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Development of the Complete Utilization Process of Steelmaking Slag

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Abstract

The complete utilization process of steelmaking slag has been developed, in which Fe and P were recovered and slag products such as cement or aggregates, phosphate fertilizer, and the hot metal for steelmaking were produced through reduction and dephosphorization. A closed type DC arc furnace was adopted as a reduction process and its characteristics were investigated through the pilot plant tests. Especially the possibility and the effectiveness of molten slag direct charging into the reduction furnace were confirmed through the actual trial. Moreover by conducting the dephosphorization test of the hot metal with high phosphorus content, it was shown that high basicity and low (T.Fe) of the slag are the key factors for producing both low phosphorus hot metal and high phosphate slag product.

1. Introduction

Currently, almost all of the steelmaking slag discharged from converters is used mainly for road and public works. New applications such as soil improving materials, silicate fertilizers, and products for seaweed bed development are under development. Meanwhile, steelmaking slag contains valuable elements: Unused iron resources that correspond to 2% of the iron yield, and a lot of phosphorus that is indispensable for human life and various industrial goods, even though all of its supply is dependent on imports in Japan. Some researchers proposed the concept of “complete utilization process of steelmaking slag.”1) In complete utilization, these valuable elements are recovered and steelmaking slag is reduced and reformed at the same time to convert the slag into that equivalent to blast furnace slag that does not pose problems of hydroscopic expansion and high pH leaching.

We have been conducting study and development on the possibility of putting this complete utilization process to practical use. **Figure 1** illustrates our intended process. Steelmaking slag is supplied to the reduction process along with carbon materials and slag modifiers. The reduced slag is used in the same way as blast furnace slag. Meanwhile, hot iron in which iron and phosphorus were enriched through reduction is dephosphorized to the level of [P][*1] of normal hot metal in the dephosphorization (phosphate concentration) process and then recycled in the steelmaking process. In addition, the slag produced in the dephosphorization process is used as high- phosphate fertilizers. In our development, we focused on direct charge of hot molten steelmaking slag into reducing furnaces to decrease energy consumption. This paper reports the development outcomes obtained to date regarding the reduction and dephosphorization processes.

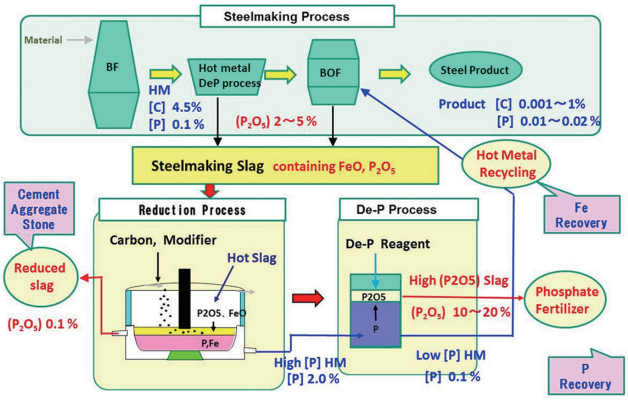

Fig. 1 Process concept for complete utilization of the steelmaking slag

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[*1] [P]: Percent by mass of P in metal

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2. Selection of Processes

As the furnace for the slag reduction process, various types such as converter type[2], arc furnace type[3, 4], and shaft furnace type[5] have been proposed. Among such, we selected the closed-type DC arc furnace. The process was developed by MINTEK in South Africa mainly for ferroalloy production.[6, 7] No air gets into the closed type unlike melting-type conventional arc furnaces and no packed beds of solid raw materials are formed unlike submerged arc furnaces of conventional reduction arc furnaces. The features of closed-type furnaces are a high reduction rate thanks to lower oxygen potential in the furnaces, high thermal efficiency thanks to low gas emissions, and charge of powder materials from the upper part due to low gas flow velocity in the furnaces. Characteristics of DC arc furnaces are a higher flow in slag, small unit consumption of electrodes, and ease of operation. In this development, considering the possibilities of CO_2 emissions reduction and direct charge of molten slag, closed-type DC arc furnaces were adopted for pilot plant tests.

