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KINETIC MODEL FOR THE REACTION BETWEEN IRON OXIDE IN MOLTEN SLAG AND CARBON IN MOLTEN IRON VIA CO-CO_2 BUBBLE

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Synopsis: The kinetic model for the reaction between iron oxide in molten slag and carbon in molten iron was developed, assuming CO and CO_2 in the bubble on slag-metal interface was a ferrying medium for oxygen and carbon. The overall reaction was assumed to be combination of reduction of FeO by CO and oxidation of C by CO_2. The slag-gas and gas-metal interfacial area were evaluated by calculating the shape of the bubble and their occupying area on the apparent slag-metal interface. The overall reaction rate was calculated, assuming the rate controlling step is either of the interfacial reactions. Various factors affecting the kinetics were discussed based on the model.

Key words: smelting reduction, steelmaking, hot metal treatment, slag, iron oxide, kinetics, simulation, bubble, interface

1. Introduction

One of the major reactions in ironmaking and steelmaking process is that between FeO in slag and C in metal: reaction (1).

$$FeO + C = Fe + CO \qquad (1)$$

There is no agreement in the literature about the theories presented to describe the kinetics of the reaction (1). One of them is based on the ferrying mechanism of C and O across the CO-CO_2 bubble existing on the slag-metal interface.[1] The overall reaction (1) is considered to be the combination of reactions (2) and (3).

$$FeO(\text{in slag})+CO=Fe+CO_2 \qquad (2)$$
$$CO_2+C(\text{in metal})=2CO \qquad (3)$$

In this work a mathematical model was developed to study the validity of the ferrying mechanism, evaluating the slag-gas and the gas-metal interfacial area.

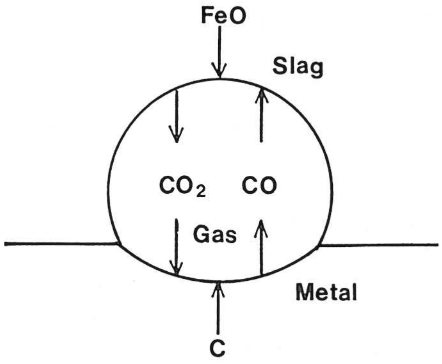

Figure 1. Schematic illustration of the reaction between FeO in slag and C in metal via CO-CO_2 bubble

2. Model

Figure 1 shows basic material flow of this model. The presence of gas halo[2] or bubble[3] around or on the metal was observed by X-ray fluoroscopy. FeO in the slag diffuses to the slag-gas interface of the bubble sitting on the slag- metal interface and react with the CO in the bubble to form CO_2. The CO_2 diffuses to the gas-metal interface of the bubble and react with carbon in the metal to generate CO. The CO diffuses back to the slag-gas interface. These sequential reactions continue until the bubble leaves the slag-metal interface.

In this work it was assumed that either of the interfacial chemical reactions was the rate controlling step. If any diffusion step is controlling the rate, the rate will be slower than that based on chemical reaction control.

2.1 Interfacial area

The slag-gas and gas-metal interfacial areas of the bubble should be estimated to calculate the overall reaction rate.

The shape of bubble and ratio of slag-gas and gas-metal interfacial area were calculated based on the static balance of forces acting upon the bubble. The ratio of the slag-gas and gas-metal interfacial area is estimated by simulating the growth and detachment of the bubbles on slag/metal interface.

2.1.1 Shape of bubble

It was assumed that the shape of the bubble nucleated on the slag- metal interface was determined by the static balance of its buoyancy force and its surface and interfacial tensions, as shown in Figure 2. Though, there have been several works in which the maximum size of the bubble on the interface were calculated, most of them, except Terashima et al.[4], assumed a half spherical bubble.

When the bubble is small, the each radius of curvature is constant in a bubble for slag-gas and gas-metal interface. The balancing equation of vertical and horizontal forces are,

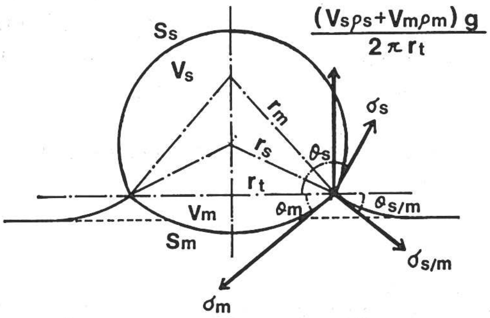

Figure 2. Static balance of the bubble on the slag-metal interface

$$2\pi r_t\ \sigma_{s/m}\sin\theta_{s/m} = (\rho_s V_s + \rho_m V_m)g \tag{4}$$

$$\sigma_s\cos\theta_s + \sigma_m\cos\theta_m = \sigma_{s/m}\cos\theta_{s/m} \tag{5}$$

$$r_t = r_m\sin\theta_m = r_s\sin\theta_s \tag{6}$$

It is assumed that the pressure inside the bubble is uniform.

