Transfer of Elements between Molten Slag and a Falling Droplet of Carbon-saturated Iron

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Synopsis

To simulate the reaction between slag and metal in the hearth of blast furnace, molten carbon-saturated iron droplet of 0.3 to 0.6 mm dia. was dropped down through the molten slag column of 25 mm dia. and 100 mm height. A new equipment was developed in order to determine the falling time, i.e., reaction time, when iron drop fell through slag melt. With the use of this equipment, the velocity of fall of carbon-saturated iron droplet either containing sulfur or free of sulfur and the transer of silicon or sulfur between these phases were measured at 1 550° and 1 600°C. The velocity of fall through this column of slag melt with the composition CaO *45%–*SiO_2 *45%–*Al_2O_3 *10% did not obey the Stokes' law and, therefore, the law should be corrected by means of Oseen's approximation and correction equation of wall effect. The velocity of fall* $\bar{V}$ *(cm/sec) determined by the measured falling time was given by the droplet diameter d (cm) as follows:* $\bar{V}=12.5\,d^{2.2}$ *at 1 550°C and* $13.7\,d^{1.8}$ *at 1 600°C for iron droplet free from sulfur. When sulfur was added to iron, because of its surface activity, the velocity of fall increased.*

The rate of silicon transfer from slag to falling droplet was 10 to 20 times higher than that for permanent contact. Under the conditions of the present experiments, the penetration theory by Higbie was applied to the rate of silicon transfer with good accuracy. The rate of sulfur transfer was also as high as that of silicon transfer.

I. Introduction

Recently, in the metallurgical processes it is remarked what the liquid droplet of metal and slag behaves chemically or hydrodynamically in a continuous media such as molten slag and metal. In blast furnace, the iron droplets produced at bosh fall through slag layer and collect in the hearth.

The authors had previously investigated desulfurization of iron melt dropping through a molten slag column and found that the rate of S transfer was much higher than that for permanent contact.[1] But then, as reaction time was calculated from the Stokes' law, it seemed that the reaction time was different from the true value.

In the present work, the detectors for finding the exact moments that an iron droplet started to fall through the molten slag in the crucible and reached its bottom were developed, and the rates of transfer of Si and S between carbon-saturated iron and slag were exactly measured at 1 550° and 1 600°C.

II. Experimental Procedure

One of the most important points in investigating the transfer of Si and S between falling iron droplet and slag melt is that the reaction time, *i.e.*, falling time, is measured with good accuracy. However, it is difficult to measure the falling time when a liquid droplet falls through the liquid media at very high temperature. The most suitable method for determining the falling time is by directly watching the motion of iron droplet through a X-ray fluoroscope. However, this method is not acceptable for several reasons.

In order to know the falling time, it is necessary that the moments of the start and finish of fall are detected in the molten slag column. And so the experimental apparatus consists mainly of two parts:

One of them is a graphite crucible in which a molten slag column, 25 mm in diameter and 100 mm in height, is formed. The graphite crucible, shown in Fig. 1 (a), possesses a molybdenum grid in the bottom. The grid is placed slightly above the bottom surface so that a thin molten slag layer is formed. This slag layer forms an unknown resistance of a Wheatstone's bridge.

The other is a graphite nozzle, shown in Fig. 1 (b), with a caliber of 3 to 6 mm dia., in which a piece of carbon-saturated iron is melted. The graphite nozzle is connected to a stainless steel pipe for introducing dried air. This pipe has a sample inlet hole and a pressure sensitive element for detecting the start time of fall of droplet.

The graphite crucible and nozzle are arranged as shown in Fig. 2. A synthetic slag, CaO 45%–SiO_2 45%—Al_2O_3 10%, is melted by induction heating and forms a slag column of about 105 mm. When the slag is melted down, the tip of the nozzle is immersed in the center of the slag surface and a piece of pig iron is charged from a sample inlet hole. As the