Regarding the dephosphorization process of hot metal with high phosphorus content that is obtained after reduction, in consideration of receiving hot metal to be discharged from the reducing furnace and charging the hot metal into the converter after treatment, pilot plant tests were performed adopting a ladle that could also be used as a transportation container.

3. Experimental Procedure

3.1 Reduction process

Three pilot tests were performed to develop reducing furnaces. **Table 1** lists the experimental conditions. In TEST 1, a closed-type DC arc furnace at SWEREA-MEFOS in Sweden was used.[8] **Figure 2** illustrates the test furnace. Actual crushed steelmaking slag and anthracite coal were charged into the iron bath in the furnace via a hollow electrode to study the reduction characteristics of the slag. In TEST 2, an industrial scale 120-t DC arc furnace at Muroran Works illustrated in **Fig. 3** was used.[9] After hot metal was charged, desiliconization with oxygen and composition adjustment were performed to melt and produce molten pseudo-steelmaking slag in the furnace. Then, granular coke was supplied from the slag door via a pipe to reduce the slag. Since this furnace was a common open-type melting arc furnace, during the reduction, air was continually suctioned into the furnace from the slag door. For TEST 3, a new pilot test furnace was constructed at Yawata Works to charge actual molten converter slag into a reducing furnace and a five-day campaign test was performed seven times in total.[10, 11]

Figure 4 outlines the test furnace. The closed-type DC arc furnace has a slag container in the upper part to store molten slag temporarily. Exhaust gas was burned with oxygen at the inlet of the container to increase the temperature of the slag in the container and melt it. The pressure inside the arc furnace was adjusted to −30 Pa by adjusting the opening degree of the slide sleeve of the off gas duct. In the reducing furnace, approximately 10-t hot metal with a depth of 200 mm continually existed as a hot heel. Reduced slag of 3 to 4 t remained in it. In the test, among molten slag discharged from the 350-t converter, approximately 8 t of it was transferred to a transfer ladle and then it was carried to the test building. Approximately 4 t of it was put into the container and charged into the reducing furnace intermittently by tilting the container.

Granular coke (reducing agent) and silica sand and brick chips (modifiers) for adjusting SiO_2 and Al_2O_3 were continuously put in from the material feeding pipe installed on the furnace cover. When the reduction of the slag discharged from the container was com-

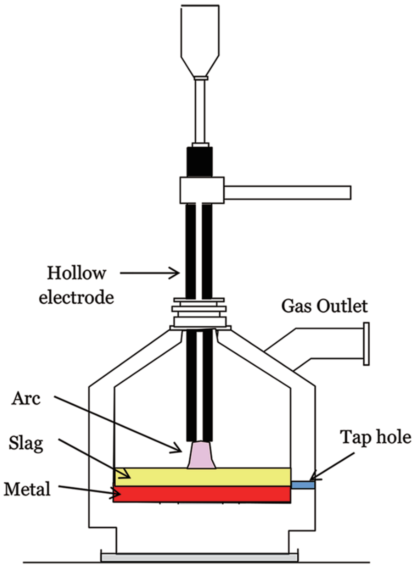

Fig. 2 Schematic diagram of the test furnace in TEST 1

Table 1 Experimental conditions of each TEST

	TEST 1	TEST 2	TEST 3
Purposes	Cold slag charge Reducing efficiency	Molten slag reduction Influence of P_{O_2}	Molten slag charge Process optimization
Furnace type	Closed-type Reducing DC arc	Open-type Melting DC arc	Closed-type Reducing DC arc
Power	1–2 MW	30 MW	2–4 MW
Heat size	Hot heel 3 t	Melt size 120 t	Hot heel 10 t
Material slag	Cold converter slag	Pseudo-converter slag	Molten converter slag
Charge method	Hollow electrode	Prepared in the furnace	Tilting-type Slag container
Reductant	Anthracite	Coke	Coke
Feed method	Hollow electrode	Injection tube	Top feed tube
Tapping	1 tap hole	Slag door / EBT	2 tap holes
Location	MEFOS / Sweden	Muroran Works	Yawata Works

