Reduction of Molten Oxide Mixture Containing Iron and Phosphorus Oxide at Temperature below Melting Point of Metallic Iron*

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Synopsis

The possibility for the production of solid iron containing little phosphorus from molten iron oxide containing phosphorus oxide was examined experimentally.

Molten iron oxide containing phosphorus, lime and silica was reduced by CO gas in an iron crucible. The samples containing 20 and 60 % FeO were used as "model" substances for steelmaking slag and iron ore, respectively, in the case of smelting reduction.

Reduction temperature were at 1350 and 1450 °C. Phosphorus contents of produced iron are always below 0.2 %. Lower phosphorus content of produced iron can be obtained, with the sample containing 60 % FeO than with that containing 20 % FeO, with the sample with CaO/SiO₂ ratio of 0.5 than with unity.

The reduction of iron oxide in the sample begins after an incubation period of a few minutes while that of phosphorus oxide in the sample has no incubation period. Namely, at very early stage of the reduction, phosphorus oxide alone is reduced. The reduced phosphorus is diluted with produced iron after beginning of reducing of iron oxide. The content of phosphorus increases again when the reducing rate of the iron oxide decreases.

The reduction rates of oxides of iron and phosphorus can be described as time-linear equations.

It is speculated that the rate determining step of the reduction is the transport process of the substances through the molten oxide.

I. Introduction

The history of iron- and steelmaking might be a history of a struggle against phosphorus. Some Japanese steel companies are recently making effort to produce steel with phosphorus content of less than 10 ppm. It is forecasted on the other hand that phosphorus content in raw material for ironmaking will increase gradually in future because of the exhaustion of iron ore with low phosphorus and the recycle of steelmaking slag.¹⁾

The present work is concerned with a method to produce solid iron of low phosphorus content from molten iron oxide with high phosphorus content. The reasons why solid iron is produced from the molten state oxide are as follows:

(1) Solubility of phosphorus in solid iron is much smaller than that in liquid iron.

(2) Produced solid iron particles can coarse easily into large particles in the molten oxide.

This procedure may be classified into a smelting reduction process. A study on the smelting reduction process has begun since about 1930.²⁾ Philbrook and Kirkbride,³⁾ Tarby and Philbrook,⁴⁾ and Shabrin⁵⁾ studied on the smelting reduction of molten mixture of lime and silica containing small amount of iron

oxide. Krainer *et al.*,⁶⁾ Fan,⁷⁾ Sugata *et al.*,⁸⁾ and Davies *et al.*,⁹⁾ have studied on the smelting reduction of molten mixture of lime and silica containing large amount of iron oxide. Recently Sasaki *et al.*,¹⁰⁻¹²⁾ Wijk and Mellberg,¹³⁾ and Sato *et al.*¹⁴⁾ have studied in some detail on this process. However these studies are concerned with the process which produces molten iron and molten slag from molten raw material. There have been no study on the process which gives solid iron from molten oxide.

The object of this work is to obtain basic data, *i.e.*, the reduction rate of iron oxide, maximum phosphorus content and physical shape of the produced iron.

II. Experimental Procedure

Nominal composition of samples is shown in Table 1. The composition of the sample was decided on the basis of the melting point of the mixed oxide. The samples containing 60 wt% FeO were used as "model" substance for iron ore in the case of smelting reduction. The samples containing 20 wt% FeO were used as "model" substance for the smelting reduction of steelmaking slag.

The samples were prepared from Fe₂O₃, SiO₂, Ca(OH)₂ and P₂O₅. These were mixed in an alumina mortar and then were melted at about 1500 °C in a pure iron crucible in air. The molten samples were quenched in water. The distributions of analyzed data of FeO contents in the quenched samples were scattered within ±3 % due to oxidation of iron crucible. The other compositions were scattered also followed by the scattering of FeO content. The quenched sample was crushed below 30 mesh pass in a stainless steel mortar.