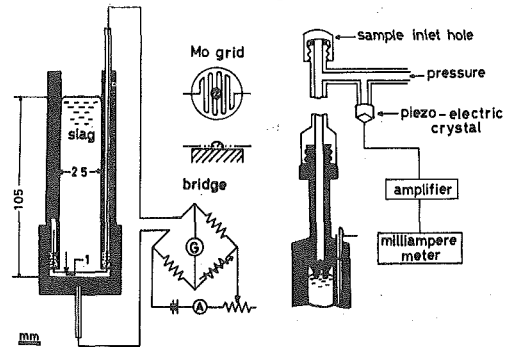

Fig. 1. Graphite crucible and nozzle
(a) Graphite crucible to form molten slag column, attached Mo grid for detecting the end time of fall
(b) Graphite nozzle to melt a droplet of iron, connected to stainless steel pipe with element for detecting the start time of fall

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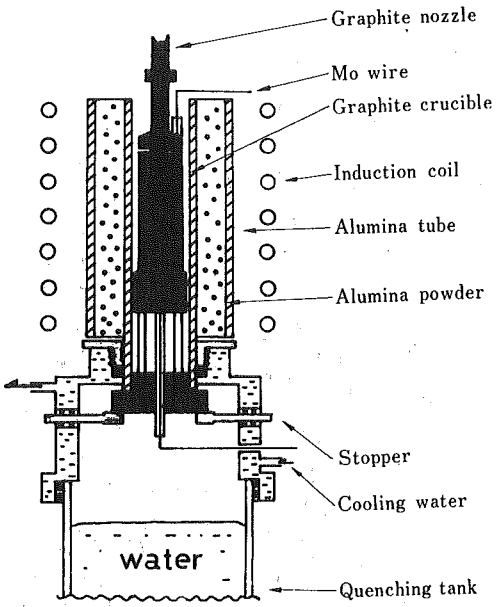

Fig. 2. Schematic diagram showing the arrangement of crucible assembly

crucible and the nozzle are heated to any desired temperature, the iron droplet is pushed into the slag melt by the pressure of a few cm H_2O, and a small change of pressure in the stainless steel pipe is synchronously detected by a pressure sensitive element. The direct current generated in this element is amplified and detected by a milliammeter. As soon as molten iron droplet reaches the bottom of the graphite crucible and the Wheatstone's bridge becomes unbalanced by short circuit, the crucible assembly is quenched into water. An iron droplet found on the bottom of graphite crucible is used for the analysis of Si or S.

III. Results and Discussions

1. Falling Time and Mean Fall Velocity

The falling time, *i.e.*, reaction time, when a molten iron droplet falls through the slag column of 100 mm height, is plotted against the weight of droplet in Fig. 3. For the larger droplet and the higher temperature, the falling time was shorter. Increasing the temperature decreases the viscosity of molten slag and the drag force acting on the liquid droplet. When C-saturated iron contains 0.5 to 0.6%S, because sulfur is the surface-active reagent and decreases the interfacial tension between the slag and iron, a droplet of iron falls slightly faster than that of pig iron free from S. Bargeron *et al.*,[2] studied the kinetics of S transfer between the slag and molten iron droplet using a device similar to our apparatus and measured the falling time of molten iron droplet (0.5 g) through the column of slag at 1 454°C. The molten iron contained

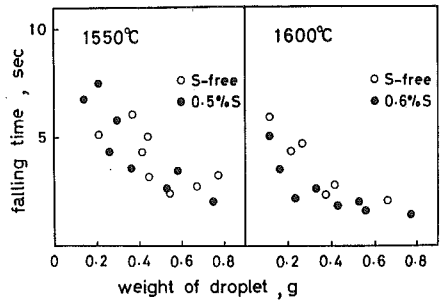

Fig. 3. Falling time of carbon-saturated iron droplet through molten slag containing 45%CaO, 45%SiO_2, and 10%Al_2O_3

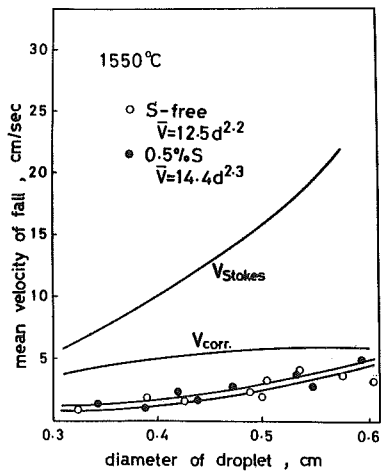

Fig. 4. Increase of fall velocity of carbon-saturated iron droplet with diameter at 1 550°C

4.2%C and 0.02%S. The slag contained 5%CaO, 9%SiO_2 and 41%Al_2O_3 and had a viscosity of 7.7 poise at this temperature.