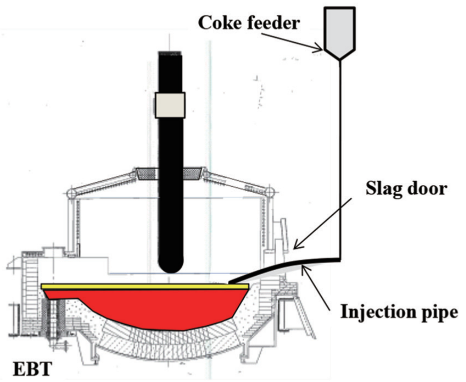

Fig. 3 Schematic diagram of the test furnace in TEST 2

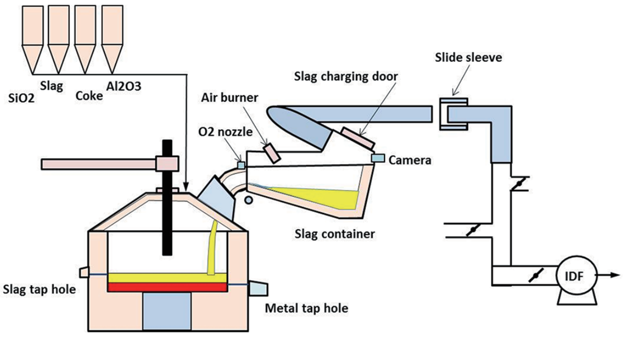

Fig. 4 Schematic diagram of the test furnace in TEST 3

pleted, the reduced slag was discharged from the slag tap hole. This cycle was set as a single test. **Figure 5** shows the slag tapping operation. These processes were repeated. When the metal level approached the slag hole level due to increased metal, the metal was discharged from the metal tap hole that was 200 mm below the slag hole.

The target composition of reduced slag was a basicity $(CaO)/(SiO_2)$ of 1.0 to 1.2 and (Al_2O_3) of 10 to 12%, being at a similar level to that of blast furnace slag. The target slag temperature was 1 823 K and target metal temperature was 1 723 K considering temperature gradient. Temperature measuring and sampling were performed with sub-lance equipment.

3.2 Dephosphorization process

In the slag reduction process, P_2O_5 is also reduced along with Fe_xO and P is concentrated in the hot metal. In the dephosphorization process, to recycle metals in the steelmaking process, [P] needs to be decreased to 0.1% — the level of the normal hot metal — and at the same time, (P_2O_5) needs to be increased, for example, to equal to or higher than 15% to produce high-value-added phosphate fertilizers. To study dephosphorization characteristics in the region with high phosphorus content, an induction melting furnace was used to perform a dephosphorization test. **Figure 6** illustrates the test furnace. Mold pig iron of 800 kg was melted. Then, [C] was adjusted to 4% and [P] was adjusted to 0.6 to 3.0%. Oxygen was blown in at 30 to 60 Nm^3/h from the top-blowing lance for dephosphorization. Calcined lime, dolomite, and silica sand were added as flux and as a coolant, iron ore was added from the upper part of the furnace. As agitating gas, Ar was blown in at 2 to 10 Nm^3/h from the porous plug at the furnace bottom. The temperature was set to 1 473 to 1 923 K.

(a) Slag tap hole

(b) The whole facilities

Fig. 5 Slag tapping operation at TEST 3

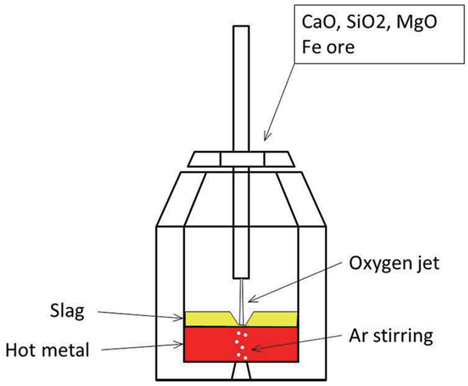

Fig. 6 Schematic diagram of the test furnace for dephosphorization process

4. Experimental Results and Discussion

4.1 Reduction process

4.1.1 In-furnace temperature distribution

In TEST 3, the temperatures of the metal bath (100 mm from the furnace bottom) and slag bath (300 mm from the furnace bottom) were measured at the same time. **Figure 7** shows the relationship between the slag and metal temperature. The slag temperature is higher by 100 to 200 K than the metal temperature. Considering that the reduction reaction proceeds in the slag phase, the inclination of the temperature in the bath can be regarded as advantageous because the metal temperature is maintained low and direct reduction by the carbon materials in the slag is accelerated.

