. The two-dimensional simulation results of Si transfer phenomena indicate that the SiO generation rate from SiO₂ in coke is about 40 times greater than that from SiO₂ in slag. The two-dimensional simulation results of Si transfer phenomena indicate that the SiO generation rate from SiO₂ in coke is about 40 times greater than that from SiO₂ in slag. Consequently the molten metal Si variation associated with changes of pulverized coal brand in an actual furnace is become to be estimated.

KEY WORDS: blast furnace; molten metal composition; silicon; pulverized coal injection; pulverized coal char.
2.1. Experimental Method

Figure 2 shows an experimental apparatus for generating SiO(g) from pulverized coal ash under gas flow using a vertical furnace-tube type electric furnace. To simulate generation of SiO(g) from SiO2 in pulverized coal ash in the vicinity of blast furnace raceway, pulverized coal char preliminarily combusted in advance was used for samples. Samples were packed (10 g) in an alumina crucible (inside diameter: 40 mm) and heated in CO gas stream (2 l/min). Heating conditions include 10°C/min for heating rate, 1500°C and 1600°C for holding temperature, and 1, 2, and 3 h for holding time. Furthermore, with traces of oxygen in CO gas taken into account, graphite (layer thickness: 80 mm) was filled below the crucible.

Table 1 shows the chemical composition of pulverized coal char used for samples. Raw char with the preliminary combustion ratio varied and carbon concentration adjusted was used for samples. Samples were packed (10 g) in an alumina crucible (inside diameter: 40 mm) and heated in CO gas stream (2 l/min). Heating conditions include 10°C/min for heating rate, 1500°C and 1600°C for holding temperature, and 1, 2, and 3 h for holding time. Furthermore, with traces of oxygen in CO gas taken into account, graphite (layer thickness: 80 mm) was filled below the crucible.

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After experiments, samples were chemically analyzed, the Al2O3 concentration was set as a reference, and the SiO2 gasification rate Δ(SiO2) (kg-SiO2/kg-char) per unit weight of char was found by Eq. (1). Furthermore, the SiO2 gasification rate Δ(SiO2) was converted into the Si concentration in molten metal during operation at 200 kg/thm PC rate with Eq. (2) used for convenience.

\[
\Delta(SiO_2) = \left[ \frac{[SiO_2]}{[Al_2O_3]} \right]_{in} - \left[ \frac{[SiO_2]}{[Al_2O_3]} \right]_{out} \cdot \frac{[ash]}{[Al_2O_3]} \cdot \frac{[PC]}{1000}\]  

where, subscript: in: before heating; out: after heating; char: before adding aqueous calcium solution.

\[
[Si]_{PC} = \Delta(SiO_2) \cdot \frac{M_{Si}}{M_{SiO_2}} \cdot \frac{100}{1000} \cdot \frac{[ash]}{[PC]_{char}} \cdot (PC) \]  

where, 
M_{Si}, M_{SiO_2}: molecular weight (–)

(PC): pulverized coal rate (kg/thm)

2.2. Experimental Results

The SiO2 reduction reaction of pulverized coal char is reduction of ash SiO2 by carbon in char and is assumed to be simultaneous reactions of reactions (3) and (4).

\[
SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \quad \text{(3)}
\]

\[
SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g) \quad \text{(4)}
\]

The experimental results are shown in Figs. 3 and 4, and calculated curves are derived in Sec. 4.1 by discussing on SiO(g) generating reaction rate from pulverized coal char.

Figure 3 shows effects of holding time and basicity on Δ[Si]_{PC} when pulverized coal char A is heated at 1600°C holding temperature. In the case of raw char A (C/S=0.12), as holding time is extended, Δ[Si]_{PC} tends to increase and become constant. This is assumed that the SiO(g)/SiO2 equilibrium or SiO(g)/SiC equilibrium is reached.
Figure 4 shows effects of ash basicity on $\Delta[Si]_{PC}$ at 1600°C holding temperature and for 3-h holding time. $\Delta[Si]_{PC}$ in raw char is susceptible to the SiO$_2$ concentration, and in particular, A with high SiO$_2$ concentration indicates a large reduction rate due to basicity.