Experimental apparatus used for the reduction is shown in Fig. 1. The prepared sample of 10 g was put into a steel crucible. The crucible of 19 mm in inner-diameter and of 70 mm in length was hung by steel wire in a mullite tube of 42 mm in inner-diameter and of 600 mm in length. Both ends of the mullite tube were closed by stoppers made of silicon rubber. The stopper at the top of the tube was equipped with an inlet for CO lance of 2 mm in inner-diameter, an outlet of CO and N₂, and a glass window to observe inside the tube. An inlet of N₂ was attached to the stopper at the bottom. A protecting tube for thermocouple was also inserted into the mullite tube through

* Presented to the 99th ISIJ Meeting, April 1980, S77, at The University of Tokyo in Tokyo. Manuscript received March 25, 1983. © 1984 ISIJ

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Table 1. Nominal composition of samples. (wt%)

Sample No.	FeO	P ₂ O ₅	CaO	SiO ₂	CaO/SiO ₂
1	60	5	17.5	17.5	1.0
2	60	5	11.7	23.3	0.5
3	20	5	37.5	37.5	1.0
4	20	5	25.0	50.0	0.5

Fig. 1. Schematic illustration of experimental apparatus.

the stopper at the bottom. The mullite tube was heated by a spiral type heating element made of silicon carbide.

The crucible containing crushed sample and the CO lance at room temperature were simultaneously put into the mullite tube heated at experimental temperature. N₂ gas was blown into the mullite tube from the bottom at the rate of about 1(S.T.P.) l·min⁻¹. After the melting of the sample and returning the temperature in the mullite tube to the experimental temperature, CO gas was blown on the surface of the molten sample at the rate of 1.5 (S.T.P.) l·min⁻¹. When the flow rate of CO increased more than 1.5(S.T.P.) l·min⁻¹, molten sample flowed out from the crucible. Velocity of CO was about 8 m·s⁻¹ at the outlet of the nozzle. A distance between the surface of the molten oxide and the nozzle of the lance was about 20 mm.

After the prescribed reduction time, CO was stopped and N₂ was introduced into the mullite tube. And then the CO lance and the crucible were pulled up to the upper part of the mullite tube where temperature was lower. When the sample was cooled to room temperature, the crucible was taken out of the mullite tube and weighed. Degree of reduction of the sample was determined on the basis of its weight decreasing during the reduction. No weight change of the crucible during reduction was confirmed prior to the measurement.

CO gas was purified over soda lime and silica gel. N₂ was dried and deoxidized over silica gel and heated magnesium, respectively.

Experimental temperatures were at 1 350 and 1 450 °C. Reduction time were varied from 15 to 240 min at every 15 min intervals.

After the measurement of weight change, the iron crucible containing the reduced sample was cut longitudinally. And then produced iron metal and residual oxide were simultaneously taken out by means of a hammer and pliers. The sample taken out of the crucible was crushed in a stainless steel mortar. The crushed sample was placed in methanol. The iron was removed by a magnet, thus remaining un-reduced part of oxide in methanol. The separated iron was again crushed in the stainless steel mortar and then was treated further by means of the magnet in methanol in order to separate a small amount of the un-reduced oxide containing in the iron. The separation was carried out five times or more.

Phosphorus content of the reduced iron was analyzed by means of a indirect atomic absorption spectrometric analysis combined with the extraction of phosphomolybdic acid.¹⁵⁾

III. Experimental Results

When CO gas was blown on the molten sample, foam evolution was observed on its surface. Some thick iron films and many thin iron films were produced as shown in Photo. 1 where the films were the surfaces of the foams reduced by CO. Many small iron particles were also produced. Configurations of the reduced sample are shown in Table 2.