4.1.2 Reduction characteristics

Figure 8 shows the relationship between (T.Fe)[*2] in the slag and [C] in the metal when each test was completed. (T.Fe) of the steelmaking slag charged in TEST 1 and TEST 3 and that of the pseudo-steelmaking slag produced in TEST 2 were 16 to 28%. The values of (T.Fe) after reduction vary even in the same test. This is because of variation of the volumes of charged carbon materials and reduction time. This figure produces the following three estimations.

The first point is the reducing power in each test. Compared with TEST 1 and TEST 3, the lower limit of (T.Fe) in TEST 2 is slightly high at 3%. This may be because in TEST 2, since the open-type furnace was used, air was drawn in and thereby the oxygen potential in the furnace was high and Fe and C were oxidized at the same time with slag reduction.

The second point is the relationship between the reducing power and [C] content in hot metal. In a process where the reduction reaction is accelerated by mixing and agitation of slag metal as in the converter type, the [C] content in hot metal works as the driving force of the reduction reaction. However, in TEST 3, even when [C] was low at 2%, (T.Fe) decreased to equal to or lower than 1%. This demonstrates that reduction proceeds in the slag phase.

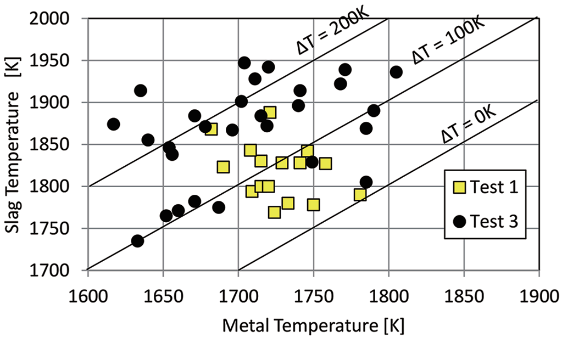

Fig. 7 Relationship between the slag and metal temperature

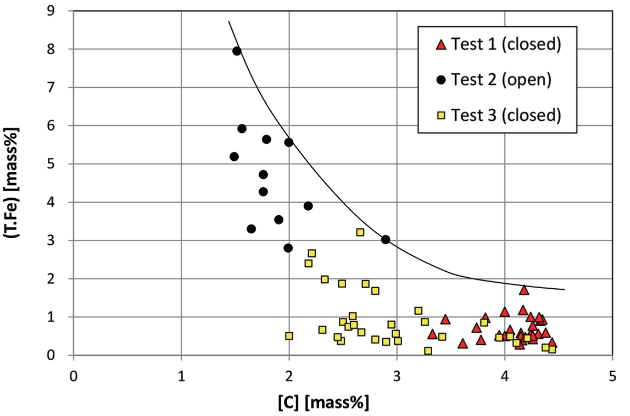

Fig. 8 Relationship between (T.Fe) and [C] in open and closed type furnaces

The third point is the relationship between the upper limit of (T.Fe) and [C] content in hot metal. As [C] is larger, the upper limit of (T.Fe) tends to be lower. That is to say, although the main site of the reduction reaction is in the slag phase, in the region close to [C] saturation, the reduction reaction at the interface between the slag and metal becomes active and (T.Fe) decreases to 1%. On the other hand, when [C] is low at 2%, slag in which (T.Fe) is 5 to 6% can stably exist.