The values given by Bargeron *et al.* were about 2 times larger than that calculated from the Stokes' law. Bargeron *et al.* considered that this discrepancy could be attributed to the nonsphericity of the molten droplets. In the present work, the deviation of the experimental data from the calculated values is larger than that of Bargeron *et al.* These results seem to be attributed to several factors other than the nonsphercity of molten droplet. In order to reveal this fact the mean fall velocity is investigated. The mean fall velocity is calculated from our data by using the following equation:

$$\bar{V} = 10.0/t \quad \text{.....(1)}$$

where $\bar{V}$ is the mean fall velocity (cm/sec) and t is falling time (sec) estimated by the two detectors. The mean fall velocity is plotted against the droplet diameter in Figs. 4 and 5. The obtained velocity is very small, even when the size of droplets is increased to 0.6 cm. The viscosity and the density of this slag

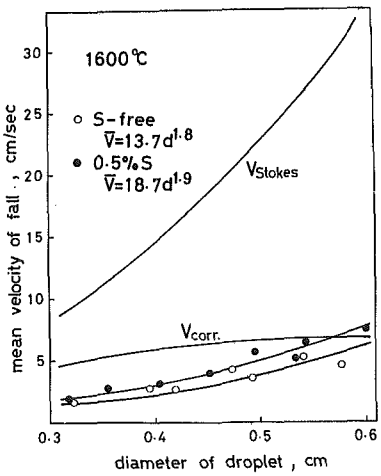

Fig. 5. Increase of fall velocity of carbon-saturated iron droplet with diameter at 1 600°C

Table 1. Viscosity and density[3]

	Viscosity (poise)		Density (g/cm³)	
	1 550°C	1 600°C	1 550°C	1 600°C
Slag	3.4	2.3	2.8	2.7
Iron (C-saturated)	0.04	0.035	6.7	6.6

and those of metal are shown in Table 1, where the effect of sulfur on these values is neglected.

In Figs. 4, and 5 V_{Stokes} represents the fall velocity calculated from the Stokes' law. According to the Stokes' law, the terminal fall velocity V of a rigid sphere is.

$$V_{\text{Stokes}} = \frac{(\rho' - \rho) g d^2}{18\eta} \quad \cdots\cdots(2)$$

where ρ, η, ρ', and d are the density and the viscosity of continuous media and the density and the diameter of a solid sphere, respectively. Substituting the values in Table 1 in the Eq. (2) gives V_{Stokes} as follows,

$$V_{\text{Stokes}} = 62d^2 \text{(cm/sec) at 1 550°C} \quad \cdots\cdots(3)$$
$$V_{\text{Stokes}} = 92d^2 \text{(cm/sec) at 1 600°C} \quad \cdots\cdots(4)$$

The observed velocities attain only 1/5 or 1/7 of the calculated ones. If the sphere is composed of fluid, the following formula known as the Hadamard-Rybczynski formula[4] is usually applied to the velocity of all liquid droplets.

$$V_{\text{Hadamard-Rybczynski}} = V_{\text{Stokes}} \frac{3\eta + 3\eta'}{2\eta + 3\eta'} \quad \cdots\cdots(5)$$

where η' is the viscosity of the fluid forming a droplet. According to this formula, if the fluid forming a droplet has a very high viscosity compared with that of media, the droplet will behave as a solid sphere. Conversely, if the fluid has a very low viscosity, the droplet should move one and a half times as fast as a solid sphere of the same size and density. According to Bond and Newton,[5] the liquid droplet behaves almost as a solid sphere, where the diameter of a falling droplet is less than a critical value given by Eq. (6).

$$d = 2\sqrt{\frac{T}{|\rho' - \rho| \cdot g}} \quad \cdots\cdots(6)$$

where T is the surface tension of contact surface between fluid media and droplet, *i.e.* interface tension. As the approximately estimated surface tension of common surface between slag and C-saturated iron is about 600 dynes/cm for molten pig iron containing 0.5%S and 800 dyne/cm for that free of sulfur, the critical value of d is about 0.8 cm. Hence, under the condition of present study, a molten metal droplet may be treated as a solid sphere.

