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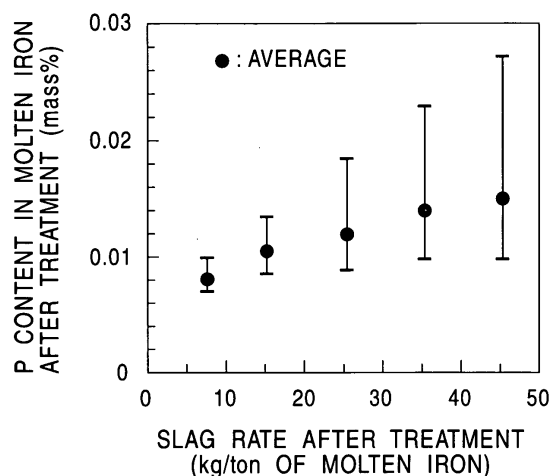
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(74) Representative: **HOFFMANN - EITLE****Patent- und Rechtsanwälte****Arabellastrasse 4****81925 München (DE)**(54) **METHOD OF MANUFACTURING LOW PHOSPHOROUS HOT METAL**

(57) The invention is to implement an efficient dephosphorization treatment without adding a large amount of CaF_2 and with a small addition amount of a refining agent. The invention is made based on the finding that a very efficient dephosphorization refinement utilizing an inhomogeneous molten state of slag can be implemented by feeding a gaseous oxygen and a refining agent onto a bath surface of a molten iron in a specific mode under conditions wherein a post-treatment slag is reduced appreciably in comparison to a conventional case. The dephosphorization treatment is performed by blowing the gaseous oxygen and at least a part of the refining agent onto the bath surface of the molten iron through a top blowing lance. Concurrently, the post-treatment slag rate is controlled to 30 kg/ton of molten iron or less, preferably to 20 kg/ton of molten iron or less, and more preferably 10 kg/ton of molten iron or less. In addition, the dephosphorization treatment be performed for an molten iron having a Si content of 0.15 mass% or less, more preferably 0.07 mass% or less, and particularly preferably 0.03 mass% or less.

FIG. 1

Description**FIELD OF THE INVENTION**

[0001] The present invention relates to a method for efficiently producing a low-phosphorous molten iron by performing a dephosphorization treatment as a molten iron preliminary treatment.

DESCRIPTION OF THE RELATED ARTS

[0002] Instead of conventional converter-using methods, molten iron preliminary treatment methods that perform a dephosphorization treatment in a molten iron stage are enjoying wide use. This is attributable to an advantage of the molten iron preliminary treatment method. In the method, as the refining temperature is lower, dephosphorization reactions are more facilitated to progress in terms of thermodynamics, and so that the dephosphorization treatment can be accomplished with a smaller amount of a refining agent.

[0003] Generally speaking, in the molten iron preliminary treatment, a desiliconization treatment is first performed by adding a solid oxygen source such as iron oxide, and the dephosphorization treatment is then performed by using a refining agent after removing slag occurred in the desiliconization treatment. Ordinarily, a CaO based refining agent, such as lime, is used as a refining agent, and a solid oxygen source (iron oxide, for example) or gaseous oxygen is used as oxygen source. As a treatment vessel, a torpedo car, a ladle (charging ladle), a converter type vessel, or the like vessel is used.

[0004] By way of example, Japanese Unexamined Patent Publication No. 07-70626 discloses as conventional dephosphorization treatment conditions: slag basicity = 0.6 - 2.5; treatment termination temperature = 1,250 - 1,400°C; bottom blowing agitation force = 1.0 kg/ton of molten iron or more; oxygen supplying rate = 2.5 Nm³/ton of molten iron or higher. This technique is described that the slag basicity is controlled to 2.5 or less for the reason that slag fluidity is deteriorated at a basicity higher than the set value. This requires the treatment to be performed at a high temperature that is disadvantageous to dephosphorization. Additionally, it is described that when the basicity is 2.5 or less, the more the slag basicity, the more the dephosphorization progresses.

[0005] In addition, Japanese Unexamined Patent Publication No. 08-311523 discloses a method of blowing CaO powder and oxygen of 0.7 to 2.0 Nm³/min/ton of molten iron in a converter-type vessel, and concurrently, blows an agitation gas of 0.5 to 0.30 Nm³/min/ton of molten iron from the bottom of a furnace or a sidewall of the converter-type vessel. This method is described that the oxygen supplying amount in top-blowing refining is optimized to implement the optimization of quick generation of slag (dissolution of the CaO) and the FeO concentration in the slag, whereby an efficient dephosphorization treatment can be implemented.

[0006] As can be known from discussions made with reference to the dephosphorization equilibrium method, conventional molten iron dephosphorization refining techniques, such as those disclosed in the Japanese Unexamined Patent Publications No. 07-70626 and No. 08-311523, are constituted on a prerequisite that post-treatment slag is equally melted, and the slag-metal conditions are close to equilibrium. As such, the slag dephosphorization capability (phosphorus distribution $L_p = \text{mass\% (P)}/\text{mass\% [P]}$; mass% (P): P concentration in the slag; and mass% [P]: P content in the metal), the slag volume, and the like are also determined under such the prerequisite, and the operation is carried out.

[0007] The phosphorus distribution L_p of the slag is dependent on the slag basicity; and the higher the slag basicity is, the lower the phosphorus distribution L_p . Conventionally, however, it has been considered that the higher the slag basicity, the lower the slag fluidity, whereby the dephosphorization conditions are worsened. On the other hand, as the slag basicity is reduced, the phosphorus distribution L_p also is reduced, so that the slag rate should be increased by adding much lime (also SiO₂ source by necessity).

[0008] As described above, according to the conventional techniques, the slag basicity necessary to secure the predetermined phosphorus distribution L_p is set, the slag rate necessary to reach the object P is determined, and the refining agent is then added. However, because of the relationship with the slag fluidity, the slag basicity cannot be increased so much. For this reason, in a normal dephosphorization treatment for a molten iron with a Si content of about 0.2 mass%, the operation is performed with a slag rate (post-treatment slag rate) of about 40-50 kg/ton of molten iron. For example, according to Japanese Unexamined Patent Publication No. 08-311523, the feed amount of CaO (refining agent) is determined in accordance with the P content; and when a pre-treatment P content is about 0.10 mass% of a normal level, the CaO is fed at a rate of about 20 kg/ton of molten iron. However, the slag existing in the refining vessel during the dephosphorization refinement consists of various substances. The substances are, for example, slag generated with the above-described CaO having been fed and various other substances such as a SiO₂ part generated by desiliconization reaction of the molten iron, a P₂O₅ part generated by dephosphorization reaction, a slag part generated from molten iron ingredients (FeO and MnO, for example), a slag part carried over from the previous processing step, a slag part (Al₂O₃ and MgO, for example) generated due to a melt loss of the furnace body,

a slag part originally adhered to the furnace body, a slag part adhered to fed scrap and carried over, and a slag part generated from added ore and the like. With these added substances, the amount of slag existing in the refining vessel is increased to about 2 to 2.5 times the amount of the CaO having been fed. As such, as described above, when the CaO of about 20 kg/ton of molten iron is fed, the post-treatment slag rate inevitably reaches the level of about 40-50 kg/ton of molten iron.

[0009] In recent years, from the viewpoints of environmental protection and the like, the amount of slag to be generated in refining steps including the dephosphorization step is required to be minimized. However, the conventional techniques as described above are limited in the capability of reducing the slag rate, so that the techniques cannot sufficiently respond to the requirements for reducing the amount of the occurring slag.

[0010] In connection with the addition of CaF_2 for accelerating dissolution of the refining agent, in recent years, the use amount of CaF_2 is required to be minimized also in refining steel, taking influence of F on the environment into consideration. As such, improvement in the dephosphorization efficiency through the addition of CaF_2 is limited.

SUMMARY OF THE INVENTION

[0011] It is an object of the invention to provide a method for producing a low-phosphorous molten iron that is capable of performing an efficient dephosphorization treatment without requiring addition of much CaF_2 and with a small addition of a refining agent, thereby enabling the generated slag to be minimized.

[0012] In a dephosphorization refinement of a molten iron, the oxygen source and a refining agent acting as a CaO source are added to the molten iron. As a method of supplying the oxygen source, methods of the type that blows a gaseous oxygen onto a bath surface of the molten iron from a top blowing lance is suitable in that that concurrently with inhibition of temperature drop, the generation of FeO can be effectively promoted. According to the oxygen supplying method of that type, the inside of a refining vessel is separated into two portions. In the one portion, the bath surface (bath surface of the molten iron) is pushed out by the energy of the gaseous oxygen to be exposed; and in the other portion, the bath surface is covered by the slag. In the inside of the refining vessel, the slag-existing state is not uniform. As such, not sticking to conventional concepts of keeping the slag to be in a uniform state, the inventors conducted research for a dephosphorization refinement method that is capable of stabilizing dephosphorization efficiency with a small addition amount of the refining agent. As a result, the inventors found that under a condition where an amount of post-treatment slag is appreciably reduced in comparison to the conventional techniques, and more preferably, under a condition where the Si content in the pre-treatment molten iron is set not higher than a predetermined level, when the gaseous oxygen and the refining agent are supplied in a specific manner onto the bath surface of the molten iron, there can be implemented a very efficient dephosphorization refinement using a nonuniform molten state to which is converse to the conventional concept of uniformly melting the slag.

[0013] A method for producing a low-phosphorous molten iron according to the present invention has been developed in accordance with the knowledge described above. A feature of the inventive method is that in a method for producing a low-phosphorous molten iron in a manner that an oxygen source and a refining agent acting as a CaO source are added into a vessel containing a molten iron and a dephosphorization treatment as an molten iron preliminary treatment is thereby performed, the method being characterized in that the dephosphorization treatment is performed by blowing a gaseous oxygen and at least a part of the refining agent onto a bath surface of the molten iron through a top blowing lance; and a post-treatment slag rate is 30 kg/ton of molten iron or smaller. In this case, preferably, the post-treatment slag rate is preferably 30 kg/ton of molten iron or smaller. More preferably, the post-treatment slag rate is 10 kg/ton of molten iron or smaller. However, the method uses a direct dephosphorization reaction in the region of the bath surface onto which the gaseous oxygen has been blown and also uses a mechanism to fix P through a solid-phase base slag in a region outside the region of the bath surface. Thereby, an efficient dephosphorization treatment can be implemented without a large addition amount of CaF_2 and with a small addition amount of the refining agent.

[0014] To make the effects of the present invention even higher, the dephosphorization treatment is preferably applied to a low Si molten iron. More specifically, the dephosphorization treatment is preferably applied to a 0.7 mass% or lower molten iron and is more preferably applied to a 0.03 mass% or lower molten iron, thereby enabling an optimal condition to be provided to stably cause the dephosphorization reaction by the above-described mechanism.

[0015] As a mode of adding refining agent fed from the top blowing lance, at least the part of the refining agent to be fed from the top blowing lance is preferably blown onto a region of the bath surface of the molten iron onto which the gaseous oxygen has been blown. More preferably, at least the part of the refining agent is blown onto a hot spot formed on the bath surface of the molten iron by blowing the gaseous oxygen. It is further preferable that at least the part of the refining agent be blown with the oxygen gas as a carrier gas. These arrangements enables the refining agent to be efficiently to melt in the region of the bath surface where a large amount of FeO are generated with the feeding of the gaseous oxygen, and consequently enables the dephosphorization reaction to be effectively promoted.

[0016] According to the present invention, an efficient dephosphorization treatment can be implemented under a condition wherein the addition amount of CaF_2 is 2 kg/ton of molten iron is smaller or CaF_2 is substantially not added.

[0017] In the present invention, it is preferable that a molten iron having a P content of 0.10 mass% or more be dephosphorized and refined to have a P content required for crude steel (steel ingredient standard value); and it is particularly preferable that the P content in the molten iron after the dephosphorization treatment be 0.010 mass% or less. In this case, substantially no slag seed material has to be used in a converter refinement in a subsequent step,

[0018] The present invention allows various preferred embodiments, as described hereunder, to be carried out under the basic conditions described above.

[0019] According to a first embodiment, a dephosphorization treatment is performed so that a supplying rate B in terms of CaO (kg/min/ton of molten iron) of the refining agent to be blown onto the bath surface of the molten iron and a supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron satisfy Equation (1) below, and preferably Equation (2) below. This optimizes the balance between a generation amount of FeO dependent on the feeding of the gaseous oxygen and a feed amount of the CaO, consequently enabling an even higher dephosphorization efficiency to be secured.

$$0.3 \leq A/B \leq 7 \quad (1)$$

$$1.2 \leq A/B \leq 2.5 \quad (2)$$

[0020] According to a second embodiment, the dephosphorization treatment is performed by using a ladle or a torpedo-car type vessel as a vessel for holding the molten iron. Concurrently, the gaseous oxygen and at least a part of the refining agent are blown onto the bath surface of a molten iron through the top blowing lance, and gas including powder is injected into the molten iron through an immersed lance and/or a blowing nozzle lance. Thereby, in the dephosphorization treatment using the ladle or the torpedo-car type vessel, an appropriate agitation effect of the molten iron can be attained, and even higher dephosphorization efficiency can be secured.

[0021] In the second embodiment, the powder to be injected into the molten iron through the immersed lance and/or the blowing nozzle is preferably the part of the refining agent. In addition, a supplying rate of the gaseous oxygen to be blown onto the bath surface of the molten iron through the top blowing lance is preferably 0.7 Nm³/min/ton of molten iron or less. Further, 80 mass% or more of the addition amount of the refining agent in the dephosphorization treatment is preferably blown onto the bath surface of the molten iron to effectively implement the process. When adding substantially all of the refining agent by being blown onto the bath surface of the molten iron through the top blowing lance and by being injected into the molten iron through the immersed lance and/or the blowing nozzle, the addition amount of the refining agent through the top blowing lance is preferably 20 to 80 mass% of the total amount of the refining agent. Thereby, the effect of blowing the refining agent on the bath surface of the molten iron and the agitation effect of blowing thereof into the molten iron can be secured with good balance.

[0022] According to a third embodiment, the dephosphorization treatment is performed so that the supplying rate of the refining agent to be blown onto the bath surface of the molten iron and the supplying rate of the gaseous oxygen to be blown onto the bath surface of the molten iron satisfy Equations (3) and (4) below:

$$(C1/D1) > (C2/D2) \quad (3)$$

$$C1 > C2 \quad (4)$$

[0023] In these equations:

C1 = average value of supplying rates in terms of CaO of the refining agent in the earlier stage of the dephosphorization treatment (kg/min/ton of molten iron);

C2 = average value of supplying rates in terms of CaO of the refining agent in the latter stage of the dephosphorization treatment (kg/min/ton of molten iron);

D1 = average value of supplying rates of the gaseous oxygen in the earlier stage of the dephosphorization treatment (Nm³/min/ton of molten iron); and

D2 = average value of supplying rates of the gaseous oxygen in the latter stage of the dephosphorization treatment (Nm³/min/ton of molten iron).

[0024] In the third embodiment, the supplying rate in terms of CaO of the refining agent and the supplying rate of

the gaseous oxygen can be continually and/or gradually varied during the dephosphorization treatment.

[0025] According to a fourth embodiment, the dephosphorization treatment is performed for a molten iron having a Si content of 0.15 mass% or lower by blowing the gaseous oxygen and at least a part of the refining agent onto the bath surface of the molten iron through the top blowing lance. In addition, lime is added as the refining agent in the dephosphorization treatment, wherein the supplying amount of the lime is the sum of a lime amount W_{CaO_P} (kg/ton of molten iron) obtained from Equation (5) below and a lime amount W_{CaO_Si} (kg/ton of molten iron) obtained from Equation (6) below.

$$W_{CaO_P} = (\text{molten iron [P]} - \text{object [P]}) \times (10/62) \times 56 \times 3/\eta_{CaO} \quad (5)$$

[0026] Where:

molten iron [P] = P content (mass%) in the molten iron before the dephosphorization treatment;
object [P] = P content (mass%) in the molten iron after the dephosphorization treatment; and
 η_{CaO} (lime efficiency) = 0.5 to 1

$$W_{CaO_Si} = (\text{molten iron [Si]} \times (10/28) \times 56 \times 2) \quad (6)$$

[0027] In the expression:

molten iron [Si] = Si content (mass%) in the molten iron before the dephosphorization treatment.

[0028] In the fourth embodiment, the lime in the amount of 80 mass% or more of the lime amount W_{CaO_P} (W_{CaO_P} obtained when $\eta_{CaO} = 1$) is preferably blown onto the bath surface of the molten iron through the top blowing lance to implement an efficient treatment. For the refining agent corresponding to the lime amount W_{CaO_Si} , at least one selected from powdered lime, massive burnt lime, massive limestone, and iron-making slags containing unreacted CaO can be used.

[0029] According to a fifth embodiment, a depth L of a concave, which occurs in the bath surface of a molten iron in association with blowing of the gaseous oxygen thereonto or blowing of the refining agent thereonto with the gaseous oxygen being used as the carrier gas, is controlled to 200 to 500 mm, the depth L being defined by Equation (7) below. Thereby, the feeding mode for the gaseous oxygen onto the hot spot, which is a reaction site, is optimized, and the dephosphorization treatment can be implemented even more efficiently with a small addition amount of refining agent.

$$L = L_0 \times \exp\{(-0.78 \times L_H)/L_0\} \quad (7)$$

$$L_0 = 63 \times \{(F_{O2}/n)/d_t\}^{2/3}$$

[0030] Where:

L_H = lance height (mm) of the top blowing lance;

F_{O2} = supplying rate (Nm³/hr) of the gaseous oxygen to be fed from the top blowing lance;

n = number of nozzle holes of the top blowing lance; and

d_t = diameter (mm) of each of the nozzle holes of the top blowing lance (which alternatively represents an average hole diameter of all the nozzle holes in a case where the nozzle diameters of the plurality of nozzle holes are different).

[0031] According to a sixth embodiment, the dephosphorization treatment is performed for an molten iron having a Si content of 0.15 mass% or lower by blowing the gaseous oxygen and at least a part of the refining agent onto the bath surface of the molten iron through the top blowing lance in a condition wherein the addition amount of CaF₂ is 1 kg/ton of molten iron or smaller or CaF₂ is substantially not added; and the temperature of the molten iron at completion of the dephosphorization treatment is controlled to 1,360°C to 1,450°C. Thereby, the dephosphorization treatment can be performed even for a high temperature process, whereby a sufficient heat can be secured in latter processing steps.

[0032] According to a seventh embodiment, a substance absorbing heat of the molten iron through a chemical reaction and/or a thermal decomposition reaction is fed onto the region of the bath surface to which the gaseous oxygen is fed. Thereby, without interfering melting of the refining agent the substance enables inhibition of the temperature

rise in the region of the bath surface whereon the gaseous oxygen is fed. Consequently, even higher dephosphorization efficiency can be secured.

[0033] In the seventh embodiment, at least a part of the substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction is preferably fed onto the hot spot occurring on the bath surface of the molten iron by being blowing the gaseous oxygen. Preferably, the substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction is at least one selected from carbon dioxide, water vapor, nitrogen oxide, metal carbonate and metal hydroxide. Particularly, it is preferable that the substance is at least one selected from metal carbonate that generates CO_2 or H_2O through thermal decomposition and metal hydroxide that generates CO_2 or H_2O through thermal decomposition. More preferably, the substance is at least one selected from CaCO_3 , Ca(OH)_2 , and $\text{CaMg(CO}_3)_2$.

[0034] Additionally, in the seventh embodiment, as the substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction, instead of the part or all of the refining agent acting as CaO source, at least one selected from CaCO_3 , Ca(OH)_2 , and $\text{CaMg(CO}_3)_2$ may be fed onto the region of the bath surface. In this embodiment, at least part of the at least one selected from CaCO_3 , Ca(OH)_2 , and $\text{CaMg(CO}_3)_2$ is preferably fed onto the hot spot occurring on the bath surface of the molten iron by blowing the gaseous oxygen.

[0035] The above-described first to seventh embodiments of the inventive method may be individually practiced; or alternatively, two or more of the conditions of the embodiments may be arbitrarily combined for practical application. In this case, the effects of the present invention may be enhanced in proportion to the increase in the number of combination conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0036]

FIG. 1 is a graph of showing the relationship between the slag rate and the P content in a molten iron after a dephosphorization treatment.

FIG. 2 is a graph showing the relationship between the Si content in the molten iron before the dephosphorization treatment and the slag rate in the molten iron after the dephosphorization treatment.

FIG. 3 is an explanatory view showing an application example of an inventive method using a converter-type vessel.

FIG. 4 is a graph showing the relationship between the ratio of the addition amount of a refining agent fed through the top blowing lance with respect to the total amount of the refining agent and the amount of necessary lime in a second embodiment of the present invention.

FIG. 5 is a graph showing the relationship between the ratio of the addition amount of the refining agent fed through the top blowing lance with respect to the total amount of the refining agent and the dephosphorization rate when adding the total amount of the refining agent by being blown onto a bath surface of the molten iron and by being injected into the molten iron through an immersed lance and/or a blowing nozzle in the second embodiment of the present invention.

FIG. 6 is an explanatory view showing an application example of the second embodiment of the present invention.

FIG. 7 is a graph showing the relationship between a CaO unit consumption necessary to cause the P content in a molten iron after the dephosphorization treatment to be 0.012 mass% and the efficiency of dephosphorization in each of a third embodiment of the present invention and a conventional method.

FIG. 8 is a graph showing the relationship between the Si content in a molten iron and the necessary amount of lime in each of a fourth embodiment of the present invention and the conventional method.

FIG. 9 is a graph showing the relationship between the necessary amount of lime for dephosphorization and a lime efficiency η_{CaO} and the P content in the molten iron after the dephosphorization treatment in each of the fourth embodiment and the conventional method.

FIG. 10 is a graph showing the relationship between a ratio $X/W_{\text{CaO_P}}$ between a lime amount X of lime and a lime amount $W_{\text{CaO_P}}$ of the lime for dephosphorization, which are blown onto the bath surface of the molten iron from the top blowing lance, and the P content in the molten iron after the dephosphorization treatment in the fourth embodiment of the present invention.

FIG. 11 shows graphs each illustrating the relationship between a depth L of a concave, which occurs in the bath surface of a molten iron in association with blowing of the gaseous oxygen thereonto or blowing the refining agent thereonto with the gaseous oxygen being used as a carrier gas, and the efficiency of dephosphorization, and the relationship between the depth L and the P content in the molten iron after the dephosphorization treatment in a fifth embodiment of the present invention.

FIG. 12 is a graph showing the relationship between the Si content in a molten iron, the molten iron temperature after the dephosphorization treatment, and the dephosphorization lime efficiency in the dephosphorization treatment without CaF_2 being added in a sixth embodiment of the present invention.

FIG. 13 is a graph showing the relationship between the amount of CaF_2 and the dephosphorization lime efficiency in the dephosphorization treatment at the molten iron temperature of 1,360 to 1,450°C after the dephosphorization treatment without CaF_2 being added in the sixth embodiment of the present invention.

FIG. 14 shows explanatory views each illustrating an example of a feeding mode using the top blowing lance for feeding the gaseous oxygen, the refining agent, and an endothermic substance onto the bath surface of the molten iron in a seventh embodiment of the present invention.

FIG. 15 shows explanatory views each schematically showing a slag/metal state at a molten iron discharge start time in each of the conventional method and the present invention.

FIG. 16 shows explanatory views each showing a slag/metal state in the vicinity of a molten iron discharge end in a molten iron discharge termination time in each of the conventional method and the present invention.

FIG. 17 is a graph showing the relationship between a ratio A/B and the P content in an molten iron after the dephosphorization treatment, the ratio A/B being a ratio between a supplying rate A of the gaseous oxygen and a supplying rate B of a CaO based refining agent in the first embodiment of the present invention.

