Oxidation Rate of Solid Iron Using an Ar–H2O Mixture through CaO–SiO2–Al2O3–FeO Slag

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1. Introduction

Various measures have been developed to control slag foaming, which often causes operational problems during the BOF process. Although anti-foaming agents, which contain carbonaceous materials such as pulverized coke, are usually added to the foamed slag, the additional carbon input during the steelmaking process causes an increase in CO2 emissions. Therefore, the development of a new anti-foaming technology that does not use general carbon-containing materials is a favorable alternative. Steam jet injection into foamed slag may control the foaming, not only mechanically but also chemically. The injected steam reacts with iron droplets in the slag according to reaction (1), producing hydrogen and FeO.

\[ \text{Fe} + \text{H}_2\text{O} = \text{FeO} + \frac{1}{2}\text{H}_2 \] ................................. (1)

Since an increased FeO concentration changes the physical properties of slag, the foaming index \( \Sigma \) (s), which gives the average foam life, as proposed by Ito and Fruehan, should be affected by reaction (1). The variation of \( \Sigma \) can be easily estimated in terms of Eq. (2), where \( m \) is the viscosity, \( \rho \) is the density, and \( \gamma \) is the surface tension of the slag.

\[ \Sigma \propto \frac{\mu}{\sqrt{\rho \gamma}} \] ................................. (2)

Although Eq. (2) was derived for foams with almost constant bubble diameters, it was confirmed experimentally that Eq. (2) is valid for various bubble sizes as long as the foam is made from uniform bubbles. Substituting the physical properties of slag into Eq. (2), the foam life of CaO–SiO2–FeO slag with CaO/SiO2=1.5 will be decreased by an order of magnitude by increasing FeO from 20 mass% to 40 mass%.

The key aspect of the technology proposed above is the oxidation rate of iron droplets in a foamed slag using a steam jet. Therefore, the oxidation rate of iron using an Ar–H2O mixture through molten CaO–SiO2–FeO–Al2O3 slag was measured at 1 673 K as a function of the slag composition.

2. Experimental

2.1. Hydrogen Analysis System

A convenient and economical hydrogen analysis system was developed in this study. A hydrogen detection semiconductor sensor (FIS Inc., SB-19) was used. The principle of this sensor is that the reduction of absorbed oxygen on the sensing element (SnO2 thin film) by hydrogen gas decreases the electrical resistance of the element. Since the existence of oxygen is required for the sensor to work properly, the sample gas was mixed with oxygen to maintain a constant partial pressure of 0.21 atm before being introduced into the detection cell. The resistance of the sensor was continuously measured and converted to the hydrogen concentration. The calibration curve shows good reproducibility within the range of 300–3 000 ppm H2 and the relative error was estimated to be 5%.

2.2. Oxidation Experiment

The slag samples were prepared by melting a mixture of CaO, FeO, and SiO2 in an alumina crucible at 1 673 K under an Ar atmosphere for 1 h. A solid iron preform, machined on a lathe for a proper fit, was placed at the bottom of the alumina crucible (I.D. 24 mm), and 20 g of slag was kept in an electric furnace for 30–40 min to attain slag-metal equilibrium under the 1 673 K Ar atmosphere. The Ar–H2O mixture was then blown onto the slag surface. The gas mixture was made by passing Ar gas through a couple of conical flasks filled with distilled water, which was kept in a thermostat bath at 343 K. The partial pressure of water was measured for each Ar flow rate using a gravimetric analysis. The reacted gas mixture was dehydrated through a cold trap and, mixed with oxygen gas, was introduced into the hydrogen analyzing system. The evolution rate of hydrogen was continuously measured during each experiment stage. The crucible was carefully removed from the furnace and quickly quenched after the experiment. It was then divided lengthwise, and the shape of the slag layer was measured. The slag sample was crushed for an X-ray fluorescence analysis to determine its chemical composition.

3. Results and Discussion

The slag compositions after the experiment are listed in Table 1, where all the iron oxide is considered as FeO. The hydrogen evolution rate, \( R_{\text{H2}} \) (mol-H2 s\(^{-1}\)), is plotted against the Ar flow rate (cm\(^3\) s\(^{-1}\)) in Fig. 2. The evolution rate increased with an increase in the flow rate and became constant at above 46 cm\(^3\) s\(^{-1}\), where the effect of the gas phase mass transfer was eliminated. Therefore, this constant value is expressed as \( R_{\text{H2}}^* \) to demonstrate its independence from the gas flow rate. Since the chemical reaction rates are considered to be faster than the mass transfer rate because of a high temperature, the value of \( R_{\text{H2}}^* \) should correlate with the mass transfer rate of oxygen through the slag layer.

Figure 3 shows an illustration of the oxidation experiment. Injected H2O reacts with Fe\(^2+\) in slag, and oxide ions and positive holes move toward the slag-iron interface.
Instead of analyzing this complex mass transfer mechanism, the concept of “oxygen permeability” proposed by Sasabe et al.\textsuperscript{8)} was introduced to analyze the experimental results. When the partial pressure of oxygen on one side of a slag film with thickness $L$ (cm) is assumed to be negligibly small compared to that on the other side, $P_o$, the permeability of oxygen, $\Pi_o$ (mol cm$^{-1}$ s$^{-1}$), is defined using Eq. (3) in terms of oxygen mass flux, $J_{o2}$ (mol cm$^{-2}$ s$^{-1}$).

$$\Pi_o = \frac{1}{a} \left( \frac{b R_{H_2}}{R T^2} \right)^n$$

Eq. (4) then gives the dependency of $\Pi_o$ on the partial pressure of oxygen $P_o$, where $\Pi_o^0$ is the permeability of oxygen measured at $P_o=1$ atm.\textsuperscript{9)}

$$\Pi_o = \Pi_o^0 P_o^n$$

Eq. (5) was derived by assuming that the slag surface was a paraboloid.