Figures 2 and 3 show relationships between degree of reduction of iron oxide as well as that of phosphorus oxide reduction time. The degrees of reduction of iron oxide, (%R_{Fe}), and of phosphorus oxide, (%R_P), are defined as follows:

(%R_{Fe})

$$= \frac{\left\{ \frac{16}{72}(\%FeO) + \frac{80}{142}(\%P_2O_5) \right\} \times \frac{62}{80} \{100 - (\%P)\}}{\frac{16}{72}(\%FeO) \times \left[\frac{62}{80} \{100 - (\%P)\} + \frac{56}{16}(\%P) \right]} \times (\%R_0) \dots\dots\dots(1)$$

(%R_P)

$$= \frac{\left\{ \frac{16}{72}(\%FeO) + \frac{80}{142}(\%P_2O_5) \right\} \times \frac{56}{16}(\%P)}{\frac{80}{142}(\%P_2O_5) \times \left[\frac{62}{80} \{100 - (\%P)\} + \frac{56}{16}(\%P) \right]} \times (\%R_0) \dots\dots\dots(2)$$

where, (%FeO), (%P₂O₅): initial percentages of FeO and P₂O₅ of the sample, respectively

(%P): percentage of phosphorus of the produced iron

(R₀): degree of overall reduction.

The degree of overall reduction is defined as total weight loss of the sample during the reduction dividing

Photo. 1. An example of the longitudinal cross section of the reduced sample. The composition of the sample is 60 % FeO and ratio of CaO to SiO₂ of unity. The reducing temperature and time are 1 450 °C and 45 min, respectively.

Table 2. Configuration of reduced sample.

Sample No.	Reduced temp. (°C)	Height of foaming	Distance between films of produced iron
1	1 350	high	wide
	1 450	low	narrow
2	1 350	high	wide
	1 450	low	narrow
3	1 350	middle	chain like
	1 450	low	chain like
4	1 350	Experiment could not be carried out.	
	1 450	Produced iron melted.	

by the initial weight of oxygen combining Fe and P. The samples with the CaO/SiO₂ ratio of unity showed larger reduction rates than that of 0.5.

Figure 4 shows relationship between phosphorus content of produced iron and degree of reduction of iron oxide. The phosphorus contents were below 0.2 %. The phosphorus content decreases at first and afterwards increases with increase of degree of reduction of iron oxide.

Lower phosphorus content of produced iron can be obtained, with the sample containing 60 % FeO than with that containing 20 % FeO, with the sample with ratio of CaO to SiO₂ of half than that with unity and when it was reduced at 1 350 °C than at 1 450 °C.

The experiment using the sample containing 20 % FeO and with CaO/SiO₂ ratio of 0.5 could not be carried out at 1 350 °C since the sample was mixture of solid and liquid phases at this temperature. When this sample was reduced at 1 450 °C, molten iron which was produced from the sample accumulated on the bottom of the crucible. Phosphorus and silicon contents of the molten iron were both more than 1 %.

Fig. 2. Relationship between degree of reduction of iron oxide and reduction time.

Fig. 3. Relationship between degree of reduction of phosphorus oxide and reduction time.

Fig. 4. Relationship between phosphorus content of produced iron, %P, and degree of reduction of iron oxide. Solid and dotted lines indicate at 1 450 and 1 350 °C, respectively.

IV. Discussion

1. Rate Determining Step

The reduction rates of oxides of iron and phosphorus can be described as time-linear equations as shown

in Figs. 5 and 6, respectively.
The rate equations can be expressed as Eqs. (3) and (4).

For reduction of iron oxide:
$$-\log (1-R_{Fe})=k_1 t+A \quad \cdots \cdots \cdots (3)$$

For reduction of phosphorus oxide:
$$-\log (1-R_P)=k_2 t \quad \cdots \cdots \cdots (4)$$

where, R_{Fe} , R_P : fractional reductions of iron oxide and phosphorus oxide, respectively
 k_1 , k_2 : rate constants of the reduction of iron oxide and of phosphorus oxide, respectively
 A : a constant.

Calculated values of k_1 , k_2 , A and apparent activation energies, E , are listed in Figs. 5 and 6.
Incubation periods of 5 to 20 min were observed in the case of iron oxide reduction. The incubation periods are identical when the samples with the same initial iron oxide contents were used at the same temperature. The incubation periods at 1450 °C are shorter than that at 1350 °C. The samples containing 20 % FeO showed longer incubation periods than that containing 60 % FeO.