DESCRIPTION OF THE EMBODIMENT

[0037] According to conventionally developed dephosphorization mechanisms, CaO added into a refining vessel reacts with SiO_2 and FeO generated with the feeding of oxygen to become a melt. Thereby, CaO- SiO_2 -FeO based slag is generated that is homogeneous and that has high dephosphorization capability, and dephosphorization of a molten iron progresses with the reaction between the slag and P in the molten iron. As described above, with the dephosphorization mechanism being used as a prerequisite, by taking the fluidity and dephosphorization capability of the slag into account, the slag basicity is determined, and the slag rate necessary for the molten iron to reach the object P is determined. In this connection, the inventors found the following. Under a condition where a amount of post-treatment slag is appreciably reduced in comparison to the conventional techniques, and more preferably, under a condition where the Si content in the pre-treatment molten iron is set not higher than a predetermined level, when a process method is employed to blow a gaseous oxygen and a refining agent through a top blowing lance onto the bath surface of the molten iron, there can be implemented a very efficient dephosphorization refinement using a mechanism that is completely different from the conventional technique.

[0038] Details of the present invention in accordance with the knowledge described above and preferred embodiments will be described hereinbelow.

[0039] An inventive method is applied in the event of making a low-phosphorous molten iron in a manner that an oxygen source and a refining agent acting as a CaO source are added into a vessel containing an molten iron and a dephosphorization treatment as a molten iron preliminary treatment is thereby performed. At this event, according to the inventive method, a dephosphorization treatment is performed by blowing gaseous oxygen and at least a part of the refining agent onto a bath surface of the molten iron through a top blowing lance. When the gaseous oxygen is blown onto the bath surface of the molten iron through the top blowing lance, the gaseous oxygen impinges on the bath surface caused a large amount FeO to occur. In this case, the condition is made a very advantageous to promote dissolution of the refining agent, and the refining agent is directly fed to a region where the large amount of FeO has been generated, whereby the dissolution of the refining agent (CaO) can be effectively promoted.

[0040] In the event of the blowing of the gaseous oxygen and the refining agent onto the bath surface of the molten iron through the top blowing lance, a carrier gas (inert gas such as N_2 or Ar) other than the refining agent and the gaseous oxygen may be used the blowing onto the bath surface of the molten iron. Even in this event, preferably, a part or the entire refining agent is blown to the region of the bath surface onto which the gaseous oxygen is fed (blown). The reasons for the above are as described hereunder. The region of the bath surface where the gaseous oxygen is fed is a region where FeO is generated with the feeding of oxygen. With the CaO being directly added onto the bath surface region, the dissolution of the CaO is effectively accelerated, a CaO-FeO contact effect is increased. In the region of the bath surface onto which the gaseous oxygen is fed, a most preferable region onto which the refining agent is to be blown is a region called a "hot spot" caused by top blowing of the gaseous oxygen. In the hot spot thus occurring in the region of the bath surface, the temperature is increased highest due to impingement on gaseous-oxygen jets, oxidation reactions caused by the gaseous oxygen are concentrated, and the molten iron is agitated with the gaseous-oxygen gas jets. As such, the hot spot can be defined as a region where the most prominent effect with the feeding of the CaO can be obtained. For this reason, the gaseous oxygen is preferably used as the carrier gas for blowing the refining agent onto the bath surface of the molten iron. In this case, the refining agent is directly fed to the hot spot, consequently causing the CaO-FeO contact effect to be increased highest.

[0041] In the inventive method, the adding mode for the gaseous oxygen and the refining agent, as described above, is aimed to cause an efficient dephosphorization reaction by use of a basic mechanism described hereunder.

[0042] More specifically, the refining agent (CaO) is blown onto the region of the bath surface (preferably, the hot spot) to which the gaseous oxygen is fed under an optimal condition through the top blowing lance. Thereby, the CaO

quickly reacts with FeO that is generated at the hot spot and is melted (dissolved) to form a CaO-FeO based melt. The generated CaO-FeO based melt is pushed out according to the kinetic energy to a region with a low oxygen potential in the periphery of the region of the bath surface from the region of the bath surface to which gaseous oxygen with the hot spot in the center is fed. Concurrently, the melt first reacts with Si in the molten iron, whereby the FeO is reduced, and a stable solid phase, such as $2\text{CaO} \cdot \text{SiO}_2$, corresponding to the Si content in the pre-treatment molten iron. When the Si content in the molten iron is reduced by the above-described reaction lower to a certain level, the CaO-FeO based melt subsequently begins to react with the phosphorus to form a $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid phase similar to the above. As a consequence, an equivalent amount (or most) of slag that is progressively generated with the progress of the dephosphorization treatment and that is sequentially pushed out to an outer region of the region of the bath surface of the molten iron from the region of the bath surface to which the gaseous oxygen with the hot spot in the center is present as the stable $2\text{CaO} \cdot \text{SiO}_2$ or $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid phase. The slag thus formed as the solid phase is so stable that the slag is never melted again even when the slag basicity is low. Thus, the direct dephosphorization reactions take place in the region having the hot spot in the center, the slag pushed out to the outer region of that region exists in the solid-state state. This enables the dephosphorization treatment to be implemented with a small addition amount of the refining agent.

[0043] Thus, the inventive method is aimed for implementing the efficient dephosphorization treatment by using the mechanism in which the direct dephosphorization reactions take place in the region of the bath surface with the hot spot in the center and P is fixed by the slag present as the solid phase object in the outer region of that region of the bath surface. However, stable dephosphorization reactions according to the mechanism cannot be implemented only by blowing the gaseous oxygen and the refining agent onto the bath surface of the molten iron. To implement stable dephosphorization reactions in the above-described mechanism, the process should be performed under conditions in which the slag rate is sufficiently small, in addition to the condition of using the above-described specific feeding mode for the gaseous oxygen and the refining agent. More specifically, the dephosphorization treatment is required under a condition the post-treatment slag rate is 30 kg/ton of molten iron, preferably 20 kg/ton of molten iron, and more preferably, 10 kg/ton of molten iron. In addition, from a similar viewpoint, an object molten iron for the dephosphorization treatment is preferably a low Si molten iron; more specifically, the Si content is preferably 0.15 mass% or lower, more preferably 0.07 mass% or lower, and even more preferably 0.03 mass% or lower.

[0044] Described hereunder are reasons that the process is performed with the small amount of slag. In order to cause the dephosphorization reactions with the above-described specific mechanism, the gaseous oxygen should be fed through the top blowing lance onto the bath surface of the molten iron with a so-called soft blow (low dynamic pressure). More specifically, in the dephosphorization reaction through the above-described specific mechanism, a FeO generation region where FeO is generated is the region of the bath surface which has the hot spot in the center and to which the gaseous oxygen is fed is a main FeO generation region. The CaO fed into this region and dissolved therein directly reacts with the FeO, whereby a CaO-FeO based melt is thereby generated. The CaO-FeO based melt directly reacts with P in the molten iron, and a stable $3\text{CaO} \cdot \text{P}_2\text{O}_5$ solid phase is thereby formed. Suppose now that the gaseous oxygen is fed with the soft blow (low dynamic pressure) in a state where the slag rate is large and a thick slag layer is generated, as in the conventional technique. In this case, the gaseous-oxygen gas jet is unable to penetrate the slag layer, so that the gaseous oxygen cannot be appropriately fed onto the bath surface of the molten iron. As such, the generation amount of the FeO on the bath surface of the molten iron is insufficient, whereby also the generation amount of the CaO-FeO based melt is small. In comparison to the above, suppose that when the gaseous oxygen is fed with a hard blow (high dynamic pressure) so that the gaseous-oxygen gas jet penetrates the slag layer generated to be thick. In this case, the feed region to which the gaseous oxygen is fed becomes a violent agitation state, so that even when FeO is generated, the FeO is reduced by C in the molten iron. Resultantly, in this case also, a necessary amount of FeO cannot be secured, whereby also the generation amount of the CaO-FeO based melt also is small. As described above, in the case where the slag rate is large, even when the gaseous oxygen is fed either the soft blow or the hard blow, the generation quantities of, for example, the FeO and CaO-FeO based melt cannot be stably secured. This makes it difficult to cause the dephosphorization reactions through the mechanism described above. For these reasons, indispensable conditions are that the gaseous oxygen be appropriately fed with the soft blow onto the bath surface of the molten iron, and the slag rate be controlled to reduce the thickness of the slag layer to be sufficiently small in order to effectively cause the dephosphorization reactions through the mechanism. In addition, for the reasons described above, the post-treatment slag rate is preferably as small as possible; particularly, the amount is preferably 20 kg/ton of molten iron or smaller, and more preferably 10 kg/ton of molten iron or smaller.

[0045] Reasons that the dephosphorization treatment is preferably performed for the low Si molten iron will be described hereunder. As already described, in the specific dephosphorization mechanism, the CaO fed into the region of the bath surface (= main FeO generation region), which has the hot spot in the center and onto which the gaseous oxygen is fed and dissolved therein, directly reacts with the FeO, whereby the CaO-FeO based melt is generated; and the CaO-FeO based melt directly reacts with P in the molten iron to thereby causes the dephosphorization to progress. In this case, when the Si content in the molten iron is high, the generated CaO-FeO based melt is consumed for the

reactions with the Si to an extent that it does not sufficiently contribute to the direct dephosphorization reaction described above. As such, optimal conditions for stably causing the dephosphorization reaction through the above-described mechanism are that the condition for the above-described post-treatment slag rate be satisfied, and concurrently, the Si content in the molten iron undergoing the dephosphorization treatment be sufficiently low. In addition, when the Si content in the molten iron is low, the SiO_2 generation amount also is low, so that this case is advantageous also to reduce the post-treatment slag rate. For these reasons, in the present invention, the dephosphorization treatment is applied preferably to a molten iron having a Si content of 0.15 mass% or lower, more preferably to a molten iron having a Si content of 0.07 mass% or lower, and even more preferably to a molten iron having a Si content of 0.03 mass% or lower.

[0046] In the present invention, the post-treatment slag rate refers to the amount of slag existing in a refining vessel (molten iron retaining vessel). The post-treatment slag rate can be obtained in various manners. For example, the slag rate was calculated from the mass balance between a amount of added lime and an intra-slag CaO concentration (slag analysis value). In another manner, for example, a post-treatment tracer concentration in the slag is analyzed; and in another manner, the thickness of the slag is directly measured.

[0047] FIG. 1 is a graph of showing the relationship between the slag rate and the P content in an molten iron after a dephosphorization treatment in accordance with the results of tests performed by the inventors. The post-treatment P content in the molten iron indicates the average value and the variation width. More specifically, FIG. 1 shows a summary of P contents in an molten iron after the dephosphorization treatment for 6 to 72 charges in units of a range of individual slag quantities after the process for a range from 5 kg/ton of molten iron to 10 kg/ton of molten iron, a range from larger than 10 kg/ton of molten iron to 20 kg/ton of molten iron, a range from larger than 20 kg/ton of molten iron to 30 kg/ton of molten iron, a range from larger than 30 kg/ton of molten iron to 40 kg/ton of molten iron, and a range from larger than 40 kg/ton of molten iron to 50 kg/ton of molten iron.

[0048] In each of the tests, a desiliconization treatment was performed for an molten iron discharged from a blast furnace on a casting bed and in an molten iron ladle by necessity, and a desulfurization process was subsequently performed in the molten iron ladle by using a mechanical agitator; and thereafter, a dephosphorization treatment was performed in a converter-type vessel (300 tons). Molten iron ingredients before the dephosphorization treatment were C: 4.5 to 4.7 mass%; Si: 0.01 to 0.28 mass%; Mn: 0.15 to 0.25 mass%; P: 0.10 to 0.11 mass%; and S: 0.001 to 0.003 mass%. Powdered lime having a particle size diameter of 1 mm or smaller was used as a dephosphorization refining agent, and the powdered lime was blown with the gaseous oxygen used as a carrier gas via a lance. During the refinement, CaF_2 was not added. The blowing time was controlled to 10 minutes as a constant time, and a nitrogen gas of 0.05 to 0.15 $\text{Nm}^3/\text{min}/\text{ton}$ of molten iron was fed from the bottom of the furnace to agitate the molten iron. While the lime and oxygen source units are variable depending on the Si content in the molten iron, the lime and oxygen were fed in the quantities corresponding to constant values each excluding the desiliconization part (dicalcium silicate: stoichiometric mixture part when $2\text{CaO} \cdot \text{SiO}_2$ is formed). The quantities of the lime and the oxygen were 3.5 kg/ton of molten iron and 9 Nm^3/ton of molten iron, respectively. The temperature of the molten iron before and after the dephosphorization treatment was controlled to 1,250 to 1,350°C. The post-treatment quantities of the slag were each calculated from the mass balance between the amount of added lime and CaO concentration (slag analysis value) in the slag.

[0049] According to FIG. 1, the larger the post-treatment slag rate is, the higher the post-dephosphorization treatment P content is and also the larger the nonuniformity on the upper limit side of the each amount is. In comparison, however, when the each post-treatment slag rate is 30 kg/ton of molten iron or smaller, the nonuniformity on the upper limit side of the P content is significantly reduced, and the P content is 0.020 mass% even at highest. When the post-treatment slag rate is 20 kg/ton of molten iron or lower, the post-dephosphorization treatment P content in the molten iron is 0.15 mass% even at highest. Also, when the post-treatment slag rate is 20 kg/ton of molten iron or lower, the post-dephosphorization treatment P content in the molten iron is 0.10 mass% even at highest. For these reasons, in the present invention, the post-treatment slag rate is controlled to 30 kg/ton of molten iron or smaller, preferably 20 kg/ton of molten iron or smaller, and particularly preferably 10 kg/ton of molten iron or smaller.

[0050] FIG. 2 is a graph showing the relationship between the Si content in the molten iron before the dephosphorization treatment and the slag rate in the molten iron after the dephosphorization treatment in the tests illustrated in FIG. 1. According to the figure, when the pre-treatment Si content is high, the amount of the lime to be added is large and the slag rate is therefore increased, so that there occurs a good relationship between the slag rate and the pre-treatment Si content. In this case, it can be known that the pre-dephosphorization treatment Si content in the molten iron should be controlled to 0.15 mass% or lower to reduce the post-treatment slag rate to 30 kg/ton of molten iron or smaller. Similarly, it can be known that the pre-dephosphorization treatment Si content in the molten iron should be controlled to 0.07 mass% or lower to reduce the post-treatment slag rate to 20 kg/ton of molten iron or smaller. Also, it can be known that the pre-dephosphorization treatment Si content in the molten iron should be controlled to 0.03 mass% or lower to reduce the post-treatment slag rate to 10 kg/ton of molten iron or smaller. For these reasons, in the present invention, the Si content is controlled to 0.15 mass% or lower, preferably 0.07 mass% or lower, and more

preferably 0.03 kg/ton or lower.

[0051] As described above, when the Si content in the molten iron is low, the ratio of the CaO-FeO based melt to be consumed to generate the reaction with Si is reduced, whereby an advantage can be obtained in that the direct dephosphorization reaction by the CaO-FeO based melt is accelerated. The results shown in FIG. 1 are considered to be reflected with the above-described advantage.

[0052] The pre-dephosphorization treatment Si content in the molten iron can be tuned in a manner described hereunder.

[0053] A molten iron is fed from a molten iron making facility, such as a blast furnace. An effective technique for reducing a Si content in the molten iron to be produced is to reduce a total charge amount of a amount of silicic acid is reduced in, for example, a preliminary treatment for an molten iron making raw material. Other known effective technique in this connection include, for example, a technique of a low temperature operation for inhibiting silicate reduction reactions in the inside of the blast furnace, and a technique of inhomogeneous charging of coke. As such, when an molten iron produced using a blast furnace or the like facility has a Si content of 0.15 mass% or lower, a dephosphorization treatment may be performed for the molten iron without performing a desiliconization treatment described below.

[0054] However, when an molten iron produced using a blast furnace or the like facility has an Si content exceeding 0.15 mass%, a desiliconization treatment is performed, for example, on a casting bed of the blast furnace or in a molten iron ladle before a dephosphorization treatment. The pre-dephosphorization treatment Si content in the molten iron is reduced thereby to 0.15 mass% or lower, and the molten iron is then subjected to the dephosphorization treatment.

[0055] Ordinarily, a desiliconization treatment for a molten iron is practiced adding substances such as solid-state oxygen source and gaseous oxygen. For example, solid-state oxygen sources such as sintered powder and mill scale are added by, for example, being top-charged onto the bath surface of the molten iron or blowing into the bath. Alternatively, for example, gaseous oxygen is added by being blown onto the bath surface of the molten iron or by being blown into the bath.

[0056] In addition, instead of using the blast-furnace casting bed or the molten iron ladle, the desiliconization treatment for the molten iron can be implemented by adding oxygen source to a molten iron flow flowing to a transportation vessel such as an molten iron ladle from, for example, a blast-furnace casting bed. Other techniques also are available. For example, an agitated gas is blown into an molten iron in a vessel to enhance the desiliconization efficiency. In addition, reduction efficiency can be enhanced in such a manner that CaO source, such as sintered lime, is added to the molten iron and the slag basicity is thereby tuned to minimize iron oxide contained in desiliconization slag.

[0057] When performing the dephosphorization treatment for a molten iron after the desiliconization treatment, it is preferable that slag such as desiliconization slag be dissolved away to minimize the ingress of silicate for the implementation of an efficient dephosphorization treatment. As such, the slag is separated from the molten iron by a mechanical dissolution apparatus and/or manual operations before the dephosphorization treatment, and then the dephosphorization treatment is done.

[0058] In the inventive method, no specific limitations are imposed on the method of blowing via the top blowing lance the gaseous oxygen and the refining agent onto the bath surface of the molten iron. As such, for example, the arrangement may be such that only the gaseous oxygen is fed onto the bath surface of the molten iron from some of a plurality of lance holes of the top blowing lance, and the refining agent using the gaseous oxygen or a gas (inert gas such as nitrogen or Ar) different from the oxygen as a carrier gas is fed onto the bath surface of the molten iron from other lance holes. This arrangement enables the refining agent to be fed onto the region of the bath surface onto which the gaseous oxygen is fed. In this arrangement, it is particularly preferable that a top blowing lance to be used has a main lance hole in the center of a lance tip and a plurality of sub-lance holes in peripheral portions of the main lance hole. In this case, the gaseous oxygen is fed onto the bath surface of the molten iron from the sub-lance holes, and the refining agent is fed thereonto by using the gaseous oxygen or the above-described gas different from the gaseous oxygen as the carrier gas from the main lance hole. Still alternatively, different top blowing lances may be individually used to blow the gaseous oxygen and to blow the refining agent with the gaseous oxygen or the gas other than the gaseous oxygen as the carrier gas. However, in any of the cases, the carrier gas for the refining agent is preferably gaseous oxygen to cause the refining agent to be most efficiently dissolved.

[0059] The gaseous oxygen to be used in the present invention may be any of a pure oxygen gas and an oxygen containing gas. As the oxygen source to be added into the refining vessel, other substances than the gaseous oxygen, such as solid-state oxygen source such as iron oxides (sintered powder and mill scale, for example) may be used. These substances may be added in an arbitrary manner, such as top-charging or blowing into the bath. However, it is preferable that 50% or more of oxygen source to be added into the refining vessel, and more preferably 70% (gaseous-oxygen equivalent amount) or more be fed onto the bath surface of the molten iron through the top blowing lance to implement an efficient molten iron dephosphorization, as described above, by feeding (blowing) the gaseous oxygen onto the bath surface of the molten iron.

[0060] A part of the gaseous oxygen may be fed by a technique other than the above-described technique of blowing

onto the bath surface of the molten iron. For example, the part of the gaseous oxygen may be fed into the bath by, for example, the technique of injection into the bath through an immersed lance or a blowing nozzle provided in a portion of, for example, a bottom portion or a sidewall portion of an molten iron retaining vessel.

[0061] Ordinarily, a CaO based refining agent (refining agent based on CaO) such as lime is used for the refining agent. In addition, a powdered form is used for the refining agent that is to be blown onto the bath surface of the molten iron through the top blowing lance.

[0062] By way of a technique alternative to the technique of blowing onto the bath surface of the molten iron through the top blowing lance, the refining agent may partly be added, for example, by being top-charged thereonto or by being blown into the bath. Even when using the aforementioned technique, the amount of the refining agent to be added is preferably 20 mass% or smaller with respect to the total amount of the refining agent. Suppose that the ratio of the refining agent added by a technique different from the technique of blowing onto the bath surface of the molten iron through the top blowing lance exceeds 20 mass% with respect to the total amount. In this case, a reduction tends to occur in the effect of dephosphorization reaction acceleration achievable through the blowing of the refining agent together with the gaseous oxygen.

[0063] In addition, the molten iron preferably undergoes gas agitation to enhance the efficiency of dephosphorization. The gas agitation in this case is carried out by injecting an inert gas such as nitrogen or Ar through, for example, an immersed lance or a blowing nozzle that is provided in a portion such as a bottom portion or a sidewall portion of the molten iron retaining vessel. The feed amount of the agitated gas is preferably 0.02 Nm³/min/ton of molten iron or more. In addition, when the agitation of the bath is too intensive, the rate at which C in the molten iron reduces the generated FeO is excessively increased, so that the feed amount is preferably 0.3 Nm³/min/ton of molten iron.

[0064] For the molten iron retaining vessel (refining vessel) used to perform the dephosphorization treatment, a converter-type vessel is most preferable in that a freeboard can be sufficiently secured. However, an arbitrary vessel such as a molten iron ladle or a torpedo car may be used.

[0065] FIG. 3 shows a state of an application example of an inventive method using a converter-type vessel, in which 1 denotes a converter-type vessel, 2 denotes a top blowing lance, and 3 denotes a bottom blowing nozzle. In the example, a refining agent with a gaseous oxygen as a carrier gas is blown onto a metal bath surface from the top blowing lance 2, and concurrently, an agitated gas is blown into an molten iron from the bottom blowing nozzle 3.

[0066] The conventional dephosphorization treatment indispensably and practically requires the addition of CaF₂ (fluorspar) to accelerate the dissolution of CaO. However, in recent years, taking influence of F on the environment into consideration, the use amount of CaF₂ is required even in the steel refinement. In this regard, according to the inventive method, even when CaF₂ is not substantially added (that is, CaF₂ except CaF₂ contained as an unavoidable impurity in the refining agent is not added) or only a small amount of CaF₂ is added, high efficiency of dephosphorization can be obtained. As such, even when adding CaF₂ to accelerate the CaO dissolution, the amount of the CaF₂ to be added is controlled to 2 kg/ton of molten iron or smaller and preferably to 1 kg/ton of molten iron. In addition, as will be described below, in comparison to the conventional method, the present invention enables obtaining the effect of significantly reducing the amount of flow-away slag. More specifically, slag fluidity can be caused lower by not adding CaF₂ or by reducing the addition amount of CaF₂, thereby enabling the above-described effect to be enhanced.

[0067] Ordinarily, the P content in a pre-dephosphorization treatment molten iron is 0.10 mass% or higher. However, in the present invention, the molten iron is preferably dephosphorized and refined to have a P content required for crude steel, that is, a P content lower than or equal to a steel ingredient standard value (normally, 0.020 mass% or lower), and more specifically to have a P content of 0.010 mass% or lower. In this case, substantially no slug seed material has to be used in intra-converter blowing in a subsequent step, and only an essential decarburization refinement can be implemented. This enables the following advantages to be secured: (1) The decarburization refinement is significantly simplified, and also the refining time can be reduced; (2) The occurrence slag rate in the decarburization refinement can be effectively reduced; and (3) since slug seed material is not substantially used the decarburization refinement, when manganese ore is added as manganese source, very high Mn yield can be secured.

[0068] Several preferred embodiments of the inventive method will be described hereunder. The efficiency of the dephosphorization reaction can be further enhanced when the inventive method is practiced in the manners of the embodiments described hereunder.