Figure 5 shows effects of holding temperature on $\Delta[Si]_{PC}$ for 3-h holding time. As the holding temperature rises, $\Delta[Si]_{PC}$ rises, and the higher the holding temperature, the greater is an increase range.

3. SiO(g)-generating Reaction Rate from Pulverized Coal Char

Yamagata et al.\textsuperscript{4) consider three elementary steps of reduction reaction of SiO$_2$ in coke ash, namely, gas diffusion in gas film, transgranular reactions, and gas diffusion in pores in coke grain, and find distribution of ash gasification reaction ratio in the radius in coke grain. In the result of Yamagata,\textsuperscript{4) at 1350–1650°C temperature range, good correlation is obtained but the rate constant obtained at 1750°C is large, and it is assumed that this would be attributed to an increase of contact area between ash and fixed carbon, because ash penetrates in pores as ash melting advances.

Since in the present experiment, for samples, pulverized coal char preliminarily combusted in advance are used to simulate generation of SiO(g) from SiO$_2$ in pulverized coal ash in the vicinity of blast furnace raceway, the interfacial area between ash and fixed carbon increases, and consequently, it is assumed that the ash composition may have affected the SiO$_2$ gasification rate of pulverized coal char. Ebizawa et al.\textsuperscript{5) presents a reaction rate equation, Eq. (5), based on slag composition.

$$J=k \cdot A \cdot a_{SiO_2} \quad \text{(5)}$$

On the other hand, because it is observed that the SiO$_2$ gase...
fication rate of pulverized coal char tends to successively approximate to a specified value as the holding time passes, the pulverized coal char which is an aggregate of ash and fixed carbon is able to have a reaction rate defined with an equilibrium concentration difference used as a driving force, and the reaction rate of Eq. (3) is defined in a linear reaction formula (6).

\[-\frac{dn}{dt} = J \cdot (n - n_{eq}) \]  \hspace{1cm} \text{(6)}

where,
\[ k : \text{reaction rate constant (mol/cm}^{2}\cdot\text{s}) \]
\[ A : \text{interfacial area between SiO}_2 \text{ and C (cm}^{2}/\text{mol}) \]
\[ a_{SiO_2} : \text{SiO}_2 \text{ activity in ash (}) \]
\[ n : \text{SiO}_2 \text{ concentration in pulverized coal char (mol/cm}^{3}) \]

In this event, the reduction reaction of SiO$_2$ in pulverized coal char is reduction of ash SiO$_2$ by carbon in char, and reactions (3) and (4) simultaneously take place. Let $\gamma$ denote a distribution factor which is the ratio of SiO$_2$ amount distributed in reaction (3) to total reaction SiO$_2$ amount; then, the mass balance Eq. (7) of SiO$_2$ is defined. where 0.2 reported by Sugiyama et al. was adopted for $\gamma$.

\[ n = n_0 - (n_{SiO_2/SiO} + n_{SiO_2/C}) \]
\[ = n_0 - \frac{1}{\gamma} n_{SiO_2/SiO} \]  \hspace{1cm} \text{(7)}

where,
\[ n_0 : \text{SiO}_2 \text{ concentration in initial concentration (mol/cm}^{3}) \]
\[ n_{SiO_2/SiO} : \text{SiO}_2 \text{ gasification concentration (mol/cm}^{3}) \]
\[ n_{SiO_2/C} : \text{SiC conversion concentration (mol/cm}^{3}) \]

The Eq. (8), SiO$_2$ gasification rate equation, is derived by Eqs. (6) and (7). Converting the SiO$_2$ (g) generation rate of Eq. (8) into [Si] in molten metal gives the following Eq. (9).

\[ n_{SiO_2/SiO} = \gamma (n_0 - n_{eq}) \cdot [1 - \exp(-k \cdot A \cdot a_{SiO_2} \cdot t)] \]  \hspace{1cm} \text{(8)}

\[ \Delta[Si]_{PC} = \gamma \cdot \frac{M_{Si}}{M_{SiO_2}} \cdot \frac{W_0 - W_{eq}}{W_0} \cdot [1 - \exp(-k \cdot A \cdot a_{SiO_2} \cdot t)] \]
\[ = 9.34 \cdot 10^{-3} \cdot \frac{W_0 - W_{eq}}{W_0} \cdot [1 - \exp(-k \cdot A \cdot a_{SiO_2} \cdot t)] \]  \hspace{1cm} \text{(9)}

where, $W$, $W_{eq}$, $W_0$: SiO$_2$ weight ratio (kg/thm).