4.1.3 In-furnace flow analysis

For a more in depth understanding of reduction characteristics, FLUENT was used to analyze the flow in an arc furnace. The shape of the furnace was determined based on the pilot test furnace in TEST 3 and a half three-dimensional model was used for simulation. **Figure 9** shows the results. At the center, a downward flow was generated due to electromagnetic force in both the slag phase and metal phase. On the surface of the slag, a flow in the radial direction occurs due to the gas drag force of the arc jet. Part of the carbon powder charged from above was led to the high-temperature region with the downward flow at the center, which contributes to the rapid slag reduction. Part of it dissolved to the metal. The other carbon powder may drift in the slag phase along the radial flow on the surface and may reduce the slag slowly in the low-temperature region. Meanwhile, the interface between the slag and metal is flat and although a counter flow exists, the flow velocity is not high. Based on the flow pattern, the slag reduction reaction may mainly occur at the center in the high-temperature region in particular, in

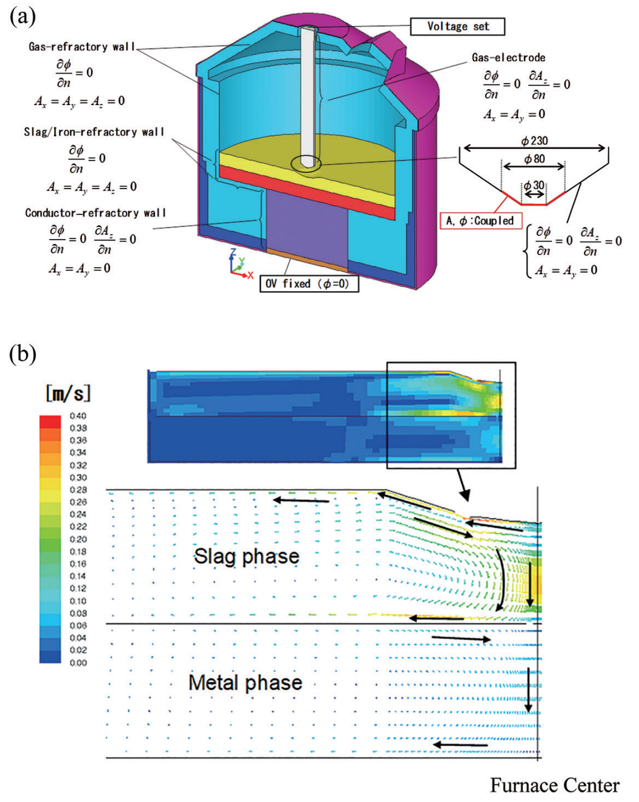

Fig. 9 (a) Calculation condition, (b) Flow pattern in the slag and metal phase

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[*2] (T.Fe): Percent by mass of total Fe in the slag

the slag phase.

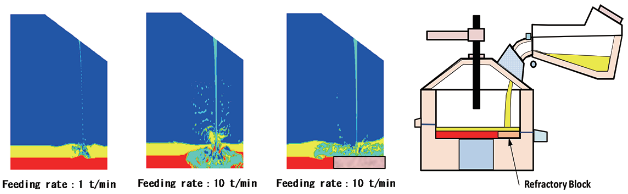
4.1.4 Possibility of charging of molten slag

The main cause of slag foaming is the reduction reaction at the interface between slag and metal.[12)] Since air bubbles generated at the interface are fine, their climbing rate is low and thereby the time during which they remain in the slag becomes longer, which tends to cause foaming. Therefore, this process in which reduction in slag is the main action can be regarded as a process in which foaming does not occur much. However, when molten slag is charged, the risk of foaming increases. Accordingly, FLUENT was used to simulate the behavior of slag and metal when molten slag is charged.

Figure 10 shows the results. When the thickness of the slag is 200 mm and the slag feeding rate is 1 t/min, the interface between the slag and metal is not disturbed; however, when the rate is 10 t/min, an emulsion of the slag and metal is formed. Under this condition, a large volume of CO gas is generated at the interface and that may induce slag foaming. To prevent this, a shallow part was provided at the drop area of the slag. As a result, the emulsion of the slag and metal disappeared and the increase in the interfacial area could be suppressed. In an industrial scale reducing furnace, brick blocks were placed at the drop area of a slag flow. As a result, foaming immediately after slag charge could be completely suppressed. Naturally, after slag is charged, it is necessary to add reducing agents continuously to prevent (T.Fe) in the bulk slag from rapidly increasing in order to suppress foaming. In such a case, as described in the preceding paragraph, using an iron bath with low [C] content can increase the upper limit of (T.Fe) against foaming.