The difference of the present experimental values from Stokes' velocity seems to result from the following major factors: the effect of Reynolds' number and the effect of the wall of crucible.

Reynolds' number calculated from V_{Stokes} is larger than unity for any droplet size in this experiment, and the term of inertia in the Navier-Stokes differential equation is not neglected. Stokes' law, therefore, is not applicable for fall velocity of the droplet. In such a case, Reynolds' number is less than 10, Oseen assumes the term of inertia to be a linear function of velocity of fluid surrounding the droplet and proposes the following equation for the drag force acting on surface of a droplet.

$$F = 3\pi\eta V d\left(1 + \frac{3}{16}\frac{\rho V d}{\eta}\right) \quad \cdots\cdots(7)$$

where, V is the velocity of a droplet. According to Eq. (7), V is related to V_{Stokes} as follows.

$$V\left(1 + \frac{3}{16}\frac{\rho V d}{\eta}\right) = V_{\text{Stokes}} \quad \cdots\cdots(8)$$

The effect of wall on the falling velocity of a droplet through the liquid media was examined independently by Ladenburg, Faxen, Kan, and Francis. All equations except the Ladenburg's give almost the same correction value with respect to the ratio of the diameter of a droplet to that of a vessel d/D. Faxen's correction coefficient f[6] is given by

$$\frac{V_{\text{corr.}}}{V} = f = 1 - 2.104\frac{d}{D} + 2.09\left(\frac{d}{D}\right)^3 - 0.95\left(\frac{d}{D}\right)^5 \quad \cdots(9)$$

where, D is the inner diameter of a cylindrical vessel and is 2.5 cm in this work.

$V_{\text{corr.}}$ in Figs. 4 and 5 are determined by multiplying the correction factor obtained from Eq. (9) to V calculated from Eq. (8). The observed values agree with $V_{\text{corr.}}$ for large droplets. For small droplets, the unknown factors such as the effect of the bottom of a crucible and the adherence of fine bubbles produced on the drop surface by chemical reaction must affect

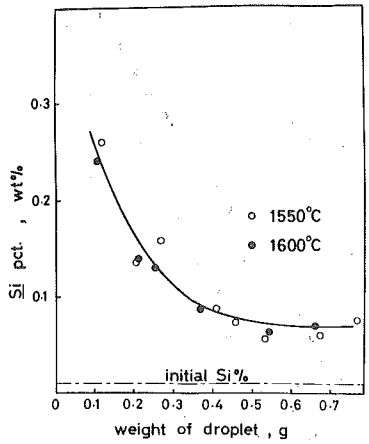

Fig. 6. Silicon contents of carbon-saturated iron droplet falling through 10 cm slag column

Table 2. Observed fall velocity

	1 550°C	1 600°C
S free	$12.5\,d^{2.2}$ (cm/s)	$13.7\,d^{1.8}$ (cm/s)
0.5%S	$14.4\,d^{2.3}$	$18.7\,d^{1.9}$

the falling behavior of molten C-saturated iron droplet. By supposing the relation between the observed fall velocity $\bar{V}$ and the droplet diameter d on longarithmic scales to be a straight line, the representative values of the velocity are shown in Table 2.

2. Transfer of Silicon

While a C-saturated iron droplet falls through molten slag, silica in the slag is reduced by carbon in iron and silicon dissolves into the droplet. The Si concentration is plotted against the weight of droplet in Fig. 6. When the droplet of 0.1 g comes into contact with the slag melt for only 10 seconds at 1 550°C, the Si concentration rises by as much as 0.25%. Increasing the weight of droplet decreases the reaction time and the Si concentration in the droplet decreases. As the falling time is not taken into account, distinction due to the reaction temperature is not revealed in Fig. 6. Therefore, the relationship between the Si concentration and falling time plotted in Fig. 7. The dependence on temperature is clearly indicated and is on a straight line. As the reaction time depends on the droplet diameter in the case of falling of a droplet, the rate of reduction is not estimated for the slope of this line, but the average mass flux of Si transfer; $\bar{N}_{Si}$ (g/cm²sec) is determined by,

$$\bar{N}_{Si} = \frac{(C_{Si} - C^{\circ}_{Si})W}{100At} \quad \text{.....(10)}$$

where, C_{Si} and C°_{Si} are the final and initial Si concentration in the pig iron (%), W is the weight of