[0069] According to a first embodiment, a dephosphorization treatment is performed so that a CaO-equivalent supplying rate B (kg/min/ton of molten iron) of the refining agent to be blown onto the bath surface of the molten iron and a supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron satisfy Equation (1) below.

$$0.3 \leq A/B \leq 7 \quad (1)$$

[0070] In addition, to secure a higher efficiency of the dephosphorization reaction, the dephosphorization treatment

is performed so that the CaO-equivalent supplying rate B (kg/min/ton of molten iron) of the refining agent to be blown onto the bath surface of the molten iron and a supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron satisfy Equation (2) below.

$$1.2 \leq A/B \leq 2.5 \quad (2)$$

[0071] As a result of the research conducted by the inventors, according to the technique of blowing the gaseous oxygen and the refining agent onto the bath surface of the molten iron, the dephosphorization reaction was verified to vary depending on the supplying rate of the gaseous oxygen and the supplying rate of CaO (refining agent). More specifically, the inventors verified that while FeO is generated in the region of the bath surface onto which the gaseous oxygen is fed, a preferable CaO supplying rate corresponding to a generation amount thereof exists. In this case, when the supplying rate of the gaseous oxygen is excessively low in the ratio between the supplying rates of the gaseous oxygen and the CaO, FeO in a amount corresponding to the CaO feed amount is not generated. As such, the dissolution of the CaO (generation of a CaO-FeO based melt) does not progress, and the CaO remains undissolved, not effectively acting for the dephosphorization. When the supplying rate of the gaseous oxygen is excessively high, CaO necessary for the dephosphorization is short with respect to the feed amount of the gaseous oxygen. In this case also, the CaO-FeO based melt is not sufficiently generated. Either of the cases makes the conditions disadvantageous to the molten iron dephosphorization that is performed by the mechanism of dephosphorization reaction, and exhibits a tendency to disable a high dephosphorization speed rate to be obtained. In addition, when the supplying rate of the gaseous oxygen is excessively high, the amount of ineffective oxygen different from oxygen necessary for the dephosphorization increases, and the ineffective oxygen is consumed for decarburization and/or the like. Thereby, the heat source becomes insufficient for subsequent processing steps, consequently leading to a significant increase in the operation costs in the decarburization process.

[0072] If the above-described ratio A/B is lower than 0.3, the CaO feed amount is excessive with respect to the feed amount of the gaseous oxygen, so that FeO in a amount corresponding to the CaO feed amount is not generated in the region of the bath surface onto which the gaseous oxygen is fed. As such, the dissolution of the fed CaO (generation of a CaO-FeO based melt) does not progress, and the CaO remains undissolved, not effectively acting for the dephosphorization, therefore causing the tendency of reducing the dephosphorization speed rate. When the supplying rate of the gaseous oxygen exceeds 7, CaO necessary for the dephosphorization is short with respect to the feed amount of the gaseous oxygen. In this case also, since a sufficient CaO-FeO based melt is not generated, there is a tendency to reduce the dephosphorization speed rate. When the ratio A/B is controlled to the range of 1.2 to 2.5, the balance between the FeO generation amount associated with the feeding of gaseous oxygen and the CaO feed amount is even more optimized, whereby a particularly higher efficiency of the dephosphorization reaction can be secured.

[0073] A second embodiment of the present invention is a method of a dephosphorization treatment to be performed using a ladle or torpedo-car type vessel. In the dephosphorization treatment using the ladle or torpedo-car type vessel, a gaseous oxygen and at least a part of a refining agent are blown onto a bath surface of an molten iron through a top blowing lance, and gas containing powder is injected into the molten iron through an immersed lance and/or a blowing nozzle lance.

[0074] The inventors conducted research regarding a method using the ladle or torpedo-car type refinement vessel for more efficiently performing the molten iron dephosphorization. As a result, the inventors verified that the method is very effective that blows the gaseous oxygen and the refining agent onto the bath surface of the molten iron through the top blowing lance and additionally injects the gas containing the powder into the molten iron through the immersed lance or the like.

[0075] In the second embodiment, the rate of the gaseous oxygen to be blown onto the bath surface of the molten iron through the top blowing lance is preferably 0.7 Nm³/min/ton of molten iron or smaller. When the supplying rate of the oxygen from the top blowing lance is excessive, slag overflow from the refinement vessel can occur because of slag foaming. Such slag foaming can be inhibited by reducing the supplying rate of the oxygen from the top blowing lance to 0.7 Nm³/min/ton of molten iron or smaller, whereby stable operation can be performed.

[0076] Also in the second embodiment, a part of the gaseous oxygen may be fed by, for example, top-charging or injection into the bath by way of a technique different from the technique of blowing onto the bath surface of the molten iron through the top blowing lance. Even in the different technique, the amount of the refining agent to be blown from the top blowing lance onto the bath surface of the molten iron is preferably 80 mass% or more of the total amount of the refining agent. When the ratio in amount of the refining agent to be added by being blown onto the bath surface of the molten iron through the top blowing lance is lower than 80% of the total amount, there can occur the tendency of reducing the effect of the dephosphorization reaction acceleration resulting from the blowing of the refining agent together with the gaseous oxygen onto the bath surface of the molten iron.

[0077] FIG. 4 is a graph in accordance with the results of tests performed by the inventors. The graph shows the

relationship between the ratio of the addition amount of a refining agent having been fed through the top blowing lance with respect to the total addition amount of the refining agent and the amount of necessary lime. The tests were each performed on an molten iron retained in a ladle type vessel (150 tons) and having a P content of 0.10 to 0.11 mass%, and an Si content of 0.07 mass% or lower. In the test, the dephosphorization treatment (process time: 15 minutes) was performed by blowing powdered lime (0 to 6 kg/ton of molten iron) having a particle size diameter of 1 mm or smaller as a refining agent with a gaseous oxygen (4.5 to 5.0 Nm³/ton of molten iron) being used as a carrier gas onto the bath surface of the molten iron and by injecting powder into the molten iron through an immersed lance. The amount of the powder to be injected through the immersed lance was controlled to a fixed amount of 30 kg/min. For a part or all of the powder, a residue of the necessary lime part is used, and dust (Fe content: 40 mass%) or coke powder was used for a shortage part. In the dephosphorization treatment described above, CaF₂ was not added to the refining agent, and the post-treatment slag rate was controlled to 20 kg/ton of molten iron or smaller. The ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was controlled to 2.0. The addition amount of the lime was controlled to fall within a range of the sum of a lime amount $W_{\text{CaO_P}}$ (kg/ton of molten iron) and a lime amount $W_{\text{CaO_Si}}$ (kg/ton of molten iron) defined by Expressions (5) and (6) described below. A depth L (value L defined by Equation (7) described below) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The temperature of the molten iron before and after the dephosphorization treatment was controlled to 1,300 to 1,320°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value). FIG. 4 shows the lime amount necessary to cause the P content in the post-treatment molten iron to be 0.02 mass% or lower.

[0078] According to FIG. 4, in line with the increase in the ratio of the refining agent to be fed through the top blowing lance with respect to the total amount of the refining agent, the amount of the necessary lime decreases; and particularly, the amount of the necessary lime decreases utmost when the ratio' is 80 mass% or lower.

[0079] No specific limitations are imposed on the type of the powder that is to be blown together with the gas into the molten iron. The powder to be used may be one or two or more types selected from, for example, a part of a refining agent such as powdered lime, dust such as converter dust occurring in a steel mill, carbon-source base powder, iron oxides such as sintered powder and mill scale, and powder of, for example, CaCO₃, Ca(OH)₂, and CaMg(CO₃)₂.

[0080] Among these substances, when the refining agent such as powdered lime is used as the powder, the refining agent is heated while floating in the molten iron, and the dissolution thereof into slag is accelerated thereby.

[0081] The use of dust occurring in a steel mill leads to effective use of waste. More specifically, since dust is in a powder form, when reusing the dust, conventional techniques require processing such as that of making it into the form of briquette. However, according to the present invention, dust can be reused as in the powder form without using time and cost for processing such as that of making it into the form of briquette. In addition, the powder composed of the carbon source carburizes the molten iron to be an effective heat source in subsequent processing steps. The powder of CaCO₃, Ca(OH)₂, or CaMg(CO₃)₂, for example, generates gases (CO₂ and H₂O), whereby the gases contribute to intensify agitation of the bath, and CaO generated by thermal decomposition functions as a refining agent. The powder of the iron oxide becomes a part of the oxygen source in the bath.

[0082] In addition, also the gas (carrier gas), which is to be blown with the powder into the molten iron, is not limited regarding the type, and the gaseous oxygen (pure oxygen gas or oxygen-containing gas) or an inert gas such as N₂ or Ar may be used. Among these gases, when the gaseous oxygen is used to blow the refining agent into the molten iron, while the agent is floating in the molten iron, a so-called transitory reaction can be expected to occur, thereby enabling the effect of accelerating the reaction to be obtained. However, since the oxygen gas is fed from, for example, the immersed lance and the blowing nozzle, FeO is generated at, for example, the lance and the nozzle tip. As such, service lives of, for example, the lance and the nozzle become a problem. In comparison, when the inert gas such as N₂ or Ar is used, while the effect in terms of reaction cannot be expected, the service lives of, for example, the lance and the nozzle are prolonged longer than in the case of using the gaseous oxygen. For these reasons, the type of the gas to be used is preferably selected in consideration of the total costs inclusive of the service lives of, for example, the lance and the nozzle.

[0083] As means of blowing the refining agent into the molten iron, the immersed lance or the blowing nozzle equipped with the refinement vessel or the both may be used. For the blowing nozzle, any type such as a bottom blowing nozzle or a horizontal blowing nozzle may be used.

[0084] In addition, in the second embodiment, suppose that substantially the total amount of the refining agent is added by being blown onto the bath surface of the molten iron through the top blowing lance and by being blown into the molten iron through the immersed lance and/or the blowing nozzle. In this case, the amount of the refining agent to be added through the top blowing lance is preferably 20 to 80 mass% of the total amount of addition of the refining agent. When the ratio in amount of the refining agent to be added by being blown onto the bath surface of the molten

iron through the top blowing lance exceeds 80 mass% of the total amount of addition of the refining agent, since the molten iron agitation effect through the blowing of the refining agent into the molten iron is low, an agitation power necessary for the dephosphorization cannot easily be obtained. On the other hand, when the ratio is lower than 20 mass%, there cannot be obtained a sufficient effect of the dephosphorization reaction acceleration resulting from the blowing of the refining agent together with the gaseous oxygen onto the bath surface of the molten iron.

[0085] FIG. 5 is a graph in accordance with the results of tests performed by the inventors for the case that the total amount of the refining agent is added by being blown onto the bath surface of the molten iron through the top blowing lance and by being blown into the molten iron through the immersed lance and/or the blowing nozzle. The graph shows the relationship between the ratio of the addition amount of a refining agent with respect to the total addition amount of the refining agent having been fed through the top blowing lance and the efficiency of dephosphorization. The tests were each performed on an molten iron retained in a ladle type vessel (150 tons) and having a P content of 0.10 to 0.11 mass%, and an Si content of 0.07 mass% or lower. In the test, the dephosphorization treatment (process time: 15 minutes) was performed by blowing powdered lime (0 to 6 kg/ton of molten iron) having a particle size diameter of 1 mm or smaller as a refining agent with a gaseous oxygen (4.5 to 5.0 Nm³/ton of molten iron) being used as a carrier gas onto the bath surface of the molten iron and by blowing the residue (0 to 6 kg/ton of molten iron) of the necessary lime part into the molten iron through an immersed lance. For a part or all of the powder, a residue of a necessary lime part is used, and dust (Fe content: 40 mass%) or coke powder was used for a shortage part. In the dephosphorization treatment described above, CaF₂ was not added to the refining agent, and the post-treatment slag rate was controlled to 20 kg/ton of molten iron or smaller. The ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was controlled to 2.0. The addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described below. The depth L (value L defined by Equation (7) described below) of a concave, which occurred in the bath surface of the molten iron in association with blowing of the refining agent thereonto with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The temperature of the molten iron before and after the dephosphorization treatment was controlled to 1,300 to 1,320°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0086] According to FIG. 5, the efficiency of dephosphorization is significantly reduced in regions where the ratio of the addition amount of the refining agent through the top blowing lance with respect to the total amount of the refining agent is lower than 20 mass% and 80 mass% or higher.

[0087] FIG. 6 shows an application example of the present embodiment in the case where the molten iron dephosphorization treatment is performed using a blast-furnace-ladle type dephosphorization facility. Depending on the Si content in the molten iron discharged from a blast furnace, a desiliconization treatment such as casting-bed desiliconization is performed by necessity before the desiliconization treatment. In the desiliconization treatment, an molten iron is charged into a blast furnace ladle 4, and powdered lime (refining agent). Then, the powdered lime (refining agent) is injected into the molten iron from a lance 5, and concurrently, the powdered lime (refining agent) together with the gaseous oxygen is blown onto the bath surface of the molten iron. At this event, the supplying rate of the powdered lime to be injected is control to enable sufficient agitation of the molten iron to be performed.

[0088] In the third embodiment, the dephosphorization treatment is performed so that the supplying rate of the refining agent to be blown onto the bath surface of the molten iron and the supplying rate of the gaseous oxygen to be blown onto the bath surface of the molten iron satisfy Equations (3) and (4) below.

$$(C1/D1) > (C2/D2) \quad (3)$$

$$C1 > C2 \quad (4)$$

[0089] In these equations:

C1 = average value of CaO-equivalent supplying rates (kg/min/ton of molten iron) of the refining agent in the earlier stage of the dephosphorization treatment;

C2 = average value of CaO-equivalent supplying rates (kg/min/ton of molten iron) of the refining agent in the latter stage of the dephosphorization treatment;

D1 = average value of supplying rates of the gaseous oxygen in the earlier stage of the dephosphorization treatment (Nm³/min/ton of molten iron); and

D2 = average value of supplying rates of the gaseous oxygen in the latter stage of the dephosphorization treatment

(Nm³/min/ton of molten iron).

[0090] In the earlier stage of the dephosphorization treatment, since the P content in the molten iron is high, there occurs an intra-slag-(P) movement rate determination region in which as the supplying rate of the refining agent is larger, the dephosphorization speed rate becomes higher. On the contrary, however, in the latter stage of the dephosphorization treatment, the P content in the molten iron becomes low, and the movement of intra-metal [P] to the reaction site is in a rate-determining step, the ratio of the refining agent that effectively contributes to the dephosphorization operation is reduced lower in comparison to the earlier stage of the dephosphorization treatment. As such, a feed-rate ratio (refining-agent supplying rate/gaseous-oxygen supplying rate) between the refining agent and gaseous oxygen to be fed onto the bath surface of the molten iron in the above-described specific mode can be reduced lower in the latter stage of the dephosphorization treatment than the feed-rate ratio in the earlier stage of the dephosphorization treatment. Thereby, an efficient dephosphorization treatment can be implemented with a smaller addition amount of the refining agent.

[0091] According to the inventive method, the reactivity of the refining agent can be effectively enhanced for the reasons described above, so that an efficient dephosphorization treatment can be implemented in the latter stage of the dephosphorization treatment with a minimum necessary amount of the refining agent being added.

[0092] FIG. 7 is a graph showing results of investigation regarding the relationship between a CaO unit consumption necessary to cause the P content in the molten iron after each dephosphorization treatment to be 0.012 mass% and the efficiency of dephosphorization. The each dephosphorization treatment was performed using a converter-type dephosphorization refinement furnace (300 ton) without CaF₂ being added under conditions (1) and (2) described below.

(1) The dephosphorization treatment was performed in the manner that a CaO-equivalent supplying rate C (kg/min/ton of molten iron) of the refining agent to be blown onto the bath surface of the molten iron is controlled to be constant throughout the total process time. Concurrently, a C/D ratio between the supplying rate C of the refining agent and a supplying rate D (Nm³/min/ton of molten iron) of the gaseous oxygen is controlled to be constant throughout the total process time.

(2) The dephosphorization treatment was performed under the conditions of (C1/D1) > (C2/D2) and C1 > C2, where C1 = average value of CaO-equivalent supplying rates of the refining agent in the earlier stage of the dephosphorization treatment (kg/min/ton of molten iron); C2 = average value of CaO-equivalent supplying rates of the refining agent in the latter stage of the dephosphorization treatment (kg/min/ton of molten iron); D1 = average value of CaO-equivalent supplying rates of the gaseous oxygen in the earlier stage of the dephosphorization treatment (Nm³/min/ton of molten iron); and D2 = average value of CaO-equivalent supplying rates of the gaseous oxygen in the latter stage of the dephosphorization treatment (kg/min/ton of molten iron).

[0093] The dephosphorization efficiency η_{CaO} was defined according to the following equation, whereby a desilicization part was excluded as 2CaO-SiO₂:

$$\eta_{\text{CaO}} = \left\{ \left(\frac{[\%P]_i - [\%P]_f}{(31 \times 2)} \right) \times 56 \times 3 \times 10 \right\} / \left\{ \left(\frac{[\%Si]_i - [\%Si]_f}{28} \right) \times 56 \times 2 \times 10 \right\} -$$

[0094] In the equation:

W_{CaO} = CaO unit consumption (kg/ton of molten iron) ;
 $[\%P]_i$ = P content (mass%) in the molten iron before the dephosphorization treatment;
 $[\%P]_f$ = P content (mass%) in the molten iron after the dephosphorization treatment;
 $[\%Si]_i$ = Si content (mass%) in the molten iron before the dephosphorization treatment; and
 $[\%Si]_f$ = Si content (mass%) in the molten iron after dephosphorization treatment molten iron.

[0095] In the test, after the converter molten iron was subjected to desilicization on the casting bed and in the molten iron ladle by necessity, the molten iron was subjected to desulfurization, was moved into a converter-type vessel, and was then subjected to the dephosphorization treatment. The P content in the molten iron before the dephosphorization treatment was 0.10 to 0.11 mass%, and the Si content therein was 0.07 mass% or lower. For the refining agent, only CaO base calcined lime not containing CaF₂ was used. For the gaseous oxygen, gaseous oxygen was mainly used and was added by being blown onto the bath surface of the molten iron from the top blowing lance; and partly, addition of a solid-state oxygen source (iron ore) was concurrently performed. The feed amount of the refining agent

was controlled to 4.6 to 9.0 kg/ton of molten iron, and the feed amount of the gaseous oxygen was controlled to 8.6 to 13.6 Nm³/ton of molten iron. For the dephosphorization treatment (1), control was performed such that C1 is 0.88 to 1.00 kg/min/ton of molten iron, C2 is 0.30 to 0.39 kg/min/ton of molten iron, C1/D1 is controlled to 0.60 to 0.83 kg/Nm³, C2/C2 is 0.38 to 0.48 kg/Nm³, and (C1/D1) × 56 to 72% = (C2/D2). The post-treatment slag rate was controlled to 20 kg/ton of molten iron. The addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described below. The depth L (value L defined by Equation (7) described below) of a concave, which occurred in the bath surface of the molten iron in association with blowing of the refining agent thereonto with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The temperature of the molten iron before and after the dephosphorization treatment was controlled to 1,300 to 1,320°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0096] According to FIG. 7, it can be known that in the dephosphorization treatment (2), the CaO source units were smaller and the efficiencies of dephosphorization were higher, in comparison to those in the dephosphorization treatment (1). This indicates that in the case (2), since sufficient dephosphorization was performed without the refining agent being added in the latter stage of the refinement, the high efficiencies of the dephosphorization were obtained.

[0097] In the third embodiment, the desired effects can be secured by controlling the refining-agent supplying rate and the gaseous-oxygen supplying rate were controlled to be (C1/D1) > (C2/D2) and C1 > C2. Particularly, however, the supplying rates are preferably controlled to fall within the range of (C1/D1) × 30 to 80% = (C2/D2) and C1 × 30 to 80% = C2. When (C1/D1) × 30% > (C2/D2) and C1 × 30% > C2, since the feed amount of the refining agent is reduced, so that the dephosphorization efficiency tends to be reduced. On the other hand, however, when (C1/D1) × 80% < (C2/D2) and C1 × 80% < C2, since a surplus feed amount of the refining agent is increased in the latter stage of the dephosphorization treatment, so that the dephosphorization efficiency tends to be reduced.

[0098] According to the third embodiment, the refining agent and the gaseous oxygen can be fed in accordance with the above-described conditions during the time of the dephosphorization treatment (the earlier stage and the latter stage of the dephosphorization treatment). Accordingly, the mode of controlling the refining-agent supplying rate the supplying rate of the gaseous oxygen to vary is arbitral, and the supplying rates can be controlled to vary in a continuous mode, in a step-by-step mode, or in both of the two modes.

[0099] According to the fourth embodiment, the dephosphorization treatment is performed for the molten iron having an Si content of 0.15 mass% or lower by blowing the gaseous oxygen and at least the part of the refining agent onto the bath surface of the molten iron through the top blowing lance. Concurrently, in the dephosphorization treatment, there is added the lime in the total amount of the lime amount W_{CaO_P} (kg/ton of molten iron) obtained from Equation (5) below and the lime amount W_{CaO_Si} (kg/ton of molten iron) obtained from Equation (6) below.

$$W_{CaO_P} = (\text{molten iron [P]} - \text{object [P]}) \times (10/62) \times 56 \times \frac{3}{\eta_{CaO}} \quad (5)$$

[0100] Where:

molten iron [P] = P content (mass%) in the molten iron before the dephosphorization treatment;
object [P] = P content (mass%) in the molten iron after the dephosphorization treatment; and
 η_{CaO} (lime efficiency) = 0.5 to 1

$$W_{CaO_Si} = (\text{molten iron [Si]} \times (10/28) \times 56 \times 2 \quad (6)$$

[0101] In the expression:

molten iron [Si] = Si content (mass%) in the molten iron before the dephosphorization treatment.

[0102] As already described, the conventional dephosphorization treatment technique is carried out on the prerequisite condition that the slag is maintained in the liquid state, wherein the slag volume is determined corresponding to the phosphorus distribution L_p, therefore requiring the refining agent of the amount larger than the refinement amount necessary for the practical P and Si fixation. However, the present invention uses the mechanism including the direct dephosphorization reaction in the region of the bath surface with the hot spot in the center and the P fixation by the solid-phase base slag in a region outside the region of the bath surface. Thereby, efficient dephosphorization reactions can be efficiently generated with a minimum necessary amount of the refining agent, as described above.

[0103] The amount of the lime consumed to practically fix P and Si in the molten iron amount can be calculated using the equation shown below. In the equation, $W_{CaO_P_0}$ is a lime amount (kg/ton of molten iron) consumed to fix the P, and $W_{CaO_Si_0}$ is a lime amount (kg/ton of molten iron) consumed to fix the Si.

$$W_{CaO_P_0} = (\text{molten iron [P]} - \text{object [P]}) \times (10/62) \times 56 \times 3$$

[0104] Where:

molten iron [P] = P content (mass%) in the molten iron before the dephosphorization treatment;
object [P] = P content (mass%) in the molten iron after the dephosphorization treatment; and

$$W_{CaO_Si_0} = (\text{molten iron [Si]} \times (10/28) \times 56 \times 2$$

[0105] In the expression:

molten iron [Si] = Si content (mass%) in the molten iron before the dephosphorization treatment.

[0106] In this case, where the total amount of addition of the lime is represented by Total CaO (kg/ton of molten iron), the lime efficiency η_{CaO} of the lime contributed to the dephosphorization can be calculated according to the following equation:

$$\eta_{CaO} = W_{CaO_P_0} / (\text{Total CaO} - W_{CaO_Si_0})$$

[0107] In the present embodiment, first, the η_{CaO} is specified as 0.5 to 1. The lower limit of η_{CaO} is specified from the viewpoint of generating an appropriate dephosphorization reaction aimed in the present invention without performing surplus lime addition. When η_{CaO} is below 0.5, substantially surplus lime addition needs to be performed. In this case, not only the advantage of the present invention that performs the efficient dephosphorization treatment with a small addition amount of the refining agent is lost, but also the addition amount of the lime is excessive relative to FeO generated under a predetermined oxygen source unit. Consequently, a large amount of non-dissoluble CaO remains, and the non-dissoluble CaO hinders the progress of the dephosphorization reaction described above.