$$2(\sigma_s/r_s - \sigma_m/r_m) = \{\rho_s r_s(1-\cos\theta_s) + \rho_m r_m(1-\cos\theta_m)\}g \tag{7}$$

The volume and surface areas of each part of the bubble are,

$$V_s = \pi r_s^3(2/3 - \cos\theta_s(1-\cos^2\theta_s/3)) \tag{8}$$

$$V_m = \pi r_m^3(2/3 - \cos\theta_m(1-\cos^2\theta_m/3)) \tag{9}$$

$$S_s = 2\pi r_s^2(1-\cos\theta_s) \tag{10}$$

$$S_m = 2\pi r_m^2(1-\cos\theta_m) \tag{11}$$

$$V_t = V_s + V_m = 4/3\,\pi r_e^3 \tag{12}$$

The contact angles and surface areas are calculated to solve these equations simultaneously for a give volume of bubble.

2.1.2 Gas-metal interfacial area

The bubbles on the apparent slag-metal interface nucleate and grow to a certain size to be released from the interface. In this work, this process was simulated and the ratio of the gas-metal interfacial area to the apparent slag-metal interfacial area: $\Sigma Sm/Sa$, was calculated. The simulation of bubble growth was carried out as follows.

(i) The bubbles nucleated at randomly distributed positions with constant rate.

(ii) The volumetric growth rate of the bubble was proportional to its gas-metal interfacial area.

(iii) When two bubbles were contact each other, they coalesced to be one bubble immediately.

(iv) When the bubble size reached a critical size, it was released from the slag-metal interface.

$\Sigma Sm/Sa$ calculation was repeated by short time steps until the $\Sigma Sm/Sa$ value reached a steady state.

2.2 Overall rate equation

Since CO and CO_2 are the only two existing species in the bubble, total pressure of the bubble is the sum of those two partial pressures.

$$P_t = P_{CO} + P_{CO2} \tag{13}$$

The pseudo-steady state of P_{CO}/P_{CO2} ratio in the bubble was assumed.

$$N_{FeO}/N_C = (Sm/Ss)\ ((2+P_{CO}/P_{CO2})/(1+P_{CO}/P_{CO2})) \tag{14}$$

When the carbon content of the melt is high, P_{CO}/P_{CO2} is much greater than unity and equation (14) can be simplified as equation (15).

$$N_{FeO} / N_C = Sm/Ss \tag{15}$$

2.2.1 Interfacial chemical reaction rates

There are several rate equations for reactions (2) and (3). In this work, equation (16) by Kim et al[5] for reaction (2) and equation (17) by Sain and Belton[6] for reaction (3) were employed.

$$N_{FeO} = \exp(-32300/RT - 1.37)(1.0 - 0.7a_{SiO2}{}^{1/3})\ (a_{FeO}P_{CO} - a_{Fe}P_{CO2}/K_{s/g})10^4 \tag{16}$$

$$N_C = \exp(-11700/T - .48)10^4 P_{CO2} \tag{17}$$

The overall rate was obtained, solving equations (13), (14), (16) and (17), simultaneously. The activities of FeO and SiO_2 were calculated by Ban-ya and Hino's[7] regular solution model.

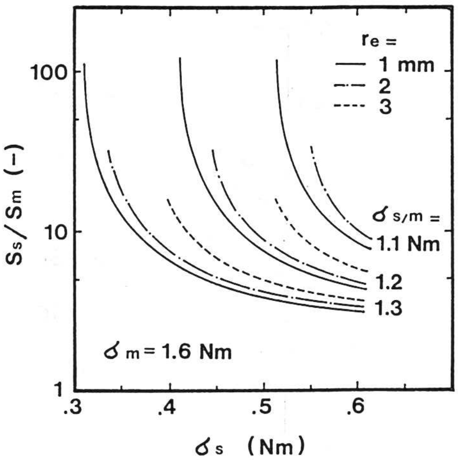

Figure 3. Relationship between Ss/Sm and surface and interfacial tensions, by the static balance calculation

3. Model calculation and discussion

3.1 Interfacial area

The ratio of slag-gas and gas-metal interfacial area of the bubble: Ss/Sm, was calculated by solving equations (4) to (12), simultaneously. Figure 3 shows calculated Ss/Sm for several values of the interfacial tension and size of the bubble. The value of Ss/Sm is over 4 for ordinary properties of metal and slag. It means the bubble is swelling deeply into the slag phase. When the volume of the bubble is too large, there is no solution in equations (4) through (12). That means there is no balancing condition for such a bubble.