Figure 6 shows experimental values of Taylor using CaO–SiO$_2$–Al$_2$O$_3$–MgO-based slag concerning $a_{SiO_2}$, SiO$_2$ activity. Conventionally, in the case of blast-furnace slag system which is comparatively on the higher C/S side, the way of Tamura’s was adopted for the estimation equation of $a_{SiO_2}$ for coal ash. On the other hand, as the ash composition of pulverized coal char is on the lower C/S side, using experimental values on the lower C/S side, $a_{SiO_2}$ was newly approximated by Eq. (10). And for the SiO$_2$ mole fraction of $N_{SiO_2}$, the way of Tamura’s was used.

\[ a_{SiO_2} = 1.235 \cdot N_{SiO_2} - 0.071 \]  \hspace{1cm} \text{(10)}

In addition, with respect to the equilibrium SiO$_2$, Gibbs free energy change $\Delta G^0$ (J/mol)$^{11}$ and equilibrium constant in reactions of Eq. (3) can be deduced from

\[ \Delta G^0 = 667 \cdot 800 - 326.2 \cdot T \]  \hspace{1cm} \text{(11)}

\[ K = \exp(-\Delta G^0 / RT) = \frac{P_{SiO_2} \cdot P_{CO}}{a_{SiO_2}} \]  \hspace{1cm} \text{(12)}

4. Discussion

4.1. SiO(g) Generating Reaction Rate from Pulverized Coal Char

With respect to generation of SiO(g) from SiO$_2$ in pulverized coal ash in the vicinity of blast furnace raceway, the interfacial area between ash and fixed carbon increases because of preliminary combustion in the raceway flight process, and consequently, the ash composition exerts influence on the SiO$_2$ gasification rate of pulverized coal char. However, since it is difficult to separate the reaction rate constant $k$ and contact interfacial area $A$, $kA$ is integrated as a reaction rate constant and the gasification characteristics of pulverized coal char is evaluated. In Eq. (9), $kA$ is found from experimental values by parameter fitting and is shown as follows by Eq. (13).

\[ kA = 6.0 \cdot 10^4 \exp(-69000/RT) \]  \hspace{1cm} \text{(13)}

Figures 3, 4, and 5 show calculation results under each experimental condition. The measured values and calculated values indicate good coincidence, and it has been confirmed that the chemical rate equation using rate constant $kA$ of Eq. (9) is appropriate. Figure 7 compares the reaction rate constant $kA$ of pulverized coal char with the reaction rate constant of coke by Yamagata.\textsuperscript{41}

The reaction rate constant of pulverized coal char is three times as much as that of coke by Yamagata,\textsuperscript{41} indicating that pulverized coal char is likely to generate SiO(g) because the contact area with carbon is large as compared to coke. This results support the assumption of Yamagata\textsuperscript{3} in that the rate constant of SiO$_2$ in coke ash obtained at 1750°C is large, and this would be attributed to an increased interfa-
4.2. Evaluation of Si Transfer Rate from Pulverized Coal

As a result of shifting to operation under intensive coal injection, Si in molten metal tends to increase, and it is also assumed that Si is varied in accord with the pulverized coal brand under an operation at high pulverized coal rate. Therefore, investigation was made on the application of Eq. (9), SiO(g) generating reaction rate equation, to blast furnace operating condition.