The nearly same rate constant, k_1 , was resulted when the samples with the same CaO/SiO₂ ratio were reduced. The reduction of the sample with CaO/SiO₂ ratio of unity gave larger k_1 value than that of 0.5. Apparent activation energies were valued between 35 and 43 kcal·mol⁻¹.
On the other hand, no incubation period was seen in the case of reduction of phosphorus oxide. The rate constants of the reduction of phosphorus oxide, k_2 , were varied with reduction temperature, content of iron oxide as well as ratio of CaO to SiO₂. It depends on the iron oxide content of the sample rather than the ratio of CaO to SiO₂. The activation energy data are between 61 kcal·mol⁻¹ and 71 kcal·mol⁻¹.

If the reaction can be described by a first order equation, following rate determining steps are conceivable.¹⁶⁾
1) Transport process of substance through gas boundary layer.
2) Chemical reaction process at reaction surface.
3) Transport process of substance through either reactant or product.

It is reviewed by Tokuda¹⁷⁾ that the rate determining step of the reduction of molten oxide with high iron oxide content is the transport process of substance through gas boundary layer, although that containing low iron oxide is transport process of iron oxide in molten oxide. However the case 1) is not rate determining step of this experiment because k_1 and k_2 did not change when the flow rate of CO decreased to 1 (S.T.P.) l·min⁻¹. The transport of a substance through produced iron was not the rate determining step, since no substantial increase of k_1 was observed at 1450 °C when the produced iron became in a molten state. Thus it is speculated that the rate determining step of reduction of iron oxide

Fig. 5. First order equation plot of reducing of iron oxide.

Fig. 6. First order equation plot of reducing of phosphorus oxide.

is either the transport process of iron oxide through molten oxide or chemical reaction process at reaction surface. Because there is no example of the rate determining step of the chemical reaction process in the above mentioned review, it is speculated that the most probable rate determining step is the transport process of substance in the molten oxide.
It is also speculated that the rate determining step of the reduction of phosphorus oxide is the transport process of phosphorus oxide through molten oxide.
If the rate determining steps are transport process

of substances through molten sample, the rate constants might be varied with reducing time because of change of properties of molten sample, especially viscosity, during the reduction. However, viscosity of the molten sample used in the present experiment is almost constant during the reduction unless the degree of reduction is 60 %.¹⁸⁾

2. Relationship between Degree of Reduction of Iron Oxide and Phosphorus Content of Produced Iron

Phosphorus content of produced iron decreased at first with increase of degree of reduction of iron oxide and then it increased with increase of degree of reduction of iron oxide. In other words, the content decreased with increase of reduction time and then it increased with increase of reduction time. The relationship can be explained by rate equation on the reduction of iron oxide, Eq. (3), and phosphorus oxide, Eq. (4). From both equations,

$$R_{Fe} = 1 - \frac{1}{B} \exp(-2.3k_1t) \dots\dots\dots(5)$$

$$R_P = 1 - \exp(-2.3k_2t) \dots\dots\dots(6)$$

where $\log B$ is equal to A in Eq. (3).

$$\begin{aligned} (\%P) &= \{ [1 - \exp(-2.3k_2t)] \times 100 \} / \{ [1 - (1/B)] \\ &\quad \times \exp(-2.3k_1t)] + [1 - \exp(-2.3k_2t)] \} \\ &\dots\dots\dots(7) \end{aligned}$$

Equation (7) can be rewritten as Eq. (8) since $R_{Fe} \gg R_P$ as shown in Figs. 2 and 3.

$$\begin{aligned} (\%P) &\div [[1 - \exp(-2.3k_2t)] / \{ 1 - (1/B) \} \\ &\quad \times \exp(-2.3k_1t)] \times 100 \dots\dots\dots(8) \end{aligned}$$

$$\begin{aligned} d(\%P)/dt &= 100B \times [\{ 2.3k_2 \exp(-2.3k_2t) \} \\ &\quad \times \{ B - \exp(-2.3k_1t) \} - \{ 2.3k_1 \\ &\quad \times \exp(-2.3k_1t) \} \{ 1 - \exp(-2.3k_2t) \}] / \\ &\quad \{ B - \exp(-2.3k_1t) \}^2 \dots\dots\dots(9) \end{aligned}$$