The calculated bubble shape indicates that the bubble volume is existing mostly in the slag phase and that the slag-gas interfacial area is larger than the gas-metal. The shape that was observed by X-ray fluoroscopy[3] during the reaction is similar to the calculated result and supports the model in this work.

Figure 4 shows a schematic view of the simulated bubble distribution in a steady state for the half sphere bubbles. The ratio of gas-metal to the apparent slag-metal interfacial area:$\Sigma Sm/Sa$ was calculated for several shapes of bubble and the relative nucleation rate, as shown in Figure 5. The ratio is saturating for high relative nucleation rate, and reaches as much as 0.35 when the shape of bubble a half sphere. When the bubble has a large Ss/Sm value, the ratio is small.

Ano et al[8] evaluated the interfacial areas of the similar reaction system, using a slit like crucible. The ratio of $\Sigma Sm/Sa$ was about 0.20 and 0.40, and Ss/Sm was about 1.5 and 3.5, for FeO content of 10.2 and 2.6%, respectively.[9] When the bubble growth

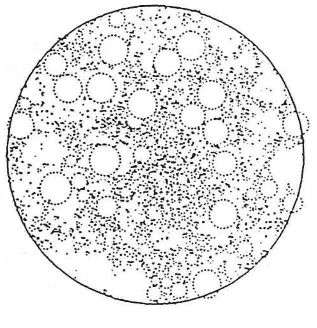

Figure 4. Schematic view of the bubble distribution on the slag-metal interface

simulation in this work was conducted in two dimensions, the ratio of gas-metal to apparent slag-metal interfacial area was saturating about 0.35 for Ss/Sm=2. Though the discussions above are not direct evidence in support of the simulation in this work, it seems to be appropriate to evaluate the interfacial areas by the model.

3.2 Overall reaction rate

Figure 6 shows the calculated N_C, the decarbarization rate per unit gas-metal interfacial area, for an imaginary CaO-SiO_2-Al_2O_3-FeO melt at 1673K and 0.1MPa. Multiplying N_C by $\Sigma Sm/Sa$, which was calculated in the previous section, gives overall reaction rate of equation (1).

There is limited experimental data to make comparisons directly with the model calculation. The available data[10,11,12,13,14] are shown in Figure 7. There are difference in slag composition and temperature among the data in Figure 7.

Qualitative discussions were made before quantitative comparison with the data.

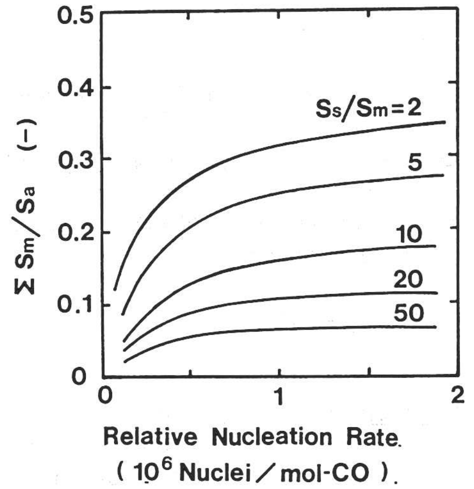

Figure 5. Ratio of the gas-metal interfacial area to the apparent slag- metal interfacial area, calculated by the bubble growth and rise simulation

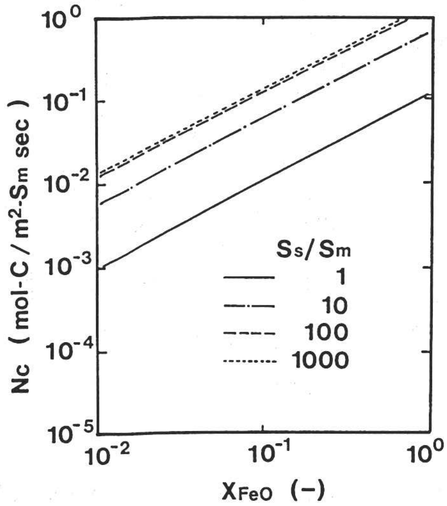

Figure 6. Calculated results of the overall reaction rate for CaO-SiO_2-Al_2O_3-FeO system at 1673K and 0.101MPa (CaO:SiO_2:Al_2O_3 = 4:4:1 in mol)