4.1.5 Energy required

Figure 11 shows the required energy intensity calculated assuming an industrial scale reducing furnace. The heat loss from the furnace body estimated from the heat loss per unit area from the furnace body that was obtained in tests is 4000 kW. Sensible heat and reaction heat were calculated from the operation conditions listed in **Table 2**. The required energy when cold slag is charged is 1063 kWh/t-slag while when molten slag at 1583 K is directly charged, it is 586 kWh/t-slag, being lower by 45%. In addition to differences in the slag sensible heat, the loss due to heat radiation is small thanks to the shorter processing time, which contributes to the low energy consumption.



Feeding rate : 1 t/min

Feeding rate : 10 t/min

Feeding rate : 10 t/min

Fig. 10 Behavior of the charged slag into the iron bath obtained by model calculation

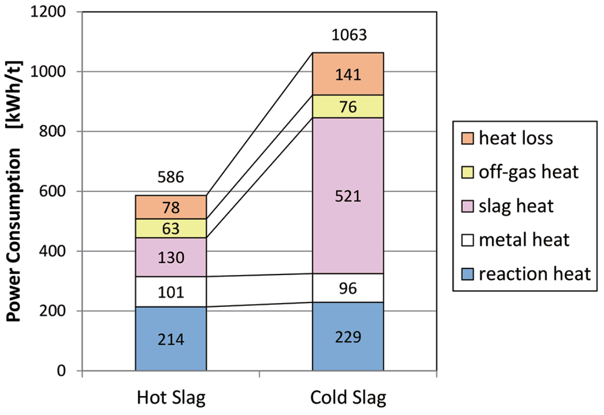


Fig. 11 Comparison of the required energy in each case of hot slag and cold slag charging

4.2 Dephosphorization process

Figure 12 shows the behavior of the (P_2O_5) content in the slag and the [P] content in the metal during dephosphorization that was obtained by continuous sampling at intervals of 10 minutes. For example, starting the initial [P] of 1.5%, as [P] decreases, (P_2O_5) increases and saturates near 30%. This may be because in the region with high (P_2O_5) content, the activity coefficient of P_2O_5 increases and thereby the equilibrium P_2O_5 concentration is suppressed. The inclination of the straight line connecting each data point and the initial [P] on the x-axis expresses the volume of slag while that of the straight line connecting each data point and original point expresses $(P_2O_5)/[P]$, i.e., phosphorus distribution. High concentration of (P_2O_5) can be easily achieved by decreasing the volume of slag and optimizing [P] at the blow-end. However, to decrease [P] to

Table 2 Preconditions for estimating the required power of the process

Furnace capacity		30 MW
Slag bath	Amount	30 t
	Temperature	1873 K
	$(CaO)/(SiO_2)$	1.2
Metal bath	Amount	100 t
	Temperature	1723 K
Charging slag	Amount	30 t
	Temperature	1583 K
	$(CaO)/(SiO_2)$	2.5
Reduced slag	Temperature	1873 K
	$(CaO)/(SiO_2)$	1.2
	(Al_2O_3)	8 %
Off-gas temperature		1573 K
Total heat loss		4000 kW

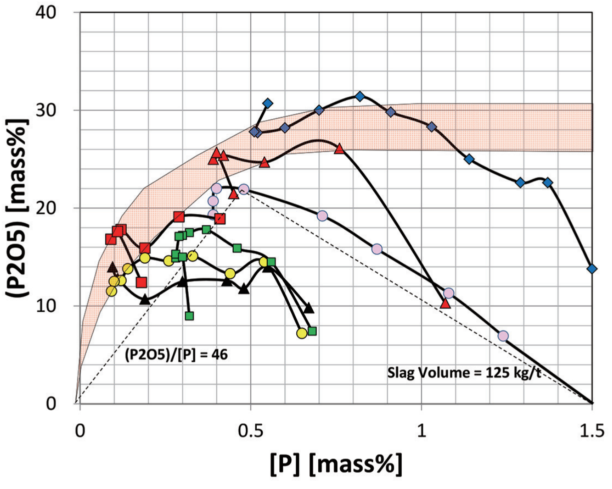


Fig. 12 Behavior of (P_2O_5) and [P] contents during dephosphorization treatment

0.1%, the phosphorus distribution needs to be improved and the upper limit curve of (P_2O_5) needs to be shifted upward as much as possible. In addition, the volume of slag needs to be optimized such that (P_2O_5) is at a high level when [P] is 0.1%.