It is difficult to determine the time that gives $d(\%P)/dt = 0$. To know whether Eq. (8) has a minimum value or not, signs of $d(\%P)/dt$ should be discussed. For example, the experiment using the sample containing 60 % FeO and with CaO/SiO₂ ratio of unity, and at 1 450 °C will be discussed, where k_1 is $5 \times 10^{-3} \text{ min}^{-1}$, k_2 is $9 \times 10^{-5} \text{ min}^{-1}$, A is -0.02 and B is 0.955 . When reducing time is 20 min, the sign of $d(\%P)/dt$ is negative. When reducing time is 60 min, the sign is positive. The above discussion shows that Eq. (8) takes a minimum value between 20 % and 50 % of the degree of reduction of iron oxide.

When $B=1$ and $t>0$, $d(\%P)/dt$ does not become zero. The plots of %P against time as well as degree of reduction of iron oxide have no minimum value. The incubation period of iron oxide reduction plays an important role in the content of phosphorus of the produced iron. At very early stage of the reduction, phosphorus oxide alone is reduced. The reduced phosphorus is diluted with produced iron after beginning of reducing of iron oxide. The content of phosphorus increases again when the reducing rate of iron

oxide decreases. The incubation period has been observed also when solid iron oxide was reduced.¹⁹⁾

3. Residual Problems on This Method

There are some problems in this smelting reduction process. One of them is slow reduction rate. Since the maximum reduction rate of iron oxide per crucible is about 40 % min⁻¹, the rate corresponds to 0.011 g oxygen min⁻¹ per crucible. When the rate of 0.011 g oxygen min⁻¹ per crucible is divided by π time the square of inner-radius of the crucible, the rate of $4 \times 10^{-3} \text{ g oxygen min}^{-1} \cdot \text{cm}^{-2}$, i.e., $2.5 \times 10^{-4} \text{ mol} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$, can be estimated. However, it is impossible to estimate exactly the reduction rate per unit area because of form evolution of the sample. It is sure that the maximum reduction rate per unit area is smaller than $2.5 \times 10^{-4} \text{ mol} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$. The rate is smaller than reduction rate of molten iron oxide by solid carbon,¹²⁾ $3 \times 10^{-3} \text{ mol} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$.

It is speculated that the difference between two reduction rates is induced by the difference of convection rate of liquid oxide phases. The convection rate during reaction between solid carbon and liquid oxide is larger than that between carbon monoxide and liquid oxide since volume change of gas produced by the solid-liquid reaction is much larger than that by the gas-liquid reaction. This problem will be solved by the device for increasing the convection force and the reaction surface.

Second problem is the separation of residual oxide from produced iron. A superior separation method is expected to be developed.

V. Summary

The possibility for the production of solid iron containing little phosphorus from molten iron oxide containing phosphorus oxide at temperature below melting point of iron was examined experimentally.

The experimental results are as follows:

(1) Phosphorus content of produced iron is less than 0.2 % when iron oxide is reduced more than 60 %.

(2) The phosphorus content takes a minimum value between 40 % and 50 % of the degree of reduction of iron oxide.

(3) The more the contents of the iron oxide, the lower the CaO/SiO₂ ratio and the lower the temperature, the lower phosphorus content of the produced iron is resulted.

(4) Reaction rates of reduction of iron oxide and phosphorus oxide can be both described by the first order equations.

Acknowledgements

The authors wish to thank M.E.S. Yamashita, a research associate of Chiba Institute of Technology, for his help for atomic absorption spectrometric analysis. The authors also wish to thank Messrs. Koyashiki, Naoe, Fukunishi, Saito and Kakishima for their experimental assistance as students of Chiba Institute of Technology.

The research was financially supported by a grant-in-aid for scientific research from The Research Committee of Chiba Institute of Technology.

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