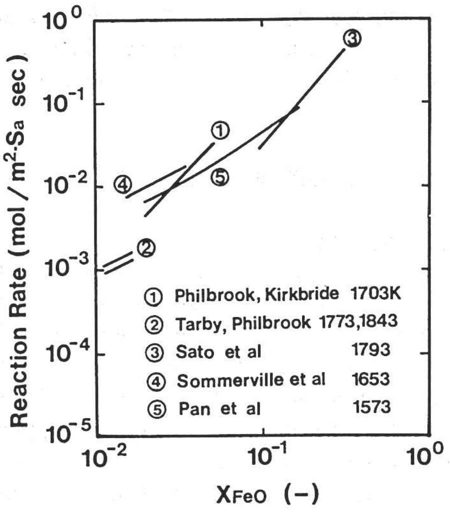

Figure 7. Experimental data of the rate of the reaction between FeO containing slag and high carbon content metal

3.2.1 Order of reaction with respect to FeO concentration

The calculated rate is almost proportional to mole fraction of FeO in Figure 6, but the reaction order is changed by the dependency of activity of FeO on slag composition, as far as the rate equations and regular solution model are applicable. The rate is also changed with Ss/Sm in one order of magnitude. When Ss/Sm is great, N_C does not depend on Ss/Sm and controlled by the gas-metal reaction. As contrary N_C is controlled by the slag-gas reaction, when Ss/Sm is less than 10.

Sommerville et al's data[13] was the first order reaction. Philbrook and Kirkbride[10] and Sato et al[12] reported their experimental rate data was proportional to the second power of FeO concentration, and pointed out that the oxygen diffusion in the slag is controlling the rate and is affected by the bubble generation rate and its stirring.

The dependency on FeO concentration in this model is the result of the rate equation (17) and the regular solution model. Since FeO is a surface active component in an oxide slag, it has influences on the shape of bubble and the interfacial area. Figure 3 indicates that the addition of a surface active agent, that decreases the slag-metal interfacial tension and the slag surface tension, leads greater value of Ss/Sm. On the other hand, the smaller surface and interfacial tensions may lead the larger gas-metal reaction area; ΣSm/Sa. Based on the homogeneous nucleation theory, the supersaturating pressure necessary to nucleate a bubble is lowered when the surface tension are reduced. If it leads to a faster nucleation rate, ΣSm/Sa will be larger , as shown in Figure 5. The order of the reaction with respect to FeO concentration may also be affected by FeO concentration itself through the interfacial properties.

3.2.2 Effects of total pressure

The effect of ambient pressure on the overall reaction rate can be also predicted by this model. Figure 8 shows the calculated result for 40mol% CaO- 40mol% SiO_2- 10mol% Al_2O_3-10mol% FeO slag at 1673K. As the rate equations (16) and (17) have linear dependency to the pressure, the overall rate is proportional to the total pressure.

The effect of the pressure was experimentally investigated.[15, 16, 17] Upadhya[17] reported the reaction rate was proportional to the pressure. MacRae[15] ,whose data at 1513 and 1608K was omitted in this work because they are below the melting point of FeO, and Lloyd et al[16] observed the increase of the rate with pressure, but the rates were not proportional to the pressure.

The interfacial area dose not change with the ambient pressure. The density of gas is so small, comparing to that of slag and metal, that the buoyancy force is not influenced much by the pressure. Therefore static forces acting on the bubble are almost the same, and the shape of bubble is not affected by the pressure.

If the mass transfer in gas phase is controlling the overall rate, the kinetic equation is expressed as,

$$N = kP \propto p^n \tag{18}$$

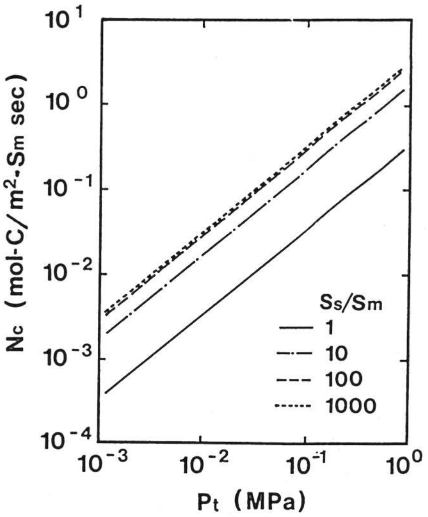

Figure 8. Effect of ambient pressure on the calculation result, for FeO-SiO_2-CaO-Al_2O_3 at 1673K (FeO:CaO:SiO_2:Al_2O_3 = 1:4:4:1 in mol)