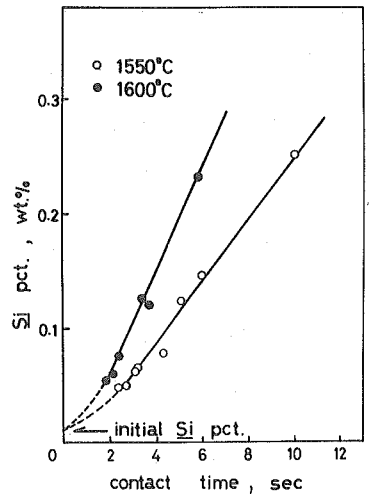

Fig. 7. Apparent linearity silicon contents with contact time, *i.e.* falling time

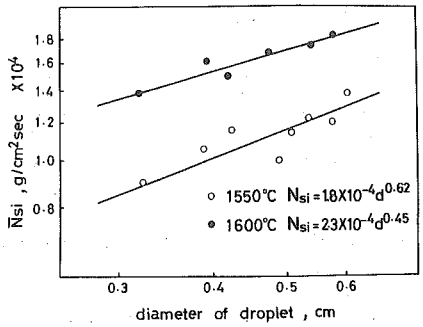

Fig. 8. Size dependence of average mass flux of silicon transfer between molten slag and falling iron droplet

droplet (g), A is the interfacial area between the slag and the pig iron (cm²), t is the reaction time (sec). $\bar{N}_{Si}$ is plotted against the droplet diameter on logarithmic scales as shown in Fig. 8. Provided that the average mass flux of Si is linearly dependent on the droplet diameter, the following relationship between $\bar{N}_{Si}$ and $\bar{d}$ is obtained.

$$\bar{N}_{Si} = 1.8\times10^{-4}\bar{d}^{0.62}\,(\text{g/cm}^2\text{sec}) \text{ at } 1\,550^{\circ}\text{C} \quad \text{.....(11)}$$

$$\bar{N}_{Si} = 2.3\times10^{-4}\bar{d}^{0.45}\,(\text{g/cm}^2\text{sec}) \text{ at } 1\,600^{\circ}\text{C} \quad \text{.....(12)}$$

Although the reduction of silica is generally controlled by chemical reaction, the controlling step in this experiment is considered to be the diffusion of silicon in the slag layer. If a segment of slag small compared with the diameter of a falling droplet is considered, the partial differential equation for convective diffusion is given[7] with respect to rectangular coordinates simply by

$$\frac{\partial C}{\partial t} = D_{Si}\frac{\partial^2 C}{\partial x^2} \quad \text{.....(13)}$$

This equation is to be solved with the following initial and boundary conditions:

$$\text{I.C. 1}: \quad t \leq 0,\ x \geq 0 \qquad C = C_{Si}^{\infty}$$
$$\text{B.C. 1}: \quad t > 0,\ x = 0 \qquad C = C_{Si}^{*}$$
$$\text{B.C. 2}: \quad x = \infty \qquad C = C_{Si}^{\infty}$$

where, C_{Si}^{∞} is the Si concentration in the slag bulk and C_{Si}^{*} is the Si concentration of slag at the slag–metal interface. The mass flux at time t is

$$N_{Si}(t) = \sqrt{\frac{D_{Si}}{\pi t}}(C_{Si}^{\infty} - C_{Si}^{*}) \quad \text{.....(14)}$$

The average flux of mass transfer of Si is

$$\bar{N}_{Si} = \frac{1}{t}\int_0^t N_{Si}(t)dt = 2\sqrt{\frac{D_{Si}}{\pi t}}(C_{Si}^{\infty} - C_{Si}^{*}) \quad \text{...(15)}$$