[0108] Accordingly, according to the present embodiment, the dephosphorization treatment is performed by the addition of lime in the total amount of a lime amount W_{CaO_P} (kg/ton of molten iron) obtained from Equation (5) below and a lime amount W_{CaO_Si} (kg/ton of molten iron) obtained from Equation (6) below.

$$W_{CaO_P} = (\text{molten iron [P]} - \text{object [P]}) \times (10/62) \times 56 \times \frac{3}{\eta_{CaO}} \quad (5)$$

[0109] Where:

molten iron [P] = P content (mass%) in the molten iron before the dephosphorization treatment;
object [P] = P content (mass%) in the molten iron after the dephosphorization treatment; and
 η_{CaO} (lime efficiency) = 0.5 to 1

$$W_{CaO_Si} = (\text{molten iron [Si]} \times (10/28) \times 56 \times 2 \quad (6)$$

[0110] Where:

molten iron [Si] = Si content (mass%) in the molten iron before the dephosphorization treatment.

[0111] In the above, when $\eta_{CaO} = 0.5$ to 1, W_{CaO_P} is a lime amount necessary fix the P in the molten iron as $3CaO \cdot P_2O_5$, and W_{CaO_Si} is a lime amount necessary to form consumed to fix the Si in the molten iron as $2CaO \cdot SiO_2$.

[0112] As an example, FIG. 8 shows the case of the dephosphorization treatment performed for an molten iron with a P content of 0.11 mass% to be dephosphorized to a P content of 0.015 mass%. Specifically, the figure comparatively shows the amount of the lime to be added corresponding to the Si content in the molten iron in the present embodiment in comparison to the amount of the lime to be added in the conventional dephosphorization treatment. In the figure,

W_{CaO_Si} represents the lime amount necessary for Si fixation; $W_{CaO_P_1}$ represents the lime amount necessary for P fixation (P-removal) when $\eta_{CaO} = 1$; $W_{CaO_P_{0.5}}$ represents the lime amount necessary for P fixation when $\eta_{CaO} = 0.5$; and W represents the lime amount of the lime to be added in the conventional method. As is shown in the figure, since the lime amount necessary in the conventional method is determined depending on the phosphorus distribution L_p and the necessary amount of slag corresponding to thereto, the lime amount W is necessary regardless of the Si content in the molten iron. In comparison, however, the lime amount to be added in the present embodiment is sufficient with $[W_{CaO_Si} + W_{CaO_P_1}]$ to $[W_{CaO_Si} + W_{CaO_P_{0.5}}]$, whereby the addition amount of the lime can be significantly reduced in comparison to the case in the conventional method.

[0113] FIG. 9 shows the relationship between the amount of necessary lime for the P-removal and the lime efficiency η_{cao} in each of the present embodiment and the conventional method, wherein the amount of necessary lime for the P-removal refers $[W - W_{CaO_Si}]$ shown in FIG. 8. According to FIG. 9, it can be known that in comparison to the conventional method, the present embodiment performs the dephosphorization treatment with high lime efficiency by using a very small amount of the P-removal lime.

[0114] Further, in the fourth embodiment, the lime of 80 mass% or more of the lime amount W_{CaO_P} (W_{CaO_P} obtained when $\eta_{CaO} = 1$, which hereinbelow will be the same) is preferably blown onto the bath surface of the molten iron through the top blowing lance. FIG. 10 is a graph in accordance with the results of tests performed by the inventors. The figure shows relationship between a ratio X/W_{CaO_P} between a lime amount X of lime and the lime amount for P-removal, which is to be blown onto the bath surface of the molten iron from the top blowing lance, and the P content in the molten iron after the dephosphorization treatment. The tests were each performed on an molten iron retained in a converter-type vessel (340 tons) and having a P content of 0.095 to 0.135 mass%, and an Si content of 0.02 to 0.10 mass%. In the test, the dephosphorization treatment (process time: 10 to 14 minutes) was performed by blowing powdered lime (4 to 10 kg/ton of molten iron) having a particle size diameter of 1 mm or smaller as a refining agent with a gaseous oxygen (10 to 15 Nm³/ton of molten iron) being used as a carrier gas onto the bath surface of the molten iron; and thereafter decarburization blowing was performed by charging the molten iron into a decarburizing converter. In the dephosphorization treatment described above, addition amount of CaF_2 was controlled to 1 kg/ton of molten iron or smaller, and the post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. The ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was controlled to 1.7. The depth L (value L defined by Equation (7) described below) of a concave, which occurred in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The temperature of the molten iron before and after the dephosphorization treatment was controlled to 1,300 to 1,320°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0115] According to FIG. 10, when the ratio of the lime amount X contained the lime amount W_{CaO_P} becomes smaller than 80 mass%, the dephosphorization rate tends to slightly be reduced. This is considered to occur for the reason that a high reaction efficiency as described above cannot relatively obtained by directly throwing the refining agent onto the hot spot, which is a reaction site, or a gaseous-oxygen feed region in the vicinity of the hot spot.

[0116] Si has a higher combustibility than Fe, so that the Si can stably exist as SiO_2 in the molten iron during the blowing. As such, the Si needs not be brought into reaction with the lime at the hot spot. For this reason, lime source corresponding to the W_{CaO_Si} that fixes the generated SiO_2 is not limited to the quicklime, but the lime source may be any substance containing unreacted lime (free lime). The refining agent corresponding to the lime amount W_{CaO_Si} may be at least one selected from powdered lime, massive calcined lime, massive limestone, and iron-making slag containing unreacted CaO. As the iron-making slag, converter slag (having a basicity of about 3 to 4) occurring in a decarburization step and ladle slag, for example, may be used.

[0117] For the above-described reasons or to enable the high efficiency of dephosphorization to be secured with a small addition amount of the refining agent, the Si content in the molten iron to be subjected to the dephosphorization treatment is preferably controlled to 0.15 mass% or lower, preferably 0.07 mass% or lower, and more preferably 0.03 mass% or lower. When the Si content in the molten iron exceeds 0.15 mass%, the effect of reducing the addition amount of the refining agent in the present embodiment is faded out thereby.

[0118] According to a fifth embodiment, a depth L, which is defined by Equation (7) below, of a concave, which occurred in the bath surface of the molten iron in association with the gaseous oxygen or blowing of the refining agent thereonto with the gaseous oxygen being used as the carrier gas is controlled to 200 to 500 mm.

$$L = L_0 \times \exp\{(-0.78 \times L_H)/L_0\} \quad (7)$$

$$L_0 = 63 \times \{(F_{02}/n)/d_t\}^{2/3}$$

[0119] Where:

L_H = lance height (mm) of the top blowing lance;

F_{02} = supplying rate (Nm³/hr) of the gaseous oxygen to be fed from the top blowing lance;

n = number of nozzle holes of the top blowing lance; and

d_t = diameter(mm) of each of the nozzle holes of the top blowing lance (which alternatively represents an average hole diameter of all the nozzle holes in a case where the nozzle diameters of the plurality of nozzle holes are different).

[0120] Optimizing the feed method for feeding, particularly, the gaseous oxygen onto the hot spot which is the reaction site was found preferable to secure high efficiency of dephosphorization with a small amount of the addition amount of the refining agent by using the aimed dephosphorization reaction mechanism in the present invention. More specifically, the feed method is to control a depth of a concave (theoretical concave depth calculated in accordance with the gaseous-oxygen supplying rate and the configuration and use conditions of the top blowing lance) to fall in an optimal range.

[0121] Suppose now that the depth of a concave which occurs in the bath surface of the molten iron in association with the blowing of the gaseous oxygen or the gaseous oxygen with the refining agent thereonto is excessively small; that is, the blowing of the gaseous oxygen or the gaseous oxygen with the refining agent is excessively gentle. In this case, foaming of slag occurs in regions other than the hot spot weak, and the foamed slag hinders the flow of a gaseous-oxygen jet, so that the feeding of the gaseous oxygen onto the hot spot is weakened, thereby making the condition to be disadvantageous for enhancing the efficiency of dephosphorization. In addition, since the feeding of the oxygen onto the hot spot is unstabilized, so that the oxygen necessary for the dephosphorization is not fed, whereby the nonuniformity in the efficiency of dephosphorization is increased, 3CaO-P₂O₅ is dissolved, and an undesirable phosphorization can take place again.

[0122] On the other hand, suppose that the depth of a concave, which occurred in the bath surface of the molten iron in association with the blowing of the gaseous oxygen or the gaseous oxygen with the refining agent is excessively large; that is, the blowing of the gaseous oxygen or the gaseous oxygen and the refining agent is excessively violent. In this case, the oxygen concentration within the hot spot is excessively increased, thereby disabling feeding of sufficient P corresponding to FeO being generated. Consequently, undesirable decarburization is caused by excessive part of the FeO to progress, also making the condition disadvantageous in terms of the enhancement of the dephosphorization efficiency.

[0123] Equation (7) below enables defining the depth L of the concave, which occurs in the bath surface of the molten iron in association with the blowing of the gaseous oxygen or the refining agent with the gaseous oxygen being used as the carrier gas.

$$L = L_0 \times \exp\{(-0.78 \times L_H)/L_0\} \quad (7)$$

$$L_0 = 63 \times \{(F_{02}/n)/d_t\}^{2/3}$$

[0124] Where:

L_H = lance height (mm) of the top blowing lance;

F_{02} = supplying rate (Nm³/hr) of the gaseous oxygen to be fed from the top blowing lance;

n = number of nozzle holes of the top blowing lance; and

d_t = diameter (mm) of each of the nozzle holes of the top blowing lance (which alternatively represents an average hole diameter of all the nozzle holes in a case where the nozzle diameters of the plurality of nozzle holes are different).

[0125] In the present embodiment, the dephosphorization treatment is performed by controlling the depth L of the concave occurring in the bath surface of the molten iron to 200 to 500 mm. FIG. 11 shows, based on the results of tests conducted by the inventors, the relationship between the depth L of a concave occurring in the bath surface of an molten iron and between the depth L and the efficiency of dephosphorization, and the between the depth L and the

P content in the molten iron after the dephosphorization treatment. The tests were each performed on an molten iron retained in a converter-type vessel (340 tons) and having a P content of 0.095 to 0.135 mass%, and an Si content of 0.02 to 0.15 mass%. In the test, the dephosphorization treatment (process time: 10 to 14 minutes) was performed by blowing powdered lime (4 to 10 kg/ton of molten iron) having a particle size diameter of 1 mm or smaller as a refining agent with a gaseous oxygen (10 to 15 Nm³/ton of molten iron) being used as a carrier gas onto the bath surface of the molten iron; and thereafter decarburization blowing was performed by charging the molten iron into a decarburizing converter. In the dephosphorization treatment, addition amount of CaF₂ was controlled to 1 kg/ton of molten iron or smaller, and the post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. The ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was controlled to 1.7. The addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The temperature of the molten iron before and after the dephosphorization treatment was controlled to 1,300 to 1,320°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration obtained as a slag analysis value.

[0126] According to FIGS. 11(a) and 11(b), compared with the range of the concave depth L from 200 to 500 mm, in the rage from smaller than 200 mm to larger than 500 mm, the efficiency of dephosphorization is lower for the reasons described above, and the post-treatment P content in the molten iron exhibits a tendency to increase.

[0127] According to a sixth embodiment, the dephosphorization treatment is performed for the molten iron having the Si content of 0.15 mass% or lower by blowing the gaseous oxygen and at least a part of the refining agent onto the bath surface of an molten iron through the top blowing lance in a condition wherein the addition amount of CaF₂ is 1 kg/ton of molten iron or smaller or CaF₂ is substantially not added (specifically, CaF₂ other than that is contained as an unavoidable impurity in the refining agent is not added). Concurrently, the temperature of the molten iron at the completion time of the dephosphorization treatment is controlled to 1,360°C to 1,450°C.

[0128] Conventionally, it is a commonly knowledge that since a dephosphorization reaction is an oxidation reaction of P, it is advantageous to perform the temperature of the molten iron at a low temperature. In addition, conventionally, when a process is performed at a high temperature, a rephosphorization from slag to metal has been contemplated to occur. As such, conventionally, it has been contemplated that even when a dephosphorization treatment is performed at a high temperature of 1,360°C or higher, it is difficult to reduce the P content in an molten iron to a low level. In this connection, the inventors verified the following. In the inventive method, in the event the dephosphorization treatment is performed under conditions in which the Si content in an molten iron to be subjected to the dephosphorization treatment is sufficiently reduced, and the addition amount CaF₂ is small or CaF₂ is not added, even when the high temperature process is performed, substantially no rephosphorization from slag to metal occurs, and high efficiency of the dephosphorization reaction can be secured. It is considered that even when the high temperature process is performed, the high efficiency of the dephosphorization reaction can thus be obtained for the following reasons. According to the inventive method, the refining agent is fed onto the region of the bath surface in which a large amount of FeO has been generated with the gaseous oxygen being added. As such, compared to the case of, for example, the method of top-charging massive lime, the area where the CaO (refining agent) is in contact with the FeO is significantly large. Consequently, the efficiency and rate of the reaction between P₂O₅ oxidized by the FeO and the CaO are increased, so that a melt-state time of the CaO-FeO based melt can be reduced. That is, the dephosphorization reaction is quickly completed, and the slag solution time thereafter is short, so that the rephosphorization rate also can be reduced.

[0129] FIG. 12 shows results of tests performed to investigate the influence of the temperature of the molten iron (temperature of the molten iron at the completion time of the dephosphorization treatment) and the Si content in the pre-dephosphorization treatment molten iron on the efficiency of dephosphorization (dephosphorization lime efficiency) after performing the dephosphorization treatment of the molten iron in a converter-type vessel (300 tons) under the condition CaF₂ is not added. The dephosphorization lime efficiency shown in FIG. 12 refers to the ratio of the lime contributed to the dephosphorization with respect to the total lime (calcined lime) added as the refining agent, and that ratio was derived from the stoichiometric mixture ratio on the prerequisite that oxides are fixed as 3CaO-P₂O₅.

[0130] In each of the tests, after the converter molten iron was subjected to desiliconization on the casting bed and in the molten iron ladle by necessity, the molten iron was subjected to desulfurization, was moved into a converter-type vessel, and was then subjected to the dephosphorization treatment. In this case, the Si content in the molten iron to be subjected to the dephosphorization treatment and the post-treatment molten iron temperature were changed to various levels. In the molten iron before the dephosphorization treatment, P content was 0.10 to 0.11 mass%, and the Si content was 0.15 mass% or lower, and the P content in the molten iron was reduced by the dephosphorization treatment to 0.02 mass% or lower.

[0131] For the refining agent, only CaO base calcined lime not containing CaF₂ was used. For the gaseous oxygen, gaseous oxygen was mainly used and was added by being blown onto the bath surface of the molten iron from the

top blowing lance; and partly, addition of a solid-state oxygen source (iron ore) was concurrently performed. Except for the desiliconization, the oxygen amount was controlled in a range of 10 to 11 Nm³/ton of molten iron. The dephosphorization treatment time was controlled to 10 to 11 minutes, and the pre-dephosphorization treatment molten iron temperature and addition amount of scrap were tuned to control the post-dephosphorization treatment molten iron temperature. The post-treatment slag rate was controlled to 30 kg/ton of molten iron.

[0132] In FIG. 12, "O" represents a test example (a) in which the molten iron temperature at the completion time of the dephosphorization treatment was controlled to 1,260 to 1,350°C; and "▲" represents a test, example (b) in which the lime (powdered lime having a particle size diameter of 1 mm or smaller) is blown onto the bath surface of the molten iron with the gaseous oxygen as the carrier gas, the molten iron temperature at the completion time of the dephosphorization treatment was controlled to 1,360 to 1,450°C. The addition amount of the lime was controlled to vary in the range of 5 to 10 kg/ton of molten iron corresponding to the Si content in the molten iron. In the test example (b), the ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was controlled to 1.7. The addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurred in the bath surface of the molten iron in association thereonto with the blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of from 200 to 500 mm. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and a CaO concentration obtained as a slag analysis value.

[0133] According to FIG. 12, regardless of, for example, the feed technique of the lime and the molten iron temperature at the completion time of the dephosphorization treatment, as the Si content in the molten iron is lower, the ratio of CaO to be consumed for a_{2CaO}^{CaO} is reduced, so that the dephosphorization lime efficiency is increased. However, the dephosphorization lime efficiency is higher in the case where both the molten iron temperature at the completion time of the dephosphorization treatment is controlled to 1,360 to 1,450°C in the method of blowing the lime with the gaseous oxygen onto the bath surface of the molten iron (test example (b)), compared to the case where the molten iron temperature at the completion time of the dephosphorization treatment is controlled to 1,260 to 1,350°C in the method of adding the lime through top-charging (test example (a)). In addition, this effect becomes more prominent as the Si content in the molten iron becomes lower. Although the dephosphorization reaction is relatively advantageous in terms of the averaging theory, the results shown in FIG. 12 is considered attributed to the fact that, in the test example (b), the rephosphorization rate was reduced by slag solubility and the fixation of dephosphorization generation substances.

[0134] FIG. 13 shows results of tests performed to investigate the influence of the CaF₂ addition amount on the efficiency of dephosphorization (dephosphorization lime efficiency) in the method that blows the refining agent with the gaseous oxygen onto the bath surface of the molten iron. In each of the tests, a converter-type vessel similar to that used in the test illustrated in FIG. 12, and also the adding technique of the refining agent and the oxygen source, the process time, and the like were arranged similar to those in the test example (b) illustrated in FIG. 13. The molten iron temperature at the completion time of the dephosphorization treatment was controlled in the range of 1,360 to 1,450°C. The CaF₂ was batch-added by top-charging. The post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller.

[0135] According to FIG. 13, when the CaF₂ addition amount reaches 1 kg/ton of molten iron or smaller, the dephosphorization lime efficiency is enhanced. CaF₂ has a function of accelerating the solution of CaO, and the addition of the CaF₂ increases the liquid phase percentage of slag. However, in the case where the process temperature (molten iron temperature) is 1,360°C, when the CaF₂ is added to increase the liquid phase percentage of slag, the rephosphorization rate from slag to metal increases and easily approaches to an equilibrium value, the dephosphorization lime efficiency is considered to be deteriorated. As such, to enhance the efficiency of dephosphorization by controlling the process temperature (molten iron temperature) to 1,360°C or higher, the CaF₂ addition amount should be minimized (1 kg/ton of molten iron or smaller, or substantially no addition).

[0136] When the molten iron temperature at the completion time of the dephosphorization treatment exceeds 1,450°C, the effect of increasing the value of the intra-molten iron P concentration is higher than the effect of increasing the temperature of the molten iron to solving the CaO. As such, the molten iron temperature at the completion time of the dephosphorization treatment should be controlled to 1,450°C.

[0137] The results described above teach that the dephosphorization treatment can be implemented with the high efficiency of dephosphorization even when the melt temperature at the completion time of the dephosphorization treatment is as high as 1,360 to 1,450°C. The highly efficient process can thus be implemented under the conditions in which the CaF₂ is added in the amount of 1 kg/ton of molten iron or is substantially not added, as described above.

[0138] In addition, as described above, the present embodiment enables the high molten iron temperature to be secured at the completion time of the dephosphorization treatment, therefore enabling a sufficient heat margin to be

secured for subsequent processing steps. Further, since the post-treatment molten iron temperature is high, intra-slag T.Fe can be mitigated low, and dephosphorization ferrous yield also can be enhanced.

[0139] Generally, the pre-dephosphorization treatment molten iron temperature is about 1,250 to 1,350°C. Ordinary techniques for tuning the molten iron temperature at the completion time of the dephosphorization treatment include, for example, a technique for restraining the feed amount of scrap for dephosphorization treatment using a converter-type dephosphorization refinement furnace that melts the scrap. In addition, for dephosphorization treatment using, for example, a ladle type vessel, such as an molten iron ladle or torpedo car, there is, for example, a technique for regulating the feed amount of solid-state oxygen source such as sintered powder. Such the techniques may be used to control the molten iron temperature at the completion time of the process to fall within the range of 1,360 to 1,450°C.

[0140] As practical control techniques for the molten iron temperature at the completion time of the dephosphorization treatment, an easiest one is to calculate an in-dephosphorization treatment molten iron temperature from gas-composition analysis values and the temperature of the exhaust gas. More specifically, in this technique, the exhaust gas is subjected to a gas composition analysis to obtain CO and CO₂ concentrations, a gas generation amount is calculated from the temperature of the exhaust gas, and the molten iron temperature is calculated therefrom.

[0141] According to a seventh embodiment, a substance absorbing the heat of a molten iron through a chemical reaction and/or a thermal decomposition reaction is fed onto the region of the bath surface to which the gaseous oxygen is fed.

[0142] The region of the bath surface onto which the gaseous oxygen is blown makes the conditions very advantageous for the decomposition acceleration of the refining agent since the gaseous oxygen impinging on the bath surface causes a large amount of iron oxides to be generated in that region. On the other hand, however, a high temperature site is formed by the oxidation reaction in the bath surface region (particularly, onto the hot spot) on which the gaseous oxygen impinges. While generation of such a high temperature site is advantageous to melt the lime, the site disadvantageously acts from the viewpoint of dephosphorization equilibrium.

[0143] To solve such problems described above, the inventors conducted research regarding means capable of making the region of the bath surface, onto which the gaseous oxygen is fed, to have temperature conditions advantageous to the dephosphorization reaction. As a result, the inventors found that effective means is to feed a substance absorbing the heat of an molten iron through a chemical reaction and/or a thermal decomposition reaction onto the region of the bath surface to which the gaseous oxygen is fed. The feeding of the substance enables a temperature rise in the region of the bath surface onto which the gaseous oxygen is fed to be appropriately restrained, and concurrently enables even higher efficiency of the dephosphorization reaction to be secured without allowing the gaseous oxygen to hinder the decomposition acceleration operation of the refining agent.

[0144] The substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction (the substance hereinbelow will also be referred to as an "endothermic substance") is added (fed) onto the bath surface of the molten iron to restrain an excessive rise in the molten iron temperature due to heat generation by the gaseous oxygen fed onto the bath surface of the molten iron. For this reason, the endothermic substance should be fed onto the bath surface of the molten iron onto which the gaseous oxygen is fed. In addition, in the region of the bath surface of the molten iron onto which the gaseous oxygen is fed, a region called "hot spot" occurring on the molten iron bath through the blowing of the gaseous oxygen through the top blowing lance is a particularly preferable region onto which the endothermic substance is to be fed. The hot spot corresponds to a region of the bath surface where the temperature is risen highest by the impingement on gaseous-oxygen gas jets, oxidation reactions (generative reactions of FeO) caused by the gaseous oxygen are concentrated, and the molten iron is agitated with the gaseous-oxygen gas jets. As such, the hot spot can be defined as a region where the most prominent effect with the feeding of the endothermic substance can be obtained.

[0145] For the endothermic substance, no specific limitations are imposed thereon, and any substance may be used as long as the substance removes (absorbs) the heat of the molten iron the chemical reaction and/or the thermal decomposition reaction or both that occur upon being added to the molten iron. As such, the endothermic substance may be either a gas or a solid.

[0146] Usable gaseous endothermic substances are, for example, carbon dioxide, water vapor, and nitrogen oxide (NOx), and at least one of them may be used for the substance. The gaseous endothermic substances are fed onto the bath surface of the molten iron, and are thereby brought into reaction primarily with Fe (for example, $\text{CO}_2 + \text{Fe} \rightarrow \text{FeO} + \text{CO}$ and $\text{H}_2\text{O} + \text{Fe} \rightarrow \text{FeO} + \text{H}_2$). In the event of the reactions, the substances absorb the heat of the molten iron. As a result, for the heat generation through the Fe oxidation ($\text{Fe} + 1/2\text{O}_2 \rightarrow \text{FeO}$) occurring with the gaseous oxygen, either the region is totally endothermic or the heat generation amount is significantly reduced. Among the gaseous endothermic substances described above, particularly the carbon dioxides or water vapor occurring in a steel mill are preferable as they are easily available and exhibit high thermal effect. In addition, even when substances such as nitrogen is entrained in the gases and the purity is somewhat reduced thereby, since the dephosphorization treatment is not performed in a final steelmaking stage, no specific problems take place. The substances such as CO and H₂ generated through reductions of the carbon dioxides and water vapor having been fed are collected as part of exhaust

gas at the time of the dephosphorization treatment, thereby exhibiting also the effect of increasing the exhaust gas calorie.