where k is the mass transfer coefficient. There are two possible values for n in equation (18) based on mass transfer theories. Based on the boundary layer model or simple diffusion theory, the mass transfer coefficient or diffusibility is inversely as pressure. That leads to a constant rate with the pressure; n=0. On the penetration theory or surface renewal theory, the mass transfer coefficient is inversely to the square root of the pressure. The rate is proportional to the square root of the pressure; n=1/2. If the published data[15, 16, 17] is expressed as equation (18), n=1 for Upadhya's data, and 0<n<1 for the data of MacRae and Lloyd et al.

If the mass transfer in the slag is controlling the rate, there should be no pressure dependency or the dependency may be negative; n=0 or <0. The number of bubble generated will decreases with the pressure. If the agitation by the bubble is contributing the oxygen diffusion in the slag phase, and ,the higher pressure will lead the slower rate.

Upadhya's[17] data support this model, but the other two[15, 16] leave the possibility of gas phase diffusion control. Since the gas phase mass transfer is suppressed by the pressure, the mass transfer control is favorable at relatively high pressure.

3.3 Quantitative comparison with experimental data

The experimental data in Figure 7 should be compared with the calculated result by multiplying ΣSm/Sa. The calculated result is necessary to be multiplied by the factor over 0.5 in order to agree with experimental data. However, such a large value of ΣSm/Sa can not be anticipated in this model. Although the ferrying mechanism in this work should be abandoned and the faster mechanism should be investigated, there are several points to be reevaluated in this work.

The mass transfer control should be also discarded because it gives slower rate than the chemical reaction control, as far as based on the ferrying model.

There were several investigations, for example[2], in which fine metallic particles were found in the slag phase, and carbon was found in them. This implies that the reaction interface is not limited to the apparent slag-metal interface. The reaction rate might be slower than those in Figure 7.

The rate equations might not be adequate. Harashima et al[18] mentioned that the oxidation rate of C in the metal by CO-CO_2 mixture might be faster than the equation (17), based on their experiment at low pressure.

The actual reaction mechanism may not be like that in this work. Other mechanism, such as nucleation of CO bubble by the reaction between dissolved C and O in the molten metal should be investigated.

4. Conclusion

The kinetic model for the reaction between FeO in molten slag and C in molten iron was proposed, based on the assumption CO-CO_2 in the bubble, which exists on the apparent slag-metal interface, is ferrying medium of oxygen and carbon. The effective interfacial area for the reaction was estimated with properties of the slag and metal. This model could predict the overall reaction rate without any phenomenological parameters and be a useful tool to discuss the reaction mechanism or the effect of slag composition or ambient pressure, if the interfacial properties were well examined.

However, the model was not successfully applied to reproduce the experimental kinetic data. The experimental kinetic data were faster than that predicted by the model. Although there are some points left to be reevaluate the model, other mechanism of the reaction should be examined.

Nomenclature

a_{Fe}: activity of Fe (-), a_{FeO}: activity of FeO (-), a_{SiO2}: activity of SiO_2, g: gravity constant (m/sec^2), $K_{s/g}$: equilibrium constant for reaction (-), N_{FeO}: Reduction rate of FeO (mol/m^2/sec), N_C: oxidation rate of C (mol/m^2/sec), P_t: pressure (Pa), P_{CO}: pressure of CO (Pa), P_{CO2}: pressure of CO_2 (Pa), R: gas constant (kcal/mol/deg), r_e: equivalent radius of bubble (m), r_m: radius of the top of bubble (m), r_s: radius of the bottom of bubble (m), r_t: radius of gas-slag-metal interface (m), Ss: slag-gas interfacial area (m^2), Sm: gas-metal interfacial area (m^2), T: temperature (K), V_m: volume of bubble surrounded by metal (m^3), V_s: volume of bubble surrounded by slag (m^3), V_t: volume of bubble (m^3), X_{FeO}: mole fraction of FeO (-), θ_m: angle between metal-gas interface and horizon (rad), θ_s: angle between slag-gas interface and horizon (rad), $\theta_{s/m}$: angle between slag-metal interface and horizon (rad), ρ_m: density of metal (kg/m^3), ρ_s: density of slag (kg/m^3), σ_m: surface tension of metal (N/m), σ_s: surface tension of slag (N/m), $\sigma_{s/m}$: slag-metal interfacial tension (N/m)

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