$$\Pi_o^0 = \frac{(1 + \frac{b}{a})^n}{2 R T^2 \ln \left( \frac{1 + \frac{b}{a}}{1 + \frac{b}{a}} \right)}$$

The value of $\Pi_o^0$ was calculated using Eq. (5), where the partial pressure of oxygen at the slag-gas interface, $P_o^g$, was estimated from the concentration of $H_2O$ and $H_2$ in the reacted gas by assuming that reaction (6) was in equilibrium. According to Wagner’s theory, power $n$ is equal to 0.25 if the ionic charge transport is predominant in a slag.\textsuperscript{7)} Sasabe et al.\textsuperscript{3)} reported that $n=0.25$ was experimentally obtained for CaO–SiO$_2$–FeO$_x$ slag containing 16 mass% T.Fe at 1 673 K; however, they also reported that the value of $n$ changed to 0.385 for the slag containing 38 mass% T.Fe.\textsuperscript{9)} The increase in iron oxide causes the increase in positive holes especially under a very high oxygen partial pressure of 0.21–1.0 atm, therefore, it is expected that the ionic charge transport became less predominant with the addition of iron oxide. Since the oxygen partial pressure used in this experiment was lower by several orders of magnitude, the concentration of positive holes in the slag was much lower than that in their experiment. Thus the ionic charge transport should be predominant and $n=0.25$ can be used for the calculation.

$$H_2 + \frac{1}{2} O_2 = H_2O$$

$$\Delta G^0 = -247.420 + 55.847 T \text{ (J mol}^{-1})$$

Table 1. Chemical composition of slag and the obtained oxygen permeability.

| slag | chemical composition (mass%) | B (basicity) | log $P_o^g$ | permeability (mol-O$_2$ cm$^{-1}$ s$^{-1}$) | log $\Pi_o$ | log $\Pi_o^0$ (n=0.25) |
|------|----------------------------|-------------|------------|-----------------------------|-----------|---------------------|
| A    | 25.2 20.3 4.0 50.5          | 1.24        | -5.886     | -6.731                      | -5.260     |
| B    | 24.1 21.6 4.2 55.1          | 3.20        | -6.031     | -6.552                      | -5.045     |
| C    | 28.8 17.0 3.1 51.1          | 1.69        | -6.031     | -6.539                      | -5.032     |
| D    | 30.3 23.0 4.7 42.0          | 1.32        | -5.481     | -6.700                      | -5.491     |

Fig. 1. Schematic drawing of experimental apparatus.

Fig. 2. Relation between the hydrogen evolution rates with Ar flow rate.

Fig. 3. Illustration of the oxidation of solid iron by Ar–H$_2$O mixture through a slag layer.
The calculated results for \( n = 0.25 \) are shown in Table 1. The relationship between the calculated value of \( \Pi_{o2}^0 \) and the slag composition is shown in Fig. 4. The value of \( \Pi_{o2}^0 \) increased with an increase in slag basicity and the concentration of FeO, which agrees with that reported by Sasabe et al.\(^9\). The dotted lines show \( \Pi_{o2}^0 \) at 1 673 K and 1 773 K for CaO–SiO\(_2\)–FeO slag with T.Fe=30 mass\%, which corresponds to the approximately 40 mass\%FeO, calculated from the same literature.\(^9\) The values of \( \Pi_{o2}^0 \) calculated from the oxidation experiment in this study were 1.4- to 3.4-times larger than those estimated from the literature, which seems to be in good agreement with the results from completely different experimental procedures.

The oxidation rate of iron \( R_{Fe} \) (mol-Fe cm\(^{-2}\) s\(^{-1}\)), which is equal to \( \Pi_{o2}^0 \), was calculated as a function of hydrogen concentration when a steam jet is injected under 1 atm. The assumptions \( \log \Pi_{o2} = -5.0 \) and \( n = 0.25 \) were made for the calculations in this study. The oxidation rate without a slag layer was estimated in terms of the rate constant of iron oxidation in a H\(_2\)O atmosphere, which was reported as Eq. (8) by Abuluwefa et al.\(^{11}\):

\[
R_{Fe} = 2.828 \times 10^4 \exp \left( \frac{-263555}{RT} \right) P_{H_2O} \text{ (mol cm}^{-2}\text{s}^{-1} \right) \text{ Eq. (8)}
\]

The calculated results are shown in Fig. 5. The value of \( R_{Fe} \) decreases with an increase in hydrogen concentration and increases with a decrease in slag layer thickness. When the hydrogen concentration is 0.1\%, the oxidation rate of iron, i.e., the evolution rate of hydrogen, was lowered by 0.01 to 0.1 times with the existence of the slag layer; however, the factor decreases with an increase in hydrogen concentration. Therefore, a high velocity jet is favorable for the acceleration of oxidation and the evolution of hydrogen since it can remove the slag from the iron droplets or at least reduce its thickness.

4. Conclusion

The oxidation of solid iron by an Ar–H\(_2\)O mixture through a slag layer was measured as a function of slag composition at 1 673 K. The reaction was expected to be controlled through a mass transfer in a CaO–SiO\(_2\)–FeO–Al\(_2\)O\(_3\) phase for a high gas flow rate region. The mass transfer of oxygen through a slag layer was analyzed in terms of \"oxygen permeability,\" avoiding a consideration of complex mass transfer mechanisms. The value of \( \Pi_{o2}^0 \) increased with the slag basicity and FeO concentration. The oxidation rate of iron at 1 773 K was estimated, which decreases with the concentration of H\(_2\), and is lower than that without a slag by a few orders of magnitude.

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