[0147] Examples of solids usable for endothermic substances are metal carbonate and metal hydroxide, and particularly preferable examples are carbonates of alkali metal and alkaline earth metal. At least one of these substances may be used. These solid endothermic substances primarily generate a thermal decomposition reaction by being fed onto the bath surface of the molten iron, exhibits an endothermic operation to remove the heat from the molten iron, and generate CO_2 or H_2O through the thermal decomposition. As described above, since the CO_2 or H_2O further function as the endothermic substances, a particularly high endothermic effect can be obtained. Examples of the carbonates are CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, MgCO_3 , NaCO_3 , FeCO_3 , MnCO_3 , and NaHCO_3 , (sodium hydrogencarbonate); and examples of metal hydroxides are $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Mn}(\text{OH})_n$, and $\text{Ni}(\text{OH})_n$; and at least one the aforementioned may be used.

[0148] Among these solid endothermic substances, CaCO_3 , $\text{Ca}(\text{OH})_2$, and $\text{CaMg}(\text{CO}_3)_2$ are particularly preferable for the reasons that the substances are not only easy to obtain, but also generate CaO through the thermal decomposition, the CaO functioning as the refining agent, thereby exhibiting a significant advantage. Ordinarily, these solid endothermic substances are added in the form of unburned, semiburned limestone, or dolomite.

[0149] When the granularity of the solid endothermic substance is excessively coarse, the thermal decomposition and the like do not rapidly progress, so that the solid endothermic substance is preferably particulate substance having an average particle size diameter of 5 mm or smaller.

[0150] The gaseous endothermic substance and the solid endothermic substances, as described above, may be together used at the same time. Alternatively, the gaseous endothermic substance may be used as a part or all of a carrier gas to feed the solid endothermic substance onto the bath surface of the molten iron.

[0151] No specific limitations are imposed on the adding technique for the endothermic substance (gas and/or solid). As such, the endothermic substance may be added either by being blown onto the bath surface of the molten iron through the top blowing lance or a different lance or by being top-charged (charged using, for example, a shooter for the solid endothermic substance). However, preferably, a lance is used to feed the endothermic substance onto the bath surface of the molten iron, and more preferably, the top blowing lance is used to feed the substance onto the bath surface of the molten iron. This manner is preferable so that the endothermic substance is securely fed onto the region of the bath surface (particularly preferably the "hot spot") onto which the gaseous oxygen is fed to secure the effects described above.

[0152] Any one of two techniques described hereunder may be used to feed the endothermic substance onto the bath surface of the molten iron through the top blowing lance. The one is a technique (1) in which the endothermic substance is mixed with the gaseous oxygen (for, a solid endothermic substance, the gaseous oxygen is used as a carrier gas) and is then fed onto the bath surface of the molten iron from same lance holes. The other is a technique is (2) in which the endothermic substance and the gaseous oxygen are separately fed through separate gas feed lines into a lance and are then fed onto the bath surface of the molten iron from separate lance holes (for a solid endothermic substance, a carrier gas different from the gaseous oxygen is used to feed the endothermic substance).

[0153] The technique (1) is preferable from the viewpoint of securely feeding the endothermic substance onto the region of the bath surface of the molten iron onto which the gaseous oxygen is fed. However, even in the technique (2), the endothermic substance having been fed through a predetermined lance hole may be fed onto the region of the bath surface onto which the gaseous oxygen is fed through a different lance hole. A practically preferable mode is that the gaseous endothermic substance is fed from, for example, a central lance hole formed at a tip of the top blowing lance, or the endothermic substance is fed using a gas other than the gaseous oxygen as a carrier gas, in which the gaseous oxygen is fed from a different lance hole formed in a peripheral portion of the central lance hole. For the carrier gas; an inert gas such as N_2 or Ar is preferable. Alternatively, the gaseous endothermic substance (CO_2 , for example) may be used as a carrier gas.

[0154] In the technique (1), only the gaseous oxygen may be fed from some of a plurality of lance holes onto the bath surface of the molten iron, and gaseous oxygen mixed with the endothermic substance (and the refining agent, depending on the case) may be fed from other lance holes onto the bath surface of the molten iron:

[0155] In any of (1) and (2) described above, the refining agent alone or together with the endothermic substance (gas and/or solid) may be mixed with the gaseous oxygen or a carrier gas other than the gaseous endothermic substance or the gaseous endothermic substance, and the mixture may be fed in the mixture state onto the bath surface of the molten iron.

[0156] Suppose that the endothermic substance (gas and/or solid) or the endothermic substance and the refining agent are to be fed in the state of being mixed with the gaseous oxygen onto the bath surface of the molten iron through the top blowing lance. In this case, the endothermic substance may be fed to a part or all of an oxygen feed line (a header, piping, a gaseous-oxygen flow path in the lance, and the like) of the top blowing lance and may then be mixed therein with the gaseous oxygen.

[0157] The endothermic substance (gas and/or solid) or the endothermic substance and the refining agent may be

fed onto the bath surface of the molten iron by using feed means (such as a different lance) other than the top blowing lance. The lance other than the top blowing lance may be a lance capable of feeding powder to a predetermined position in the furnace, as in the case of the top blowing lance. For this lance, ordinarily, a sub-lance or the like used for sampling and temperature measurement may be used as long as the lance has no problem in cooling capability in the furnace.

Alternatively, even a top throwing apparatus such as a shooter or a flow-in apparatus may be used as long as the apparatus has no problems in, for example, durability at high temperature and accuracy in a throw position.

[0158] Further, as described above, the dephosphorization reaction can be accelerated most effectively by blowing (projecting) the refining agent onto the region (particularly, the "hot spot" region, as described above) of the bath surface of the molten iron onto which the gaseous oxygen is fed, and concurrently, by directly feeding the endothermic substance onto that region. In this event, the technique of blowing onto the bath surface of the molten iron the gaseous oxygen, the refining agent, and the endothermic substance (gas and/or solid) in the mixed state. Alternatively, however, a different technique can be used. For example, only the gaseous oxygen can be fed onto the bath surface of the molten iron from some of a plurality of lance holes of the top blowing lance. Concurrently, from other lance holes, the refining agent and the endothermic substance (gas and/or solid) can be fed by necessity onto the bath surface of the molten iron by using, as a carrier gas, the gaseous oxygen or a gas (an inert gas such as nitrogen or Ar, for example) other than the gaseous oxygen. In this case, it is particularly preferable to use a top blowing lance that has a main lance hole in a center at a tip of the lance and that has a plurality of sub-lance holes in peripheral portions of the main lance. Thereby, the gaseous oxygen is fed onto the bath surface of the molten iron from the sub-lance holes. Concurrently, from the main lance hole, the refining agent and the endothermic substance (gas and/or solid) are fed by necessity onto the bath surface of the molten iron by using, as a carrier gas, the gaseous oxygen or a gas other than the gaseous oxygen. Still alternatively, different top blowing lances may be individually used to blow the gaseous oxygen and to blow the refining agent. However, in any of the cases, the refining agent and the endothermic substance (gas and/or solid) are preferably blown with the gaseous oxygen onto the bath surface of the molten iron to cause the refining agent to be most efficiently dissolved.

[0159] FIGS. 14(a) to 14(e) show several examples of feeding modes using a top blowing lance for feeding a gaseous oxygen, a refining agent, and an endothermic substance(s) onto the bath surface of the molten iron. FIG. 14(a) shows a mode of feeding (blowing onto the bath surface of the molten iron) the gaseous oxygen, the refining agent, and the endothermic substance (gas and/or solid) in the form of a mixture from lance holes. FIG. 14(b) shows a mode of feeding (blowing onto the bath surface of the molten iron) the gaseous oxygen and the refining agent from some lance holes and feeding the gaseous oxygen and the endothermic substance (gas and/or solid) from other lance holes. FIG. 14(c) shows a mode of feeding (blowing onto the bath surface of the molten iron) the gaseous oxygen and a carrier gas other than the gaseous oxygen from some lance holes and feeding the gaseous oxygen and the endothermic substance (gas and/or solid) from other lance holes. FIG. 14(d) shows a mode of feeding (blowing onto the bath surface of the molten iron) a gaseous endothermic substance and the refining agent from some lance holes and feeding the gaseous oxygen and the endothermic substance (gas and/or solid) from other lance holes. FIG. 14(e) shows a mode of feeding (blowing onto the bath surface of the molten iron) the gaseous oxygen and the refining agent from some lance holes and feeding the gaseous endothermic substance or the gaseous endothermic substance and a solid endothermic substance from other lance holes. However, the feeding modes of the gaseous oxygen, the refining agent, and the endothermic substance(s) to the bath surface of the molten iron are not limited to those illustrated.

[0160] As described above, among the solid endothermic substances, CaCO_3 , Ca(OH)_2 , and $\text{CaMg(CO}_3)_2$ each generate CaO through the thermal decomposition, and the CaO functions as the refining agent. As such in the present embodiment, the dephosphorization treatment can be performed in the manner that the above-described solid endothermic substance can be fed instead of a part or all of a CaO-based refining agent (primarily, quicklime), and the CaO generated from the above-described substance is used as an essential refining agent. That is, in this case, instead of a part or all of the CaO-based refining agent, at least one selected from CaCO_3 , Ca(OH)_2 , and $\text{CaMg(CO}_3)_2$ (which hereinbelow will be referred to as a "refining-agent generation/endothermic substance") is fed onto the region of the bath surface onto which the gaseous oxygen as a refining-agent generation substance and concurrently as a substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction.

[0161] According to the method described above, the following advantages and/or effects can be obtained. The refining-agent generation/endothermic substance fed onto the bath surface of the molten iron is thermally decomposed to absorb the heat of the molten iron, the thermal decomposition generates CaO acting as the refining agent and CO_2 or H_2O acting as the endothermic substance, and the CO_2 or the H_2O reacts with Fe to further absorb the heat of the molten iron. Concurrently, an effect can be obtained that is similar to the effect of feeding both the CaO-based refining agent and endothermic substance onto the region of the bath surface of the molten iron onto which the gaseous oxygen is fed. Consequently, a high efficiency of the dephosphorization reaction can be secured.

[0162] In this case also, for reasons similar to those described above, it is preferable that the refining-agent generation/endothermic substance be fed to, particularly, a region called "hot spot" occurring in association with the feeding of oxygen in the region of the bath surface of the molten-iron onto which the gaseous oxygen is fed.

[0163] Ordinarily, the refining-agent generation/endothemic substance is added in the form of unburned, semiburned limestone, or dolomite. When the granularity of the refining-agent generation/endothemic substance is excessively coarse, the thermal decomposition and the like do not rapidly progress, so that the refining-agent generation/endothemic substance is preferably particulate substance having an average particle size diameter of 5 mm or smaller.

[0164] The refining-agent generation/endothemic substance may be used together with the gaseous endothermic substance at the same time. Alternatively, the gaseous endothermic substance may be used as a part or all of a carrier gas to feed the refining-agent generation/endothemic substance onto the bath surface of the molten iron.

[0165] No specific limitations are imposed on the adding technique for the refining-agent generation/endothemic substance. As such, the refining-agent generation/endothemic substance may be added either by being blown onto the bath surface of the molten iron through the top blowing lance or a different lance or by being top-charged (charged using, for example, a shooter). However, preferably, a lance is used to feed the substance onto the bath surface of the molten iron, and more preferably, the top blowing lance is used to feed the refining-agent generation/endothemic substance onto the bath surface of the molten iron. This manner is preferable so that the refining-agent generation/endothemic substance is securely fed onto the region of the bath surface (particularly preferably the "hot spot") onto which the gaseous oxygen is fed to secure the effects described above.

[0166] Any one of two techniques described hereunder may be used to feed the refining-agent generation/endothemic substance onto the bath surface of the molten iron through the top blowing lance. The one is a technique (1) in which the refining-agent generation/endothemic substance is mixed with the gaseous oxygen (the gaseous oxygen is used as a carrier gas) and is then fed onto the bath surface of the molten iron from a same lance hole. The other is a technique (2) in which the refining-agent generation/endothemic substance and the gaseous oxygen are separately fed through separate gas feed lines into a lance and are then fed onto the bath surface of the molten iron from separate lance holes (a carrier gas different from the gaseous oxygen is used to feed the refining-agent generation/endothemic substance).

[0167] The technique (1) is preferable from the viewpoint of securely feeding the refining-agent generation/endothemic substance onto the region of the bath surface of the molten iron onto which the gaseous oxygen is fed. However, even in the technique (2), the refining-agent generation/endothemic substance having been fed through a predetermined lance hole may be fed onto the region of the bath surface onto which the gaseous oxygen is fed through a different lance hole. A practically preferable mode is that the refining-agent generation/endothemic substance is fed from, for example, a central lance hole formed at a tip of the top blowing lance, or the refining-agent generation/endothemic substance is fed using a gas other than the gaseous oxygen as a carrier gas, in which the gaseous oxygen is fed from a different lance hole formed in a peripheral portion of the central lance hole. For the carrier gas, an inert gas such as N_2 or Ar is preferable. Alternatively, the gaseous endothermic substance (CO_2 , for example) may be used as a carrier gas.

[0168] In the technique (1), only gaseous oxygen may be fed from some of a plurality of lance holes onto the bath surface of the molten iron, and gaseous oxygen mixed with the refining-agent generation/endothemic substance may be fed from other lance holes onto the bath surface of the molten iron.

[0169] Suppose that the refining-agent generation/endothemic substance is to be fed in the state of being mixed with the gaseous oxygen onto the bath surface of the molten iron through the top blowing lance. In this case, the refining-agent generation/endothemic substance may be fed to a part or all of an oxygen feed line (a header, piping, a gaseous-oxygen flow path in the lance, and the like) of the top blowing lance and may then be mixed therein with the gaseous oxygen.

[0170] The refining-agent generation/endothemic substance may be fed onto the bath surface of the molten iron by using feed means (such as a different lance) other than the top blowing lance. The lance other than the top blowing lance may be a lance capable of feeding powder to a predetermined position in the furnace, as in the case of the top blowing lance. For this lance, ordinarily, a sub-lance or the like used for sampling and temperature measurement may be used as long as the lance has no problem in cooling capability in the furnace. Alternatively, even a top throwing apparatus such as a shooter or a flow-in apparatus may be used as long as the apparatus has no problems in, for example, durability at high temperature and accuracy in a throw position.

[0171] The gaseous oxygen to be used to feed the refining-agent generation/endothemic substance may be any of a pure oxygen gas and an oxygen containing gas.

[0172] The above-described first to seventh embodiments of the inventive method may either be practiced alone or be practiced by combining the conditions of two or more of the embodiments (however, the second embodiment is limited to the case where the ladle or torpedo-car type vessel is used for the refinement vessel). Needless to say, in proportion to the increase in the number of the conditions to be combined, the effect of the inventive method are enhanced higher.

[0173] As described above, according to the present invention, the efficient dephosphorization treatment can be performed with a minimized addition amount of the refining agent. As additional effects, the inventive method exhibits a significant advantage in that since generated slag is in the solid-phase dominant state, the slag can be appropriately

prevented from flowing away at the melt-discharge time after the process.

[0174] Following an increase in the efficiency of the dephosphorization reaction in the dephosphorization treatment, the phosphorous concentration in the slag increases. As such, it is important to prevent the slag from flowing out together with the metal at the molten iron discharge time after the dephosphorization treatment (especially, at the time of iron-metal discharge from a refinement vessel such as a converter-type vessel having an molten iron discharge end). More specifically, suppose that a dephosphorization treatment with a phosphorus distribution of about 200, and the post-treatment P content in the molten iron is 0.015 mass% (specified value: 0.020 mass%). In this case, when slag of about 5 kg/ton of molten iron flows out, as much as 0.015 mass% into a decarburization blowing converter, so that dephosphorizing coal is required also in the decarburization blowing converter. However, the inherent purposes of the molten iron preliminary treatment cannot be achieved in the case described above. As such, the prevention of flow-out of the dephosphorization slag is important.

[0175] Conventionally, methods as described hereunder by way of example are used to minimize slag outflow to a subsequent processing step after a dicalcium silicate using a converter-type vessel. The methods are: (1) slag cut technique used during molten iron discharge from the converter-type vessel; (2) technique of reducing slag fluidity by controlling the slag composition after the process; and 3) technique of removing slag (skimming slag) from a ladle after molten iron discharge.

[0176] However, these techniques have such problems as that slag outflow cannot stably be prevented, a high cost is required since consumption articles are used, and the molten iron temperature is reduced since it takes a time for operation, and the ferrous yield is reduced in association with slag removal.

[0177] However, as described above, according to the inventive method, the slag generated in the bath surface of the molten iron having the hot spot in the center and serially pushed outwardly of the hot spot is formed into the stable solid-phase dominant state. As such, the slag at the completion time of the dephosphorization treatment has a very low fluidity in comparison with slag generated in the conventional dephosphorization treatment methods. Consequently, slag outflow can be effectively prevented at the time molten iron discharge time after completion of the dephosphorization treatment (particularly, at the time of molten iron discharge from a refinement vessel as a converter-type vessel having an molten iron discharge end). In addition, as described above, the effects described above can be further enhanced by not adding CaF_2 or by reducing the addition amount of CaF_2 to 1 kg/ton of molten iron or smaller and by restraining the increase in slag fluidity.

[0178] A description will be given hereinbelow regarding a mechanism of preventing slag outflow at the molten iron discharge time for slag generated with the inventive method in comparison with slag generated by the conventional method. FIG. 15 shows slag/metal states at an molten iron discharge start time. In the conventional case shown in FIG. 15(a), the slag was positively melted by, for example, reducing the slag basicity or adding a large amount of CaF_2 , so that the slag is in a foaming state, and the slag thickness is increased. As such, when the furnace is tilted at the molten iron discharge time, the slag travels through the molten iron discharge end, thereby unavoidably causing slag outflow. In comparison, in the inventive method shown in FIG. 15(b), the slag exists in a solid-phase dominant state, so that the slag thickness is very small, and slag outflow occurring at the molten iron discharge start time is at a negligible level.

[0179] FIG. 16 shows slag/metal states at an molten iron discharge start time. Immediately before completion of molten iron discharge, the metal depth decreases, thereby causing whirl streams of the metal to be generated. In the conventional method shown in FIG. 16(a), since molten slag existing over the metal is swirled into the whirl streams, and the slag flows out. In comparison, in the inventive method shown in FIG. 16(b), since the slag is in a solid-phase dominant state, pieces of the slag interfere with one another to be aggregated, cases almost do not take place in which the slag is swirled into whirl streams.

EXAMPLES

[Example 1]

[0180] A desiliconization treatment was performed for an molten iron discharged from a blast furnace on a casting bed and in an molten iron ladle by necessity, and a desulfurization process was subsequently performed in the molten iron ladle by using a mechanical agitator. Thereafter, a dephosphorization treatment was performed in a converter-type vessel (300 tons). Molten iron ingredients were C: 4.5 to 4.7 mass%; Si: 0.01 to 0.28 mass%; Mn: 0.15 to 0.25 mass%; P: 0.10 to 0.11 mass%; and S: 0.001 to 0.003 mass%. Powdered lime having a particle size diameter of 1 mm or smaller was used as a dephosphorization refining agent, and the powdered lime was blown with gaseous oxygen used as the carrier gas via a lance. CaF_2 was not added into the refining agent. The blowing time was controlled to 10 minutes as a constant time, and a nitrogen gas of 0.05 to 0.15 $\text{Nm}^3/\text{min}/\text{ton}$ of molten iron was fed from the bottom of the furnace to agitate the molten iron. While the lime and oxygen source units are variable depending on the Si content in the molten iron, the lime and oxygen were fed in the quantities corresponding to constant values each excluding the

desiliconization part (dicalcium silicate: stoichiometric mixture part when $2\text{CaO} \cdot \text{SiO}_2$ is formed) = The quantities of the lime and the oxygen were 3.5 kg/ton of molten iron and 9 Nm³/ton of molten iron, respectively. The ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was controlled to 1.7. The addition amount of the lime was controlled to fall within the range of the sum of the lime amount $W_{\text{CaO_P}}$ (kg/ton of molten iron) and the lime amount $W_{\text{CaO_Si}}$ (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The temperature of the molten iron before and after the dephosphorization treatment was controlled to 1,250 to 1,350°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0181] The results of individual application examples together with the dephosphorization treatment conditions are shown in Table 1. Individual average values are values averaged for 6 to 72 charges in units of a range of individual slag quantities after the process for a range from 5 kg/ton of molten iron to 10 kg/ton of molten iron, a range from larger than 10 kg/ton of molten iron to 20 kg/ton of molten iron, a range from larger than 20 kg/ton of molten iron to 30 kg/ton of molten iron, a range from larger than 30 kg/ton of molten iron to 40 kg/ton of molten iron, and a range from larger than 40 kg/ton of molten iron to 50 kg/ton of molten iron.

TABLE 1

No.	Post-treatment Slag rate (kg/T)	Number of Tests (ch)	Average Lime Amount (kg/T)	Average Oxygen Amount Nm ³ /T	Molten iron Ingredients (mass%)					Average Dephosphorization Rate (%)	Classification
					Pre-dephosphorization		Post-dephosphorization				
					Average [Si]	Average [P]	Average [P]	Maximum [P]	Minimum [P]		
1	5 to 10	16	5.1	9.3	0.04	0.113	0.008	0.010	0.007	93	Inventive Example
2	Larger than 10 to 20	72	6.2	9.5	0.07	0.111	0.011	0.014	0.009	91	Inventive Example
3	Larger than 20 to 30	13	8.1	9.9	0.12	0.112	0.012	0.019	0.009	89	Inventive Example
4	Larger than 30 to 40	6	11.7	10.6	0.21	0.110	0.014	0.023	0.010	87	Comparative Example
5	Larger than 40 to 50	9	13.4	11.0	0.25	0.111	0.015	0.027	0.010	86	Comparative Example

[Example 2]

[0182] A desiliconization treatment was performed for an molten iron discharged from a blast furnace on a casting

bed and in an molten iron ladle by necessity, and a desulfurization process was subsequently performed in the molten iron ladle by using a mechanical agitator. Thereafter, a dephosphorization treatment was performed in a converter-type vessel (300 tons). In the molten iron before the dephosphorization treatment, the P content was 0.10 to 0.11 mass%, and the Si content was 0.15 mass% or lower. The molten iron temperature before and after the dephosphorization treatment was controlled to 1,250 to 1,350°C. As a dephosphorization refining agent, CaO-based calcined lime sieved screened to a granularity of 200 mesh or lower was used, and the CaO source unit was controlled to 5 to 15 kg/ton of molten iron corresponding to the Si content in the molten iron.

[0183] In the dephosphorization treatment, feeding of the refining agent and the oxygen source (blowing time: 10 minutes) was performed by flowing the refining agent with the gaseous oxygen as the carrier gas onto the bath surface through a top blowing lance. In this event, operations were performed various different conditions each including a different ratio A/B between the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen and the supplying rate B (kg/min/ton of molten iron) of the refining agent. As an agitation gas, a nitrogen gas was blown at a flow rate of 0.05 to 0.15 Nm³/min/ton of molten iron into the molten iron from the bottom of the furnace. CaF₂ was not added into the refining agent, and the post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. The addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as a carrier gas, was controlled to fall within the range of 200 to 500 mm. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0184] FIG. 17 shows the relationship FIG. 17 shows the relationship between the ratio A/B, which is between the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen and the supplying rate B (kg/min/ton of molten iron) of the refining agent, and the P content in the molten iron. According to the figure, when the ratios A/B in the inventive examples are in the region of 0.3 to 7, the post-dephosphorization treatment P contents in the molten iron are lower than or equal to 0.015 mass% that corresponds to the object [P] concentration. Particularly, when the pre-dephosphorization treatment Si contents in the molten iron are in the region of 0.3 to 7, the post-dephosphorization treatment P contents in the molten iron are lower than or equal to 0.010 mass%, "[P] ≤ 0.010 mass%", which is a low P standard, is stably satisfied. When the A/B ratios are in the region of 1.2 to 2.5, an especially low level [P] concentrations are obtained, from which it can be known that the highest efficiency of the dephosphorization reaction can be obtained in that region.