The investigation by Sugiyama5) has clarified that generation of SiO(g) can be kinetically defined in an area within 3 m around the raceway, that is, a temperature field of 1700°C or higher. Therefore, as a prerequisite for the calculation, pulverized coal rate was designated to 200 kg/thm, average temperature of SiO(g) generating place to 1800°C, and SiO(g) generating time to 1000 s,12) and the Si transfer rate from pulverized coal char was expressed by Eq. (14) from Eqs. (9), (11) and (12).

$$\text{D}[\text{Si}]_{\text{PC}}/\text{H}11005 \times 3\cdot \text{W}_0 \cdot [1 - \exp(-3.18 \cdot a_{\text{SiO}_2})] \quad \cdots \cdots (14)$$

Figure 8 shows changes of hot metal [Si] and calculated [Si] when the pulverized coal brand is changed. The calculated [Si] is expressed by a total sum of $\text{D}[\text{Si}]_{\text{PC}}$ derived from pulverized coal and $\text{D}[\text{Si}]_{\text{coke}}$ derived from coke. $\text{D}[\text{Si}]_{\text{PC}}$ derived from pulverized coal was calculated from Eqs. (14) and (10) for pulverized coal ash. In addition, $\text{D}[\text{Si}]_{\text{coke}}$ derived from coke was calculated by the method of Tamura3) using the estimation equation of $a_{\text{SiO}_2}$ on the higher C/S side based on the tuyere slag composition with pulverized coal ash excluded bosh slag composition.

Because calculated [Si] nearly coincides with the measured value and hot metal [Si] decreases as $\text{D}[\text{Si}]_{\text{PC}}$ derived from pulverized coal decreases, and the decrease ranges coincide, the adequacy of rate equation was confirmed. With respect to generation of SiO(g) from SiO$_2$ in pulverized coal ash in the vicinity of blast furnace raceway, as the interfacial area between ash and fixed carbon increases because of preliminary combustion in the raceway flight process, so the change of ash composition by coal brand exerts influence on the SiO$_2$ gasification rate of pulverized coal char by newly approximated Eq. (11). Also it is confirmed that the estimation equation of $a_{\text{SiO}_2}$ with pulverized coal ash excluded as bosh slag composition is applicable to SiO(g) generation rate from coke under intensive coal injection.

Consequently, it is assumed that the effect of pulverized coal brand on [Si] in molten metal can be explained by the SiO(g) generation rate quantitatively and the Si absorption process to molten metal is not rate-controlling in the Si transfer process from SiO derived from pulverized coal to molten metal.

5. Conclusion

As shifting to operation with intensive pulverized coal injection progresses, Si in molten metal tends to increase, and basic experiments on SiO(g) generation from pulverized coal char packed in a crucible were carried out under flow of reducing gas for a purpose of formulating the gasification reaction rate of SiO from SiO$_2$ in pulverized coal. The results of the work carried out allow us to draw the following conclusions.

(1) With respect to generation of SiO(g) from SiO$_2$ in pulverized coal ash, the contact area between ash and fixed carbon increases because of preliminary combustion at the raceway flight step, and consequently, the SiO$_2$ gasification rate of pulverized coal char is influenced by the ash composition.

(2) Based on the present experimental results, the SiO(g) generating reaction rate from pulverized coal char was formulated. The measured values and calculated values indicate good coincidence, and it has been confirmed that the chemical rate equation using rate constant is appropriate.

(3) It was determined that the reaction rate constant of pulverized coal char is 3 times as much as that of coke. This would be attributed to an increased interfacial area between ash and fixed carbon because ash permeates in pores as ash melting progresses.

(4) The molten metal [Si] variation associated with changes of pulverized coal brand in an actual furnace was estimated from the reaction rate equation, and because the
estimation result coincided with the actual molten metal [Si] variation, the adequacy of the reaction rate equation was confirmed.

(5) It is assumed that the effect of pulverized coal brand on [Si] in molten metal can be explained by the SiO(g) generation rate and the Si absorption process to molten metal is not rate-controlling in the Si transfer process from SiO derived from pulverized coal to molten metal.

In the future, in order to pursue the control of molten metal quality while efforts are made to cut molten metal cost, it is essential to improve the operational flexibility that can accommodate changes of material and fuel conditions as well as production rate, and still more sophisticated control of in-furnace reactions are required.

REFERENCES