Figure 13 shows the behavior of [C] and [P] during dephosphorization. In the region with high [P] content, the dephosphorization reaction is dominant while after the transition point, the decarbonization rate quickly increases and the dephosphorization reaction gets delayed. The transition point does not depend on [P]. That is to say, the transfer of phosphorus in metal is not the key factor. **Figure 14** shows changes in (P)/[P] and d[C]/d[P] during dephosphorization. Once (P)/[P] reaches the maximum point, d[C]/d[P] starts rapidly increasing. This shows that the transition point is the point of dephosphorization equilibrium. To avoid the decarbonization rate from rapidly increasing until [P] decreases to 0.1% or lower, the phosphorus distribution in the region with [P] of 0.1% needs to be improved and the upper limit curve of (P_2O_5) needs to be shifted upward as much as possible.

Figures 15 and **16** show the relationship between (P_2O_5) and [P] when (P)/[P] reached the maximum point in each test. Figure 15 shows the relationship in the case of (CaO)/(SiO_2) and Fig. 16 shows it when stratified with (T.Fe). These figures show that to improve the phosphorus distribution and shift the upper limit of (P_2O_5) upward, increasing (CaO)/(SiO_2) and decreasing (T.Fe) are effective.[12)] For slag with high (P_2O_5) content, to settle P_2O_5 in the slag as $3CaO\text{-}P_2O_5$ and $5CaO\text{-}P_2O_5\text{-}SiO_2$, a considerable volume of CaO is required and thereby it is more important to increase the basicity compared with regions with low (P_2O_5) content.

On the other hand, regarding (T.Fe), correlation different from the relationship between oxygen potential and phosphorus distribution was observed. It should be interpreted that although (T.Fe) is naturally required to some extent to oxidize phosphorus, the necessary (T.Fe) is smaller than 10% and (T.Fe) more than necessary decreases (P_2O_5) conversely. Possible two reasons are as follows: The first point is that as (T.Fe) increases, the concentration of (P_2O_5) relatively decreases due to mass balance. The second point is that decrease in (T.Fe) increases the melting point and the slag solidifies. At that time, P_2O_5 is linked to CaO to become $3CaO\text{-}P_2O_5$ and $5CaO\text{-}P_2O_5\text{-}SiO_2$ without phosphor transfer and they remain in the solidified slag.

The results above have confirmed that high basicity and low (T.Fe) content are important factors to achieve dephosphorization of high phosphorous hot metal.