[0185] In comparison, when the ratios A/B are in the region of lower than 0.3 to higher than 7, the post-dephosphorization treatment P contents in the molten iron reach the level lower than or equal to 0.015 mass%, which is the object [P] concentration, for any items.

[Example 3]

[0186] After a desiliconization treatment performed for an molten iron discharged from a blast furnace on a casting bed, the molten iron was received by an molten iron ladle, and slag skimming was conducted therefor. The molten iron ladle was then moved to a dephosphorization station, and a dephosphorization treatment was performed therein.

[0187] In the dephosphorization treatment, powdered lime (refining agent) was blown with the gaseous oxygen being used as the carrier gas onto the bath surface of the molten iron through a top blowing lance, and the powdered lime was injected into the molten iron through the immersed lance. For comparative examples, the blowing of powdered lime through the top blowing lance was not performed, but the powdered lime was injected into the molten iron through the immersed lance. In any of the cases, the process time was controlled to 20 minutes. The post-treatment slag rate was controlled to 20 kg/ton of molten iron. For the inventive examples, the addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The molten iron temperature before and after the dephosphorization treatment was controlled to 1,300 to 1,320°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0188] The results of individual application examples together with the dephosphorization treatment conditions are shown in Table 2.

TABLE 2

No.	Pre-dephosphorization Molten iron Ingredients		Molten iron Temperature		Dephosphorization Conditions				Post-dephosphorization Molten iron [P] (mass%)	Dephosphorization Rate (%)	Classification
	[Si] (mass%)	[P] (mass%)	Pre-dephosphorization (°C)	Post-dephosphorization (°C)	Refining-agent Addition Amount (kg/T) *1		CaF ₂ Addition Amount (kg/T)	Gas Addition (Nm ³ /T)			
					Top Blowing Lance	Immersed Lance					
1	0.05	0.112	1312	1325	3.9	1.0	-	13	0.005	96	Inventive Example
2	0.04	0.120	1342	1330	3.3	1.5	-	10	0.004	97	Inventive Example
3	0.02	0.115	1338	1320	2.3	1.5	-	6	0.007	94	Inventive Example
4	0.06	0.118	1310	1328	2.8	2.7	-	7	0.006	95	Inventive Example
5	0.07	0.116	1348	1332	1.8	4.0	0.6	6	0.005	96	Inventive Example
6	0.02	0.116	1325	1324	-	3.8	-	15	0.019	84	Comparative Example
7	0.07	0.113	1343	1325	-	5.8	-	5	0.026	77	Comparative Example
8	0.03	0.120	1330	1326	-	4.4	0.4	4	0.022	82	Comparative Example
9	0.04	0.110	1329	1328	-	4.5	1.5	3	0.031	72	Comparative Example

*1) Top Blowing Lance: Blowing onto Bath Surface of Molten iron
Immersed Lance: Injection into Molten iron

[Example 4]

[0189] A desiliconization treatment was performed for an molten iron discharged from a blast furnace on a casting bed and in an molten iron ladle by necessity, and a desulfurization process was subsequently performed in the molten iron ladle by using a mechanical agitator. Thereafter, a dephosphorization treatment was performed in a converter-type vessel (300 tons). In the dephosphorization treatment, the molten iron temperature before and after the process was controlled to 1,250 to 1,350°C. The gaseous oxygen was blown onto the bath surface of the molten iron through a top blowing lance. Concurrently, the refining agent was added according to any one of techniques: (1) in which powdered lime (refining agent) having a particle size diameter of 1 mm or smaller is blown with the gaseous oxygen being used as a carrier gas; and (2) in which powdered lime (refining agent) having a particle size diameter of 1 to 3 mm is top-charged into the molten iron. The molten iron was agitated with the nitrogen gas blown into the molten iron at a feed amount of 0.05 to 0.15 Nm³/min/ton of molten iron from the bottom of the furnace, and concurrently, the dephosphorization treatment was performed for 9 minutes. The post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. For the inventive examples, the addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0190] The results of individual application examples together with the dephosphorization treatment conditions are shown in Table 3.

TABLE 3

No.	Pre-dephosphorization Molten iron ingredients (mass%)		Dephosphorization treatment Conditions										Post-dephosphorization Molten iron [P] (mass%)	Dephosphorization Rate (%)	Classification
	[S]	[P]	Refining-agent Addition Amount (kg/T)	CaF ₂ Addition Amount (kg/T)	Gas Addition Amount (Nm ³ /T)	C1 *1	C2 *1	D1 *1	D2 *1	Cl/D1 (kg/Nm ³)	C2/D2 (kg/Nm ³)	Refining-agent Addition Technique *2			
1	0.07	0.111	5.8	-	8.6	1.00	0.36	1.21	0.76	0.83	0.47	Blowing	0.009	92	Inventive example
2	0.06	0.105	4.4	-	9.3	0.85	0.30	1.42	0.85	0.60	0.35	Blowing	0.011	90	Inventive example
3	0.03	0.103	4.6	-	9.6	0.88	0.33	1.45	0.88	0.61	0.38	Blowing	0.012	88	Inventive example
4	0.04	0.108	5.5	-	9.6	0.91	0.36	1.33	0.85	0.68	0.42	Blowing	0.008	93	Inventive example
5	0.05	0.111	5.0	0.2	9.2	0.88	0.39	1.36	0.85	0.65	0.46	Blowing	0.010	91	Inventive example
6	0.01	0.108	5.0	0.7	9.1	0.88	0.30	1.28	0.79	0.69	0.38	Blowing	0.009	92	Inventive example
7	0.03	0.114	7.9	-	10.2	0.88	0.88	1.42	0.91	0.62	0.97	Blowing	0.015	87	Inventive example
8	0.07	0.112	6.7	1.5	10.4	0.91	0.61	1.45	0.91	0.63	0.67	Blowing	0.011	90	Inventive example
9	0.06	0.105	10.0	-	13.1	-	-	1.45	-	-	-	Top-Charging	0.015	86	Comparative example
10	0.06	0.108	12.0	0.3	13.6	-	-	1.52	-	-	-	Top-Charging	0.014	87	Comparative example
11	0.02	0.113	5.8	1.3	12.8	-	-	1.42	-	-	-	Top-Charging	0.039	65	Comparative example

*1 C1: Average value of Lime Supplying rates in Earlier Stage of Process (kg/min/T)

C2: Average value of Lime Supplying rates in Latter Stage of Process (kg/min/T)

D1: Average value of Gaseous-oxygen Supplying rates in Earlier Stage of Process (Nm³/min/T)

D2: Average value of Gaseous-oxygen Supplying rates in Latter Stage of Process (Nm³/min/T)

*2 Blowing: Blowing of Powdered Lime (Refining Agent) onto Bath Surface of Molten Iron through Top Blowing Lance

Top-Charging: Top-charging of Lime (Refining Agent)

※ Where: (C1/D1) ≤ (C2/D2)

[Example 5]

[0191] After a desiliconization treatment performed for an molten iron discharged from a blast furnace on a casting bed, the molten iron was received by an molten iron ladle, and slag skimming was conducted therefor. Thereafter, the molten iron was charged into a converter-type vessel (300 tons), and a dephosphorization treatment was then performed.

[0192] In the dephosphorization treatment, powdered lime (refining agent) was blown with the gaseous oxygen being used as a carrier gas onto the bath surface of the molten iron through a top blowing lance, and the top-charging of massive lime was concurrently conducted for some application examples. For comparative examples, the blowing of powdered lime through the top blowing lance was not performed, but the massive lime was added by being top-charged. For each of the application example, the nitrogen gas was blown at a feed amount of 0.07 to 0.12 Nm³/min/ton of molten iron was fed from the bottom of the furnace, and the dephosphorization treatment was performed for 8 to 14 minutes. In the dephosphorization treatment, the molten iron temperature before and after the process was controlled to 1,250 to 1,350°C, and the post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. For the inventive examples, the ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was controlled to 1.7. The molten iron temperature before and after the process was controlled to 1,250 to 1,350°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0193] The results of individual application examples together with the dephosphorization treatment conditions are shown in Tables 4 through 7.

TABLE 4

No.	Molten iron ingredients (mass%)			Calculated Value of Lime Amount #1			Lime Addition Amount #2		Steelmaking-Slag Addition Amount #3		Classification
	Pre-dephosphorization [Si]	Desired value [P]	Post-dephosphorization [P]	W _{cao_si} (kg/T)	W _{cao_p} (kg/T)	Sum	Blowing (kg/T)	Top-Charging (kg/T)	Addition Amount (kg/T)	CaO Part #4 (kg/T)	
1	0.15	0.115	0.013	6.0	2.76 to 5.53	8.76 to 11.53	4.23	4.88	-	-	Inventive example
2	0.13	0.112	0.013	5.2	2.68 to 5.37	7.88 to 10.57	4.38	3.85	-	-	Inventive example
3	0.12	0.108	0.013	4.8	2.57 to 5.15	7.37 to 9.95	5.18	2.55	-	-	Inventive example
4	0.08	0.132	0.013	3.2	3.22 to 6.45	6.42 to 9.65	5.14	1.64	-	-	Inventive example
5	0.02	0.125	0.013	0.8	3.03 to 6.07	3.83 to 6.87	3.93	0.26	-	-	Inventive example
6	0.03	0.107	0.013	1.2	2.55 to 5.09	3.75 to 6.29	2.91	1.19	-	-	Inventive example
7	0.07	0.099	0.013	2.8	2.33 to 4.66	5.13 to 7.46	3.81	1.68	-	-	Inventive example
8	0.04	0.118	0.013	1.6	2.85 to 5.69	4.45 to 7.29	4.15	0.65	-	-	Inventive example
9	0.09	0.113	0.013	3.6	2.71 to 5.42	6.31 to 9.02	6.00	0.66	-	-	Inventive example
10	0.05	0.108	0.013	2.0	2.57 to 5.15	4.57 to 7.15	4.06	0.87	-	-	Inventive example
11	0.08	0.116	0.013	3.2	2.79 to 5.58	5.99 to 8.78	5.26	1.08	-	-	Inventive example
12	0.03	0.117	0.013	1.2	2.82 to 5.64	4.02 to 6.84	2.97	0.25	3.20	0.80	Inventive example
13	0.08	0.099	0.013	3.2	2.33 to 4.66	5.53 to 7.86	2.93	1.80	4.00	1.00	Inventive example

*1 W_{cao_p}: Calculated Value of Equation (1)W_{cao_si}: Calculated Value of Equation (2)Sum: W_{cao_p} + W_{cao_si}

*2 Blowing: Blowing of Powdered Lime (Refining Agent) onto Bath Surface of Molten iron through Top Blowing Lance

*3 Top-Charging: Top-charging of Lime (Refining Agent)

*4 Top-Charging Insert

*4 Free Lime Amount in Steelmaking Slag

TABLE 5

No.	Concave Depth in Bath Surface of Molten iron (mm)	Dephosphorization Rate (%)	Lime Efficiency (-)	Blowing Lime Amount/Lime Amount W_{CaO_P} *1	Classification
1	300	88.7	0.887	1.53	Inventive example
2	325	85.7	0.857	1.63	Inventive example
3	256	85.2	0.852	2.01	Inventive example
4	268	90.2	0.902	1.59	Inventive example
5	289	87.2	0.872	1.29	Inventive example
6	295	84.1	0.841	1.14	Inventive example
7	312	88.9	0.889	1.63	Inventive example
8	415	90.7	0.907	1.46	Inventive example
9	210	88.5	0.885	2.21	Inventive example
10	450	83.3	0.833	1.58	Inventive example
11	480	92.2	0.922	1.88	Inventive example
12	290	88.0	0.990	1.05	Inventive example
13	360	91.9	0.973	1.26	Inventive example

*1 W_{CaO_P} : Lime Amount calculated with $\eta_{CaO} = 1$

TABLE 6

No.	Molten Iron Ingredients (mass%)				Calculated Value of Lime Amount (kg/T) *1	Lime Addition Amount *2		Classification
	Pre- dephosphorization		Desired value [P]	post- dephosphorization [P]		Blowing (kg/T)	Top-Charging (kg/T)	
	[Si]	[P]						
14	0.10	0.122	0.013	0.015	13.97	-	13.97	Comparative example
15	0.07	0.108	0.013	0.011	12.18	-	12.18	Comparative example
16	0.02	0.113	0.013	0.009	12.82	-	12.82	Comparative example

*1 Slag Basicity: Necessary Lime Amount calculated from 3, $L_p = 240$

*2 Blowing: Blowing of Powdered Lime (Refining Agent) onto Bath Surface of Molten iron through Top Blowing Lance
Top-Charging: Top-charging of Lime (Refining Agent)

TABLE 7

No.	Concave Depth in Bath Surface of Molten iron (mm)	Dephosphorization Rate (%)	Lime Efficiency (-)	Classification
14	450	87.7	0.330	Comparative example
15	450	89.8	0.299	Comparative example
16	330	92.0	0.320	Comparative example

[Example 6]

[0194] After a desiliconization treatment performed for an molten iron discharged from a blast furnace on a casting bed, the molten iron was received by an molten iron ladle, and slag skimming was conducted therefor. Thereafter, the molten iron was charged into a converter-type vessel (300 tons), and a dephosphorization treatment was then performed. In the dephosphorization treatment, the gaseous oxygen was blown onto the bath surface of the molten iron through a top blowing lance. Concurrently, the refining agent was added according to any one of techniques: (1) in which powdered lime (refining agent) having a particle size diameter of 3 mm or smaller is blown with the gaseous oxygen being used as the carrier gas; and (2) in which massive lime (refining agent) is top-charged thereinto. The molten iron was agitated with a nitrogen gas blown into the molten iron at a feed amount of 0.1 to 0.15 Nm³/min/ton of molten iron from the bottom of the furnace, and concurrently, the dephosphorization treatment was performed for 10 to 11 minutes. The pre-dephosphorization treatment molten iron temperature and the addition amount of scrap were tuned, and the molten iron temperature at the completion time of the dephosphorization treatment was thereby controlled. The post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. For the inventive examples, the addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0195] The results of individual application examples together with the dephosphorization treatment conditions are shown in Table 8.

TABLE 8

No.	Pre-dephosphorization Molten iron ingredients		Molten iron Temperature		Dephosphorization Conditions				Post-dephosphorization Molten iron [P] (mass%)	Dephosphorization Rate (%)	Classification
	[Si] (mass%)	[P] (mass%)	Pre-dephosphorization (°C)	Post-dephosphorization (°C)	Refining-agent Amount (kg/T)	CaF ₂ Addition Amount (kg/T)	Refining-agent Addition Technique *2	Gas Addition Amount (Nm ³ /T)			
1	0.05	0.106	1320	1375	6.5	-	Blowing	10.2	0.012	89	Inventive Example
2	0.04	0.110	1315	1400	6.1	-	Blowing	9.5	0.014	87	Inventive Example
3	0.08	0.102	1285	1446	7.7	-	Blowing	10.3	0.015	85	Inventive Example
4	0.02	0.115	1267	1440	5.3	-	Blowing	9.6	0.014	88	Inventive Example
5	0.09	0.106	1354	1421	8.1	-	Blowing	10.2	0.012	89	Inventive Example
6	0.06	0.108	1302	1367	6.9	-	Blowing	10.1	0.008	93	Inventive Example
7	0.07	0.110	1314	1385	7.3	0.2	Blowing	9.7	0.011	90	Inventive Example
8	0.03	0.107	1298	1375	5.7	0.7	Blowing	10.2	0.014	87	Inventive Example
9	0.06	0.108	1315	1410	6.9	1.6	Top-Charging	10.4	0.032	70	Comparative Example
10	0.15	0.106	1320	1403	10.5	-	Top-Charging	10.2	0.034	68	Comparative Example
11	0.05	0.106	1343	1465	6.5	-	Top-Charging	10.1	0.039	63	Comparative Example
12	0.06	0.112	1298	1321	6.9	-	Top-Charging	9.9	0.033	71	Comparative Example

*2 Blowing: Blowing of Powdered Lime (Refining Agent) onto Bath Surface of Molten iron through Top Blowing Lance

Top-Charging: Top-charging of Lime (Refining Agent)

[Example 7]

[0196] After a desiliconization treatment performed for an molten iron discharged from a blast furnace on a casting bed, the molten iron was received by an molten iron ladle, and slag skimming was conducted therefor. Thereafter, the molten iron was charged into a converter-type vessel (300 tons), and a dephosphorization treatment was then performed. In the dephosphorization treatment, powdered lime (refining agent) having a particle size diameter of 1 mm or smaller and an endothermic substance were blown onto the bath surface of the molten iron through a top blowing lance. For the endothermic substance, one of CaCO_3 and Ca(OH)_2 (each having a particle size diameter of 1 mm or smaller), the substance was preliminarily mixed with the powdered lime to have a predetermined ratio. The molten iron was agitated with a nitrogen gas blown into the molten iron at a feed amount of $0.1 \text{ Nm}^3/\text{min/ton}$ of molten iron from the bottom of the furnace, and concurrently, the dephosphorization treatment was performed for 10 to 11 minutes. The pre-dephosphorization treatment molten iron temperature and the addition amount of scrap were tuned, and the molten iron temperature at the completion time of the dephosphorization treatment was thereby controlled. The post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. For the inventive examples, the addition amount of the lime was controlled to fall within the range of the sum of the lime amount $W_{\text{CaO_P}}$ (kg/ton of molten iron) and the lime amount $W_{\text{CaO_Si}}$ (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0197] The results of individual application examples together with the dephosphorization treatment conditions are shown in Table 9.

TABLE 9

No.	Pre-dephosphorization Molten iron Ingredients		Molten iron Temperature		Dephosphorization Conditions						Post-de-phosphorization Molten iron [P] (mass%)	De-phosphorization Rate (%)	Classification
	[Si] (mass%)	[P] (mass%)	Pre-de-phosphorization (°C)	Post-de-phosphorization (°C)	Refining-agent Addition Amount (kg/T)	CaF ₂ Addition Amount (kg/T)	Refining-agent Addition Technique *1	Gas Addition Amount (Nm ³ /T)	Endothermic Substance Type	Endothermic Addition Amount (kg/T)			
1	0.03	0.108	1319	1423	5.7	-	Blowing	10.6	CaCO ₃	3.1	0.009	92	Inventive Example
2	0.05	0.111	1347	1426	6.5	-	Blowing	10.8	CaCO ₃	2.3	0.010	91	Inventive Example
3	0.08	0.105	1299	1447	7.7	-	Blowing	9.9	CaCO ₃	6.5	0.011	90	Inventive Example
4	0.03	0.106	1275	1412	5.7	-	Blowing	10.5	Ca(OH) ₂	2.1	0.012	89	Inventive Example
5	0.04	0.111	1297	1385	6.1	0.3	Blowing	10.2	CaCO ₃	3.4	0.008	93	Inventive Example
6	0.06	0.104	1311	1374	6.9	0.8	Blowing	10.5	Ca(OH) ₂	2.3	0.009	91	Inventive Example

*1 Blowing: Blowing of Powdered Lime (Refining Agent) onto Bath Surface of Molten iron through Top Blowing Lance

[Example 8]

[0198] After a desiliconization treatment performed for an molten iron discharged from a blast furnace in an molten iron ladle, slag skimming was conducted therefor. Thereafter, the molten iron was charged into a converter-type vessel (300 tons), and a dephosphorization treatment was then performed. In the dephosphorization treatment, the molten iron was agitated with the agitation gas (nitrogen) blown into the molten iron at a feed amount of 0.1 Nm³/min/ton of molten iron from the bottom of the furnace, and concurrently, the gaseous oxygen, powdered lime (CaO-based refining agent), and a gaseous endothermic substance were fed onto the bath surface of the molten iron from an upper portion of the bath surface by using a top blowing lance. CaF₂ was not added into the refining agent. The post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. The ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was set to 1.7. The addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as a carrier gas, was controlled to fall within the range of 200 to 500 mm. The molten iron temperature before and after the process was controlled to 1,250 to 1,350°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

[0199] The top blowing oxygen-feed lance having one central hole and three peripheral holes as lance holes was used.

[0200] The powdered lime having a particle size diameter of 3 mm or smaller was used. The gaseous oxygen was allotted out of a cut-out apparatus as the carrier gas and was delivered through piping to be fed to the top blowing lance, and the powdered lime was fed together with the gaseous oxygen onto the bath surface of the molten iron from the central hole. In addition, the gaseous oxygen was fed into the top blowing lance through a different piping line to be fed onto the bath surface of the molten iron from the peripheral holes. The total oxygen feed amount was controlled to 1.5 Nm³/min/ton of molten iron.

[0201] The gaseous endothermic substance was added to the gaseous-oxygen lines to have a predetermined concentration. For the gaseous endothermic substance, carbon dioxide and water vapor were used, in which the mixture ratio of the substance to the gaseous oxygen was controlled to 10 to 40 vol.% (corresponding number to 100% oxygen gas).

[0202] For comparative examples, the gaseous oxygen was fed onto the bath surface of the molten iron from the top blowing lance, and massive lime (CaO-based refining agent) was top-charged.

[0203] The results of individual application examples together with the dephosphorization treatment conditions are shown in Table 10.

TABLE 10

	Molten iron Ingredients (mass%)			Dephosphorization Conditions				
No.	Predephosphorization [Si]	[P]		Endothermic Substance		Lime Use Amount (kg/T)	Dephosphorization Time (Min.)	Classification
		Predephosphorization	Postdephosphorization	Type	Addition Amount (%) *1			
1	0.09	0.110	0.011	CO ₂	5	5.6	6.4	Inventive example
2	0.08	0.108	0.010	CO ₂	10	5.2	6.1	Inventive example
3	0.07	0.109	0.008	CO ₂	25	4.6	5.2	Inventive example
4	0.07	0.109	0.007	CO ₂	40	4.3	5.0	Inventive example
5	0.13	0.109	0.010	CO ₂	25	5.8	6.6	Inventive example
6	0.07	0.107	0.010	H ₂ O	10	5.1	5.9	Inventive example
7	0.07	0.110	0.008	H ₂ O	25	4.8	5.5	Inventive example
8	0.07	0.105	0.015	-	-	8.0	11.0	Comparative example
9	0.08	0.108	0.014	-	-	8.5	11.5	Comparative example

*1) Corresponding Number (Vol.%) with respect to 100% Gaseous Oxygen

[Example 9]

[0204] After a desiliconization treatment performed for an molten iron discharged from a blast furnace in an molten iron ladle, slag skimming was conducted; and subsequently, a dephosphorization treatment was performed therefor in the ladle. In the dephosphorization treatment, the molten iron was agitated with a nitrogen gas of 3 Nm³/min from an immersed lance, and concurrently, the gaseous oxygen, powdered lime (CaO-based refining agent), and a gaseous endothermic substance were fed from an upper portion of the bath surface by using a top blowing lance by using any one of modes (1) to (4) described below. CaF₂ was not added into the refining agent. The post-treatment slag rate was controlled to 30 kg/ton of molten iron or smaller. The ratio A/B between the supplying rate B (kg/min/ton of molten iron) of the lime to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron was set to 1.7. The addition amount of the lime was controlled to fall within the range of the sum of the lime amount W_{CaO_P} (kg/ton of molten iron) and the lime amount W_{CaO_Si} (kg/ton of molten iron) defined by Expressions (5) and (6) described above. The depth L (value L defined by Equation (7) described above) of a concave, which occurs in the bath surface of the molten iron in association with blowing of the refining agent with the gaseous oxygen being used as the carrier gas, was controlled to fall within the range of 200 to 500 mm. The molten iron temperature before and after the process was controlled to 1,250 to 1,350°C. The post-treatment slag rate was calculated from the mass balance between the amount of added lime and an intra-slag CaO concentration (slag analysis value).

(1) Inventive example: Gaseous oxygen, powdered lime, and CO₂ are fed through a top blowing lance.

(2) Inventive example: Gaseous oxygen, powdered lime, and CaCO₃ (limestone) or Ca(OH)₂ (slaked lime) are fed through a top blowing lance.

(3) Inventive example: Gaseous oxygen, powdered lime, CO₂, and CaCO₃ (limestone) are fed through a top blowing lance.

(4) Inventive example: Gaseous oxygen and CaCO₃ (limestone) or Ca(OH)₂ (slaked lime) are fed through a top blowing lance.