By replacing t by $d/\bar{V}$,

$$\bar{N}_{Si} = 2\sqrt{\frac{D_{Si}\bar{V}}{\pi d}}(C_{Si}^{\infty} - C_{Si}^{*}) \quad \text{.....(16)}$$

By substituting Si concentration which is calculated from the activity of silica a_{SiO_2}[8] in the present slag into $(C_{Si}^{\infty}-C_{Si}^{*})$ in Eq. (16) and using D_{Si} in Table 3, N_{Si} is predicted as follows:

$$\bar{N}_{Si} = 1.4\times10^{-4}d^{0.6}\,(\text{g/cm}^2\,\text{sec}) \text{ at } 1\,550°\text{C} \quad \text{...(17)}$$

$$\bar{N}_{Si} = 1.8\times10^{-4}d^{0.4}\,(\text{g/cm}^2\,\text{sec}) \text{ at } 1\,600°\text{C} \quad \text{...(18)}$$

The Eqs. (17) and (18) agree fairly well with experimental Eqs. (11) and (12).

3. *Transfer of Sulfur*

The transfer of S from the molten C-saturated iron to slag melt is investigated by the same method as for Si transfer. The S content in iron is plotted against the weight of sample in Fig. 9. While a droplet of 0.1 to 0.2 g falls through a slag column of 10 cm, almost all S in molten iron is removed without exception. $\bar{N}_S$ is estimated by applying the equation same as that for Si and plotted against the droplet diameter on logarithmic scales in Fig. 10. The average mass flux of S transfer increases as the droplet diameter increases. However, when the droplet size exceeds a critical value, $\bar{N}_S$ has a tendency of decreasing.

Desulfurization is a rapid reaction at contact surface and is rate-controlled by diffusion of S in the slag at high temperature. Therefore, the penetration theory by Higbie may be more acceptable in this case than that of Si transfer. However, the steady state solution can not be obtained because of the rapid decrease of S content in the droplet during the fall.

IV. Conclusions

The transfer of silicon and sulfur between a falling carbon-saturated iron droplet and molten slag was studied with the use of an apparatus for measuring the falling time, *i.e.*, reaction time.

The measured falling time was a few times longer than the value calculated from the Stokes' law. It seemed that the fact could be attributed to the effect of Reynolds' number and the wall of crucible.

The rate of silicon transfer was 10 to 20 times higher than that for permanent contact under the same conditions as the present work and the penetration theory was applicable for rapid rates with good accuracy. However, this theory was not applied to the sulfur transfer because of the rapid decrease of sulfur content in the droplet during the fall.

Table 3. D_{Si}[9] and a_{SiO_2}

	1 550°C	1 600°C
D_{Si} (cm²/sec)	4×10^{-7}	5×10^{-7}
a_{SiO_2}	0.045	0.05

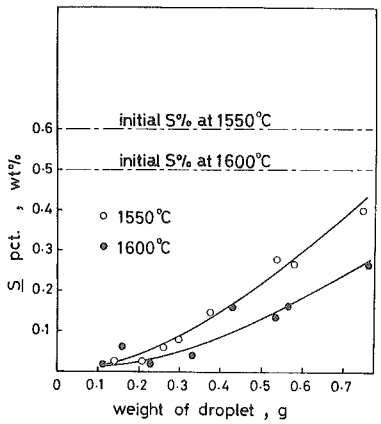

Fig. 9. Sulfur contents of carbon-saturated iron droplet containing S falling through 10 cm slag column

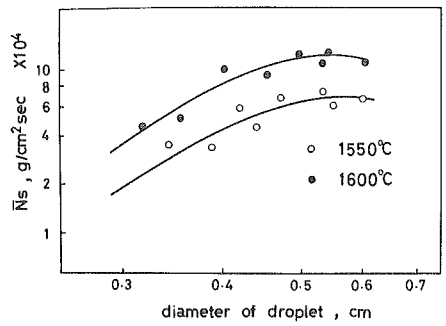

Fig. 10. Size dependence of average mass flux of sulfur transfer between molten slag and falling iron droplet

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