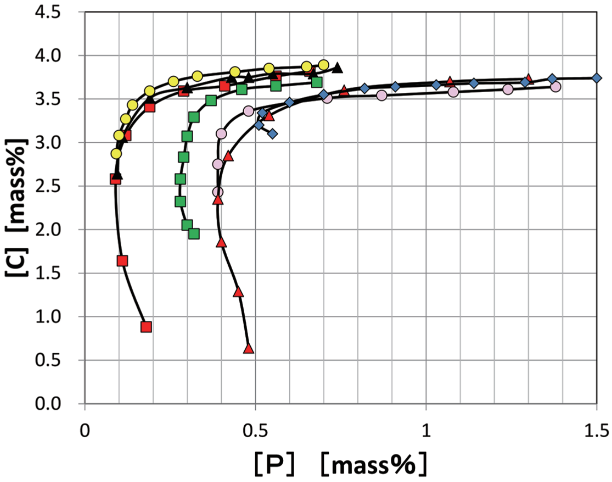


Fig. 13 Behavior of [C] and [P] contents during dephosphorization treatment

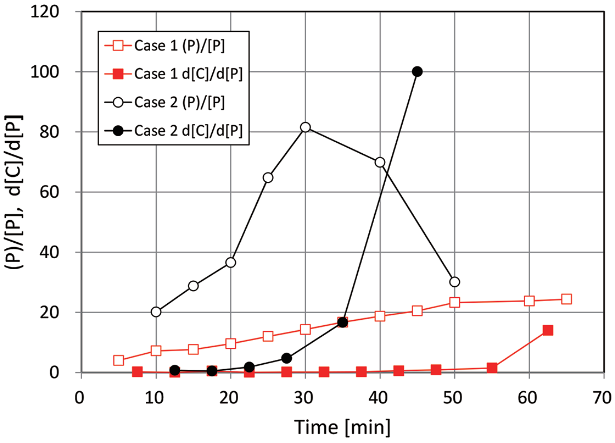


Fig. 14 Behavior of (P)/[P] and d[C]/d[P] during dephosphorization treatment

5. Conclusions

To realize the complete utilization process of steelmaking slag, pilot plant tests of the reduction and dephosphorization processes

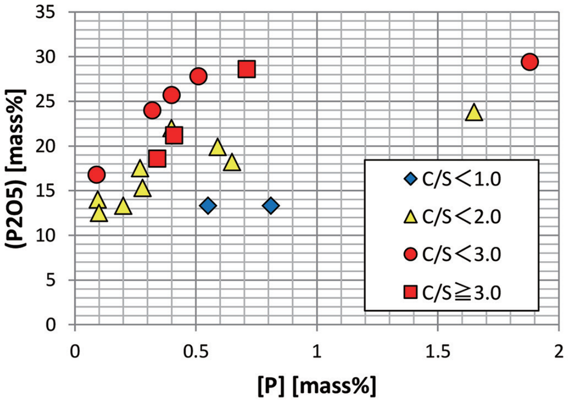


Fig. 15 Influence of (CaO)/(SiO_2) upon maximum (P_2O_5) at each heat

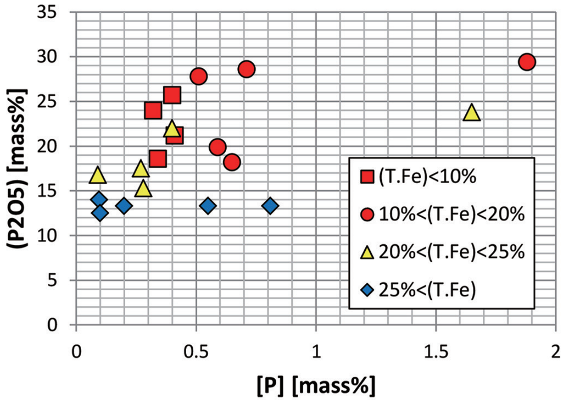


Fig. 16 Influence of (T.Fe) upon maximum (P_2O_5) at each heat

were performed and the following knowledge was acquired.

(1) (T.Fe) can be decreased to 1% or lower by reducing steelmaking slag with C using a closed-type DC arc furnace with air shut off.

(2) Since the reduction reaction mainly proceeds in the slag phase, the reduction of steel is possible even when the [C] content is low and foaming is suppressed since the interference between the slag and metal is small.

(3) When molten slag is charged, a shallow part provided at the drop area can prevent the slag from mixing with the metal and thereby the slag can be quickly charged while slag foaming is suppressed.

(4) Direct reduction of molten slag can decrease the energy consumption to half compared with when cold slag is used.

(5) To dephosphorize hot metal to [P] of 0.1% or lower and at the same time obtain slag with high (P_2O_5) that can be phosphate fertilizers, (P)/[P] needs to be improved and the volume of slag needs to be optimized.

(6) To improve (P)/[P], improving (CaO)/(SiO_2) and decreasing (T.Fe) are necessary.

The complete utilization process of steelmaking slag is a drastic reform of the refining process. That may solve issues in the future to provide energy saving by using hot slag, CO_2 emissions reduction by using electric energy, recovery of unused iron and phosphorus resources, slag with higher value added, effective use of waste, and environmental measures against dust. We will work to seek economical rationality of manufacturing processes and improve the commercial values of fertilizers and other products.

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