[0205] The powdered lime, CaCO₃ (limestone), and Ca(OH)₂ each having a particle size diameter of 1 mm or smaller were used. The gaseous oxygen was allotted out of a cut-out apparatus as the carrier gas, was delivered through piping to be fed to the top blowing lance, was merged at an inlet of the top blowing lance with the gaseous oxygen fed through a different piping, and fed together with gaseous-oxygen jets onto the bath surface from three lance holes provided at a tip of the top blowing lance. The total oxygen feed amount was controlled to 6,000 Nm³/hour.

[0206] The CO₂ was controlled to have a mixture ratio of 25 vol.% (corresponding number with respect to 100% gaseous oxygen) to the gaseous oxygen. The powdered lime, CaCO₃ (limestone), and Ca(OH)₂ (slaked lime) were added to be a CaO equivalent amount of 70 to 80 kg/min.

[0207] For comparative examples, the gaseous oxygen was fed onto the bath surface of the molten iron through the top blowing lance, and concurrently, the powdered lime was injected through the immersed lance.

[0208] The results of individual application examples together with the dephosphorization treatment conditions are shown in Table 11.

TABLE 11

No.	Molten iron ingredients (mass%)			Dephosphorization Conditions						Classification
	Pre-dephosphorization [Si]	[P]		Endothermic Substance			Lime Use Amount (kg/T)	Dephosphorization Time (Min.)		
		Pre-dephosphorization	Post-dephosphorization	Gas	Solid					
					Type	Addition Amount (kg/T)				
1	0.08	0.115	0.008	CO ₂	-	-	5.0	9.8	Inventive example	
2	0.07	0.114	0.008	CO ₂	CaCO ₃	1.1	4.4	9.7	Inventive example	
3	0.12	0.116	0.011	CO ₂	CaCO ₃	1.2	5.9	13.0	Inventive example	
4	0.08	0.115	0.009	-	CaCO ₃	3.6	3.3	13.2	Inventive example	
5	0.08	0.114	0.010	-	CaCO ₃	8.5	-	14.2	Inventive example	
6	0.07	0.113	0.011	-	Ca(OH) ₂	3.5	2.2	11.5	Inventive example	
7	0.07	0.113	0.010	-	Ca(OH) ₂	6.0	-	11.6	Inventive example	
8	0.06	0.114	0.017	-	-	-	7.9	16.5	Comparative example	
9	0.15	0.114	0.021	-	-	-	10.5	20.1	Comparative example	

INDUSTRIAL APPLICABILITY

[0209] The present invention is used to produce molten iron having a low phosphorus content in steel making process.

Claims

1. A method for producing a low-phosphorous molten iron, comprising introducing an oxygen source and a refining agent acting as a CaO source into a vessel holding a molten iron to carry out a dephosphorization treatment as a preliminary treatment,
characterized in that the dephosphorization treatment is performed by blowing a gaseous oxygen and at least a part of the refining agent onto a bath surface of the molten iron through a top blowing lance; and a slag rate after the dephosphorization treatment is 30 kg/ton of molten iron or less.
2. The method according to claim 1, **characterized in that** said at least a part of the refining agent to be fed from the top blowing lance is blown onto a region of the bath surface of the molten iron onto which the gaseous oxygen is blown.
3. The method according to claim 2, **characterized in that** said at least a part of the refining agent to be fed from the top blowing lance is blown onto a hot spot generating in the bath surface of the molten iron in association with blowing the gaseous oxygen.
4. The method according to claim 2 or 3, **characterized in that** said at least a part of the refining agent is blown with the gaseous oxygen as a carrier gas.
5. The method according to any one of claims 1 to 4,
characterized in that the dephosphorization treatment is performed for a molten iron having a Si content of 0.15 mass% or less.
6. The method according to any one of claims 1 to 4,
characterized in that the dephosphorization treatment is performed for a molten iron having a Si content of 0.07 mass% or less.
7. The method according to any one of claims 1 to 4,
characterized in that the dephosphorization treatment is performed for a molten iron having a Si content of 0.03 mass% or less.
8. The method according to any one of claims 1 to 7,
characterized in that the slag rate after the dephosphorization treatment is 20 kg/ton of molten iron or less.
9. The method according to any one of claims 1 to 7,
characterized in that the slag rate after the dephosphorization treatment is 10 kg/ton of molten iron or less.
10. The method according to any one of claims 1 to 9,
characterized in that a supplying rate B in terms of CaO (kg/min/ton of molten iron) of the refining agent to be blown onto the bath surface of the molten iron and a supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron satisfy the following Equation (1):

$$0.3 \leq A/B \leq 7 \quad (1)$$

11. The method according to claim 10, **characterized in that** the supplying rate B in terms of CaO (kg/min/ton of molten iron) of the refining agent to be blown onto the bath surface of the molten iron and the supplying rate A (Nm³/min/ton of molten iron) of the gaseous oxygen to be blown onto the bath surface of the molten iron satisfy the following Equation (2) :

$$1.2 \leq A/B \leq 2.5 \quad (2)$$

12. The method according to any one of claims 1 to 11, **characterized in that**:

a ladle or a torpedo-car type vessel is used as the vessel for holding the molten iron;
the gaseous oxygen and the at least a part of the refining agent are blown onto the bath surface of the molten iron through the top blowing lance;
and
gas including powder is injected into the molten iron through an immersed lance and/or a blowing nozzle.

13. The method according to claim 12, **characterized in that** the powder to be injected into the molten iron through the immersed lance and/or the blowing nozzle is a part of the refining agent.

14. The method according to claim 12 or 13, **characterized in that** a supplying rate of the gaseous oxygen to be blown onto the bath surface of the molten iron through the top blowing lance is 0.7 Nm³/min/ton of molten iron or less.

15. The method according to any one of claims 12 to 14, **characterized in that** 80 mass% or more of a total amount of the refining agent in the dephosphorization treatment is blown onto the bath surface of the molten iron through the top blowing lance.

16. The method according to any one of claims 12 to 15, **characterized in that**:

substantially all of the refining agent is added by being blown onto the bath surface of the molten iron through the top blowing lance and by being injected into the molten iron through the immersed lance and/or the blowing nozzle;
and
the amount of the refining agent through the top blowing lance is 20 to 80 mass% of the total amount of the refining agent.

17. The method according to any one of claims 1 to 16, **characterized in that** the dephosphorization treatment is performed so that the supplying rate of the refining agent to be blown onto the bath surface of the molten iron and the supplying rate of the gaseous oxygen to be blown onto the bath surface of the molten iron satisfy the following Equation (3) and Equation (4):

$$(C1/D1) > (C2/D2) \quad (3)$$

$$C1 > C2 \quad (4),$$

where:

C1 = average value of supplying rates in terms of CaO of the refining agent in the earlier stage of the dephosphorization treatment (kg/min/ton of molten iron);

C2 = average value of supplying rates in terms of CaO of the refining agent in the latter stage of the dephosphorization treatment (kg/min/ton of molten iron);

D1 = average value of supplying rates of the gaseous oxygen in the earlier stage of the dephosphorization treatment (Nm³/min/ton of molten iron); and

D2 = average value of supplying rates of the gaseous oxygen in the latter stage of the dephosphorization treatment (Nm³/min/ton of molten iron).

18. The method according to claim 17, **characterized in that** the supplying rate in terms of CaO of the refining agent and the supplying rate of the gaseous oxygen are continually and/or gradually varied during the dephosphorization treatment.

19. The method according to any one of claims 1 to 18, **characterized in that** the dephosphorization treatment is performed for the molten iron having a Si content of 0.15 mass% or less by blowing the gaseous oxygen and at least the part of the refining agent onto the bath surface of the molten iron through the top blowing lance; and lime is added as the refining agent in the dephosphorization treatment, wherein the supplying amount of the lime is the sum of a lime amount W_{CaO_P} (kg/ton of molten iron) obtained from Equation (5) below and a lime amount W_{CaO_Si}

(kg/ton of molten iron) obtained from Equation (6):

$$W_{\text{CaO-P}} = (\text{molten iron [P]} - \text{object [P]}) \times (10/62) \times 56 \times 3/\eta_{\text{CaO}} \quad (5),$$

where:

molten iron [P] = P content (mass%) in the molten iron before the dephosphorization treatment;

object [P] = P content (mass%) in the molten iron after the dephosphorization treatment; and

η_{CaO} (lime efficiency) = 0.5 to 1; and

$W_{\text{CaO-Si}} = (\text{molten iron [Si]} \times (10/28) \times 56 \times 2) \quad (6);$

where:

molten iron [Si] = Si content (mass%) in the molten iron before the dephosphorization treatment.

20. The method according to claim 19, **characterized in that** the lime in an amount of 80 mass% or more of the lime amount $W_{\text{CaO-P}}$ ($W_{\text{CaO-P}}$ obtained when $\eta_{\text{CaO}} = 1$) is blown onto the bath surface of the molten iron through the top blowing lance.

21. The method according to claim 19 or 20, **characterized in that** for the refining agent corresponding to the lime amount $W_{\text{CaO-Si}}$, one or more are selected from powdered lime, massive burnt lime, massive limestone, and iron-making slags containing unreacted CaO.

22. The method according to any one of claims 1 to 21, **characterized in that** a depth L of a concave, which occurs in the bath surface of the molten iron in association with blowing of the gaseous oxygen thereonto or blowing of the refining agent with the gaseous oxygen being used as the carrier gas, is controlled to 200 to 500 mm, the depth L being defined by the following Equation (7):

$$L = L_0 \times \exp\{(-0.78 \times L_H)/L_0\} \quad (7)$$

$$L_0 = 63 \times \{(F_{02}/n)/d_t\}^{2/3}$$

where:

L_H = lance height (mm) of the top blowing lance;

F_{02} = supplying rate (Nm^3/hr) of the gaseous oxygen to be fed from the top blowing lance;

n = number of nozzle holes of the top blowing lance;

and

d_t = diameter (mm) of each of the nozzle holes of the top blowing lance (which alternatively represents an average hole diameter of all the nozzle holes in a case where the nozzle diameters of the plurality of nozzle holes are different).

23. The method according to any one of claims 1 to 22, **characterized in that** the dephosphorization treatment is performed in a condition wherein the addition amount of CaF_2 is 2 kg/ton of molten iron or less or CaF_2 is not substantially added.

24. The method according to any one of claims 1 to 22, **characterized in that** the dephosphorization treatment is performed for the molten iron having an Si content of 0.15 mass% or less by blowing the gaseous oxygen and at least the part of the refining agent onto the bath surface of the molten iron through the top blowing lance in a condition wherein the addition amount of CaF_2 is 1 kg/ton of molten iron or less or CaF_2 is not substantially added; and the temperature of the molten iron at the completion time of the dephosphorization treatment is controlled to 1,360°C to 1,450°C.

25. The method according to any one of claims 1 to 24, **characterized in that** a substance absorbing heat of the molten iron through a chemical reaction and/or a thermal decomposition reaction is fed onto the region of the bath surface to which the gaseous oxygen is fed.

26. The method according to claim 25, **characterized in that** at least a part of the substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction is supplied onto the hot spot generating in the bath surface of the molten iron in association with blowing the gaseous oxygen.

27. The method according to claim 25 or 26, **characterized in that** the substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction is at least one selected from carbon dioxide, water vapor, nitrogen oxide, metal carbonate and metal hydroxide.

28. The method according to claim 27, **characterized in that** the substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction is at least one selected from metal carbonate that generates CO_2 or H_2O through thermal decomposition and metal hydroxide that generates CO_2 or H_2O through thermal decomposition.

29. The method according to claim 28, **characterized in that** the substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction is at least one selected from CaCO_3 , $\text{Ca}(\text{OH})_2$, and $\text{CaMg}(\text{CO}_3)_2$.

30. The method according to any one of claims 1 to 24, **characterized in that** as the substance absorbing the heat of the molten iron through the chemical reaction and/or the thermal decomposition reaction, instead of the part or all of the refining agent acting as CaO source, at least one' selected from CaCO_3 , $\text{Ca}(\text{OH})_2$, and $\text{CaMg}(\text{CO}_3)_2$ is fed onto the region of the bath surface.

31. The method according to claim 30, **characterized in that** at least part of the at least one selected from CaCO_3 , $\text{Ca}(\text{OH})_2$, and $\text{CaMg}(\text{CO}_3)_2$ is fed onto the hot spot generating in the bath surface of the molten iron by blowing the gaseous oxygen.

32. The method according to any one of claims 1 to 31, **characterized in that** a molten iron having a P content of 0.10 mass% or more is dephosphorized and refined to have a P content required for crude steel (steel component standard value).

33. The method according to claim 32, **characterized in that** the P content of the molten iron after dephosphorization treatment is 0.010 mass% or less.

FIG. 1

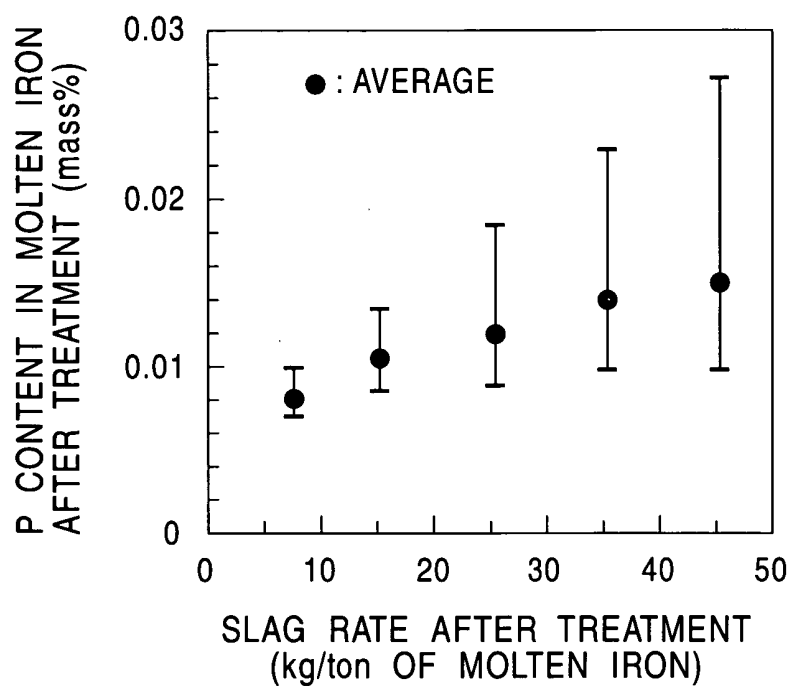


FIG. 2

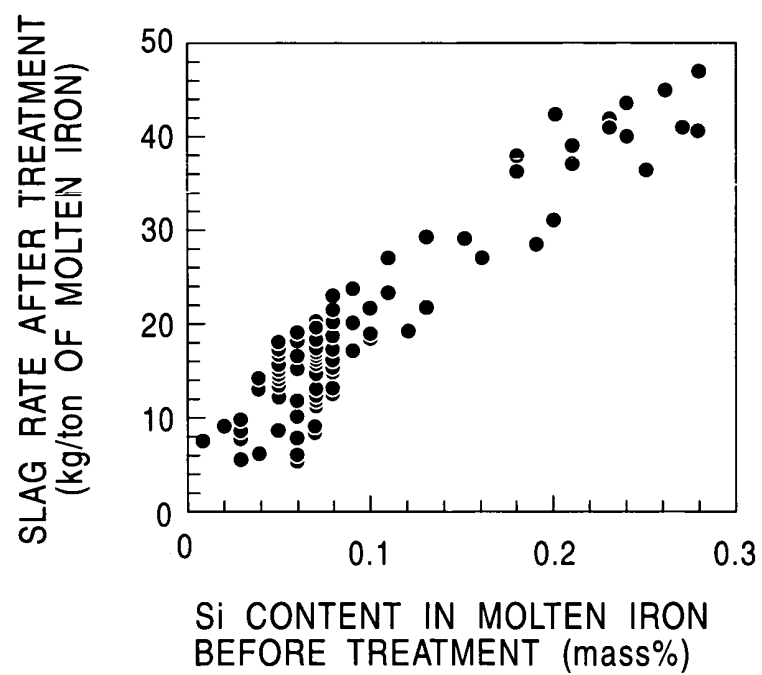


FIG. 3

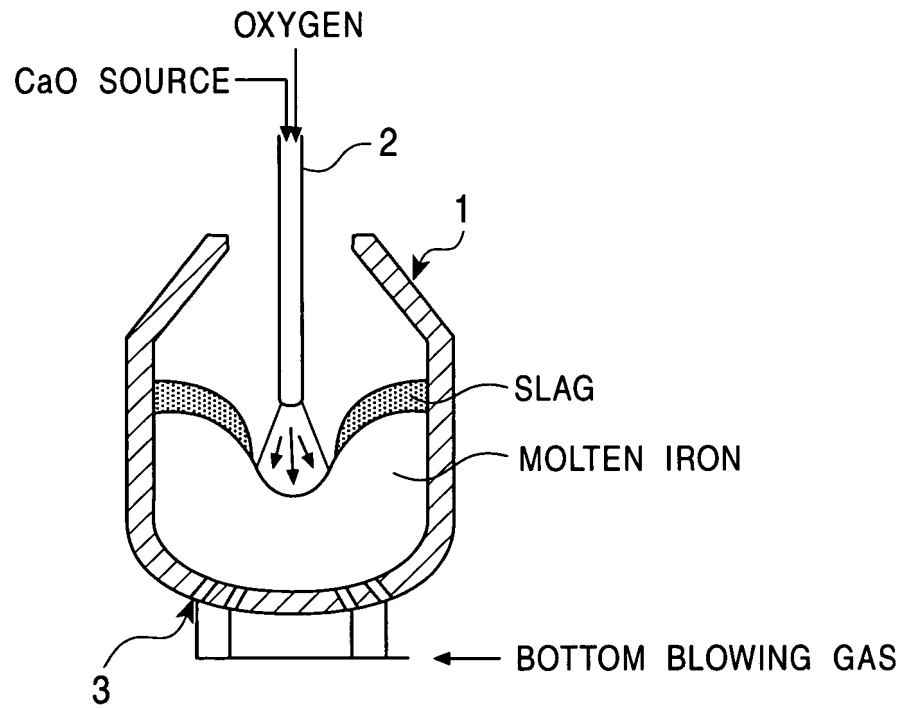


FIG. 6

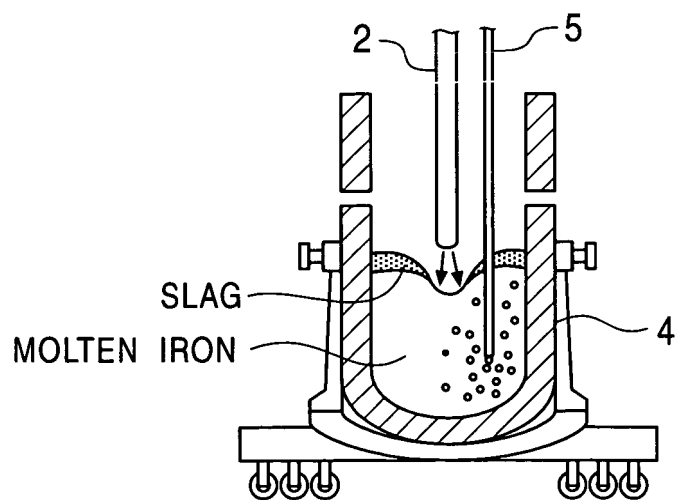


FIG. 4

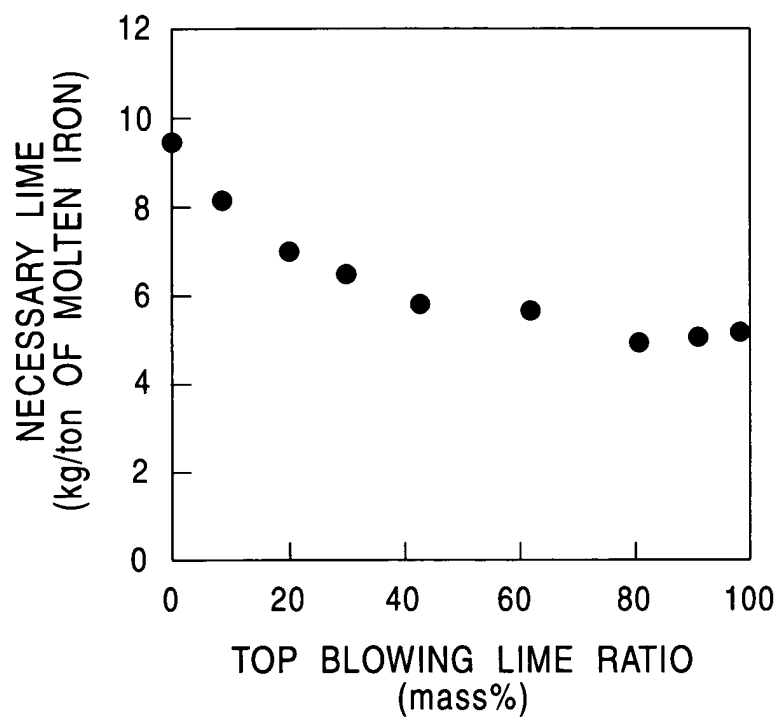


FIG. 5

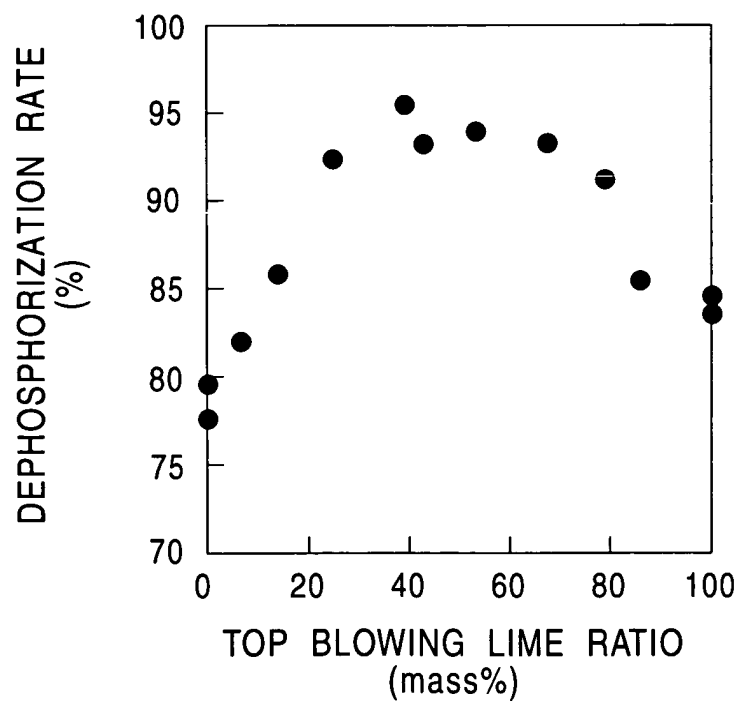


FIG. 7

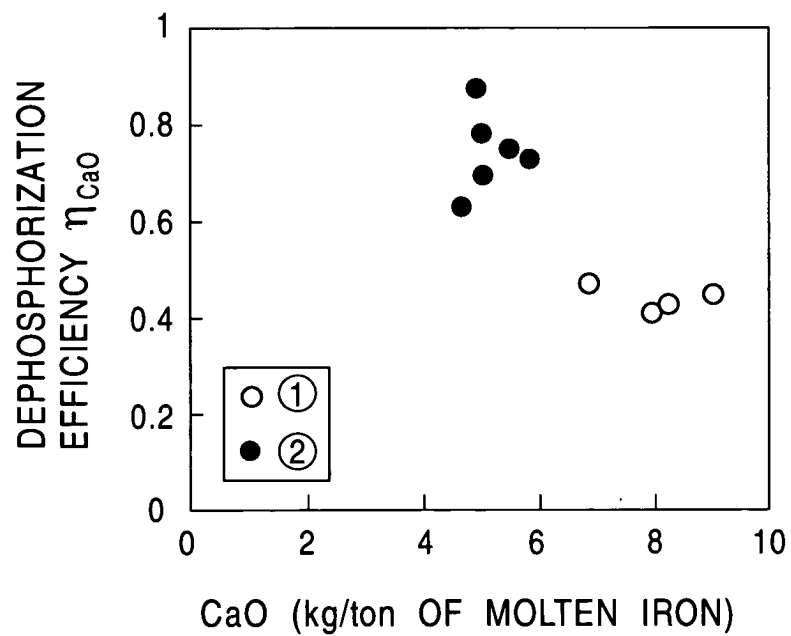


FIG. 10

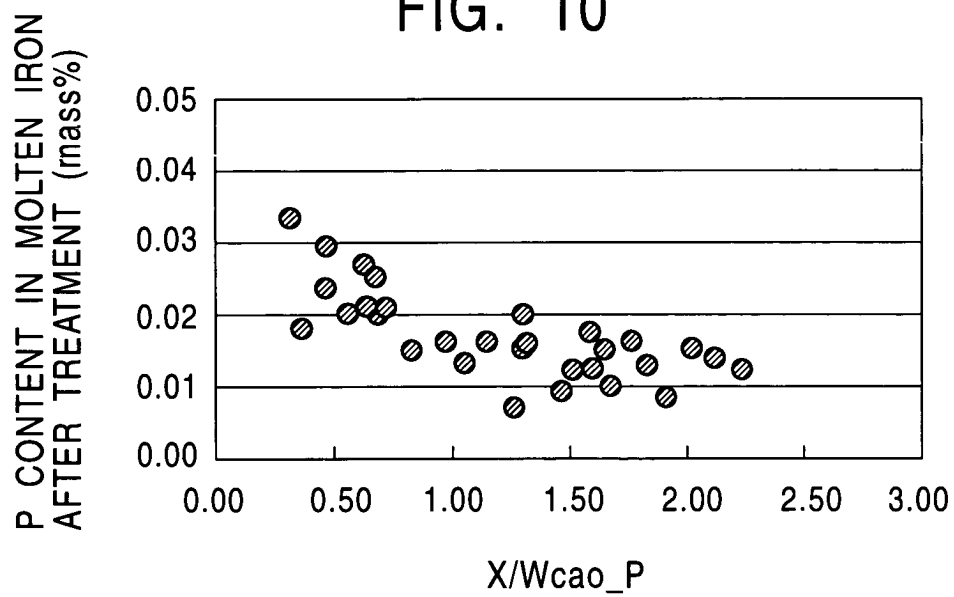


FIG. 8

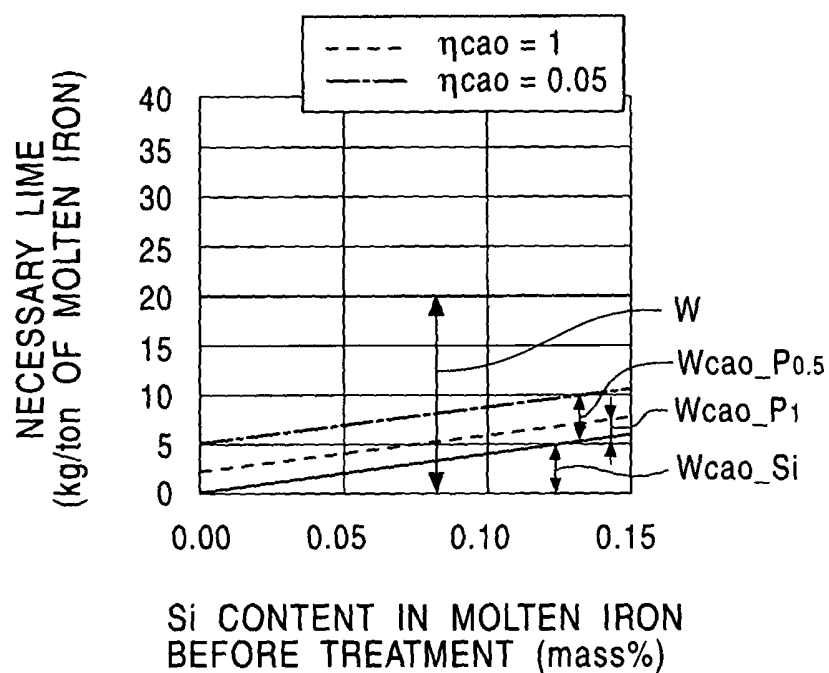


FIG. 9

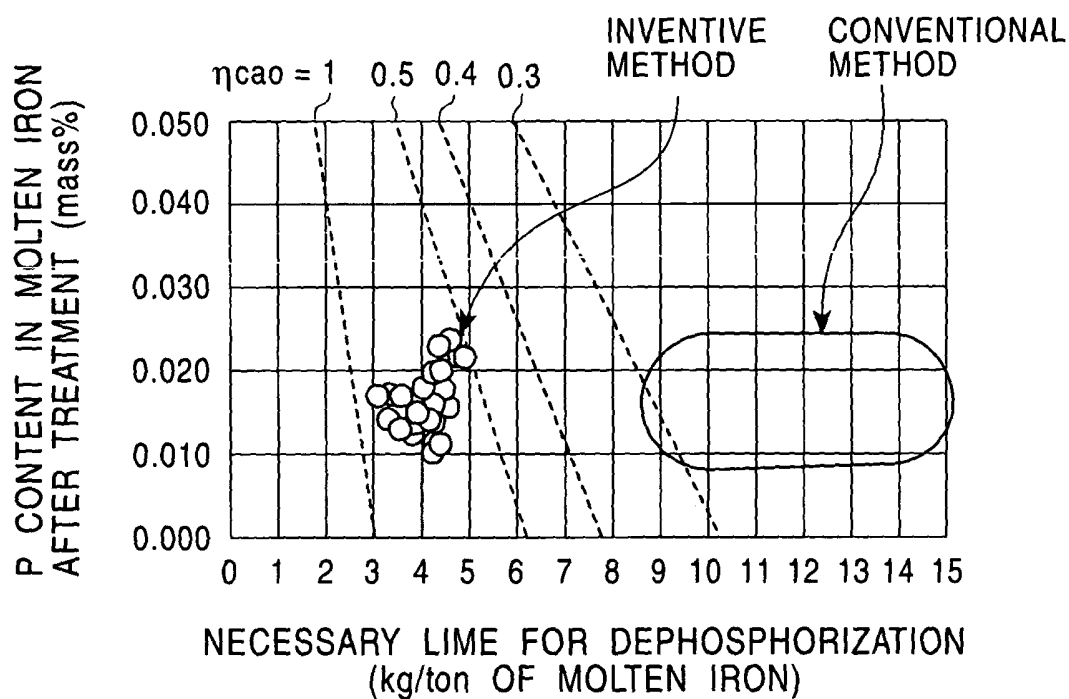


FIG. 11(a)

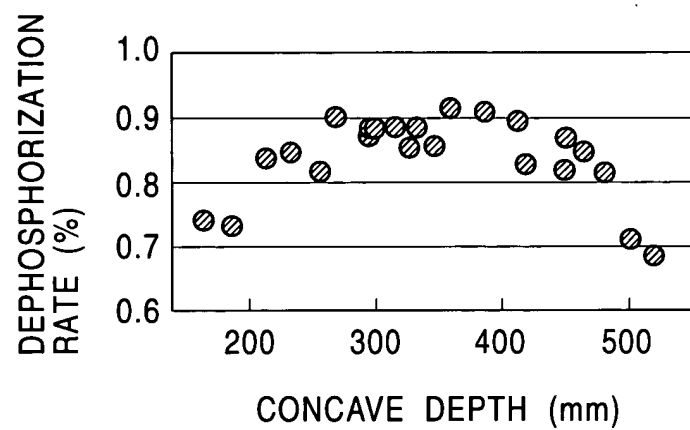


FIG. 11(b)

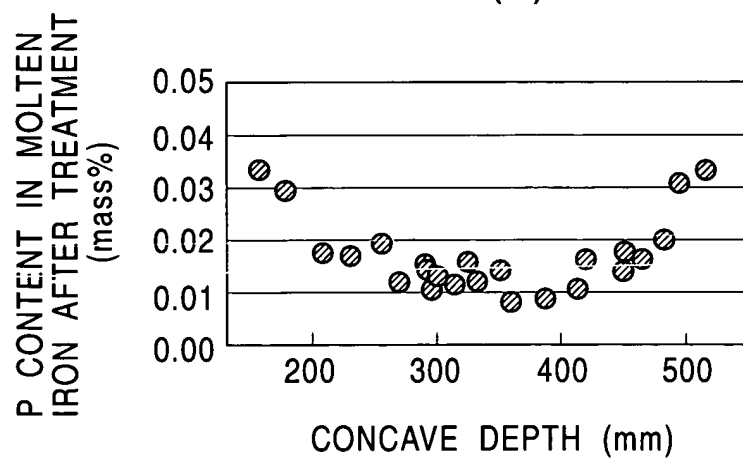


FIG. 12

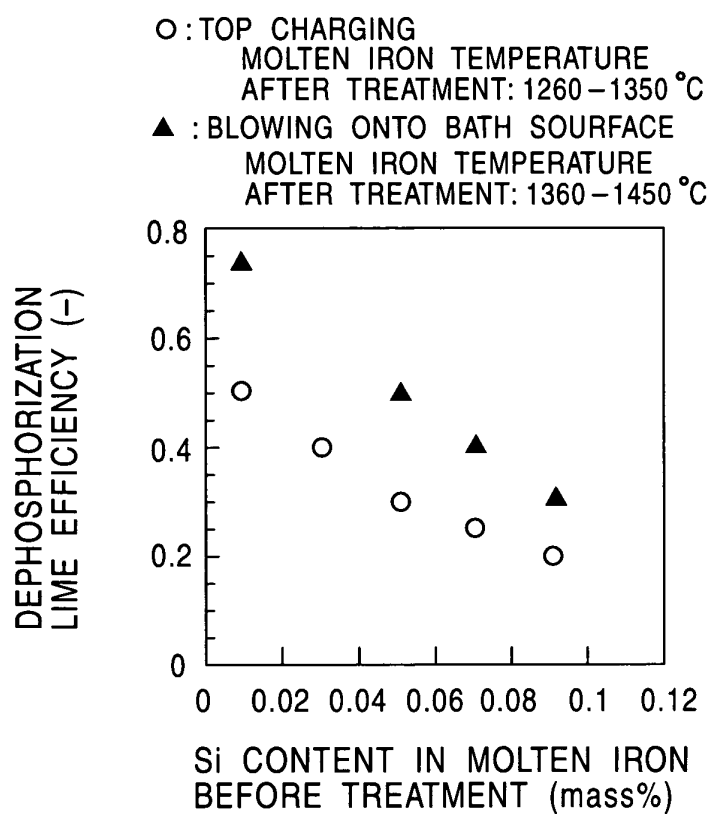


FIG. 13

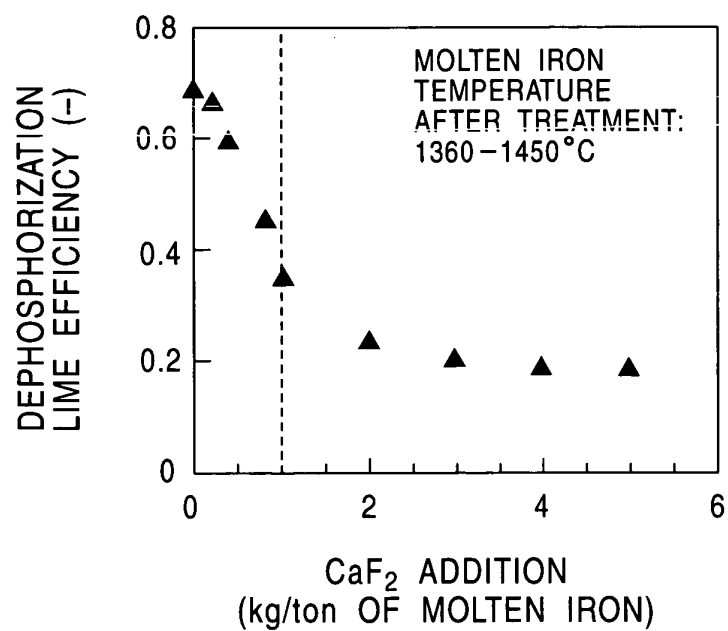


FIG. 14(a)

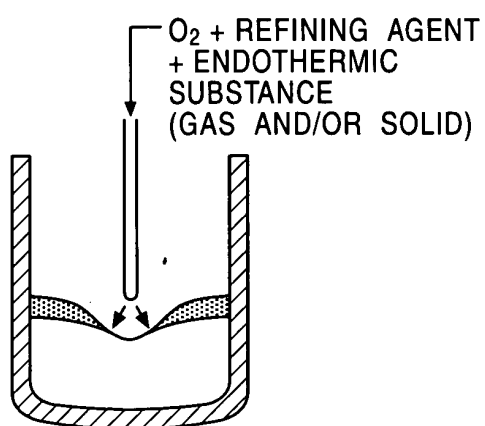


FIG. 14(b)

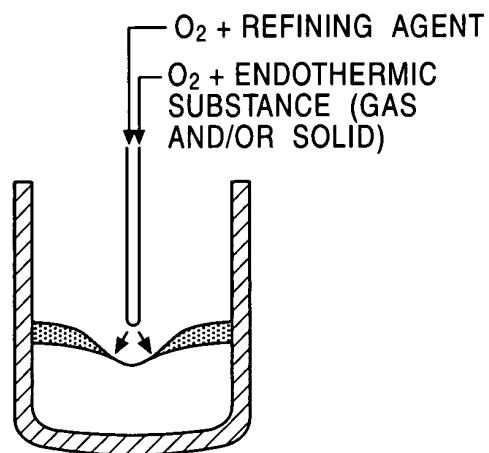


FIG. 14(c)

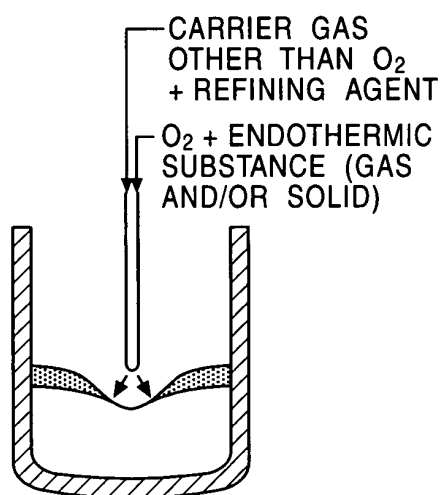


FIG. 14(d)

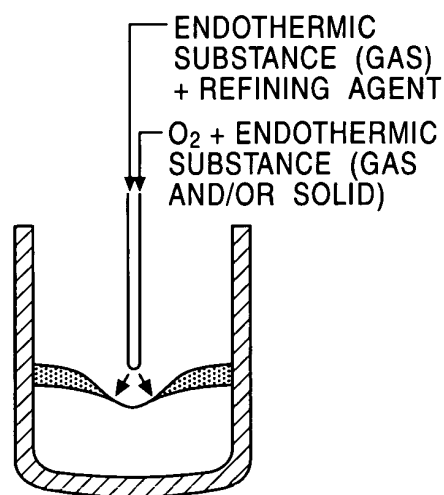


FIG. 14(e)

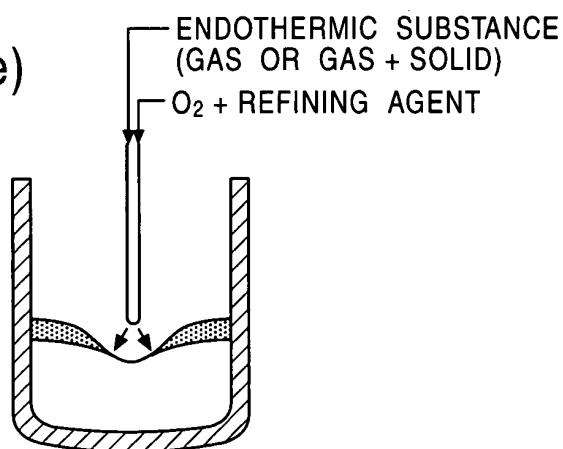


FIG. 15(a)

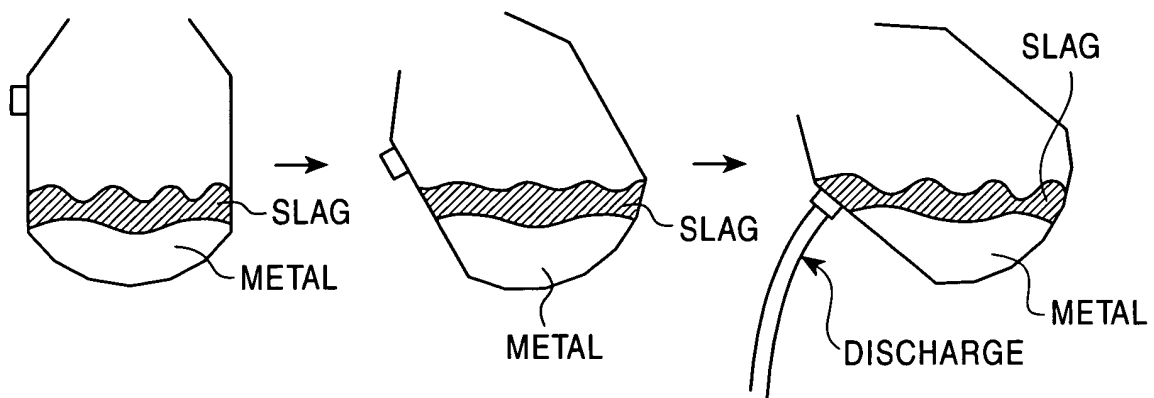


FIG. 15(b)

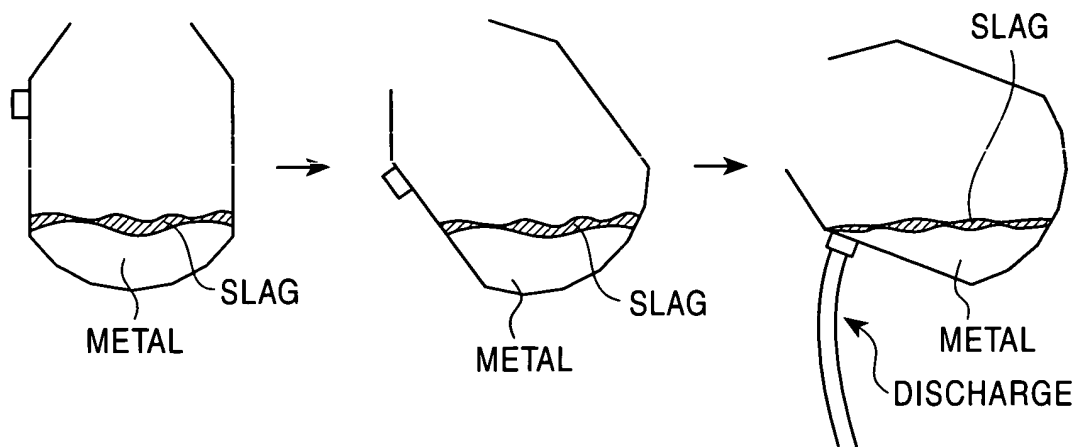


FIG. 16(a)

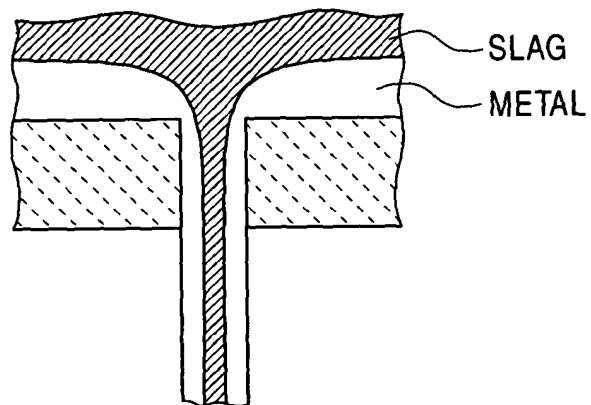


FIG. 16(b)

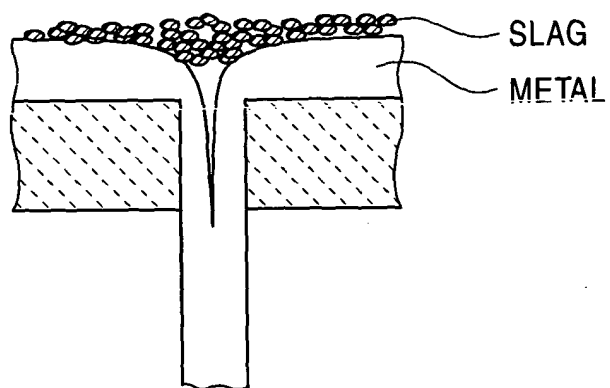
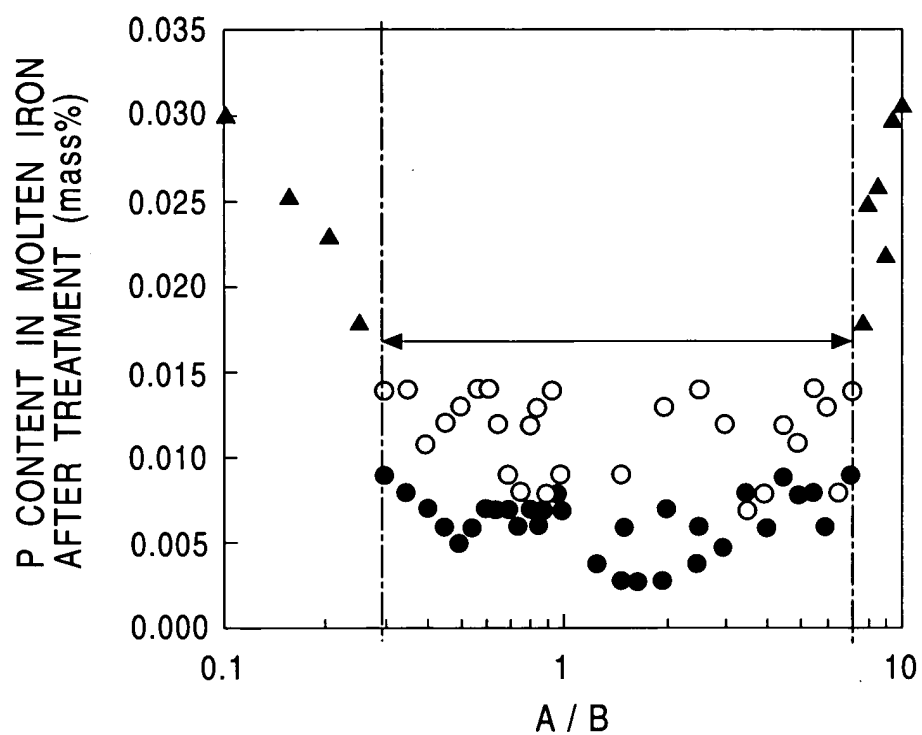


FIG. 17



- INVENTIVE EXAMPLE
Si CONTENT IN MOLTEN IRON
BEFORE TREATMENT:
0.1 mass% OR LESS
- INVENTIVE EXAMPLE
Si CONTENT IN MOLTEN IRON
BEFORE TREATMENT:
MORE THAN 0.1 mass% TO
0.15 mass% OR LESS
- ▲ COMPARATIVE EXAMPLE

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/08604

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C21C1/02 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C21C1/02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2002 Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2001-181724 A (NKK Corp.), 03 July, 2001 (03.07.01), Column 1, lines 2 to 10; column 8, lines 10 to 24; column 10, lines 12 to 14; table 1 (Family: none)	1-9, 12-14, 23, 32, 33 10, 11 15-22, 24-31
Y A	JP 2000-73111 A (NKK Corp.), 07 March, 2000 (07.03.00), Column 2, lines 6 to 12 (Family: none)	10-11 1-9, 12-33
A	JP 11-323419 A (NKK Corp.), 26 November, 1999 (26.11.99), (Family: none)	1-33
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 21 November, 2002 (21.11.02)		Date of mailing of the international search report 03 December, 2002 (03.12.02)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)