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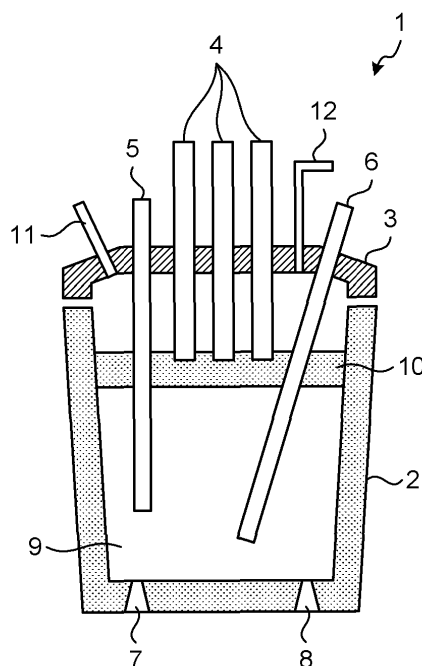
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(54) **DESULFURIZATION TREATMENT METHOD FOR MOLTEN STEEL, AND DESULFURIZATION AGENT**

(57) A desulfurization processing method of molten steel according to the invention includes adding a desulfurization agent containing quicklime into a ladle holding the molten steel, and stirring the molten steel in the ladle to reduce a sulfur concentration in the molten steel. The used desulfurization agent contains quicklime satisfying that a sum of volumes of pores having a pore diameter ranging from 0.5 to 10 μm in the quicklime is equal to or larger than 0.1 mL/g. As a result, the desulfurization processing can be efficiently performed without using CaF_2 and pre-melt flux.

FIG.1



Description

Field

5 **[0001]** The present invention relates to a desulfurization processing method of molten steel and a desulfurization agent.

Background

10 **[0002]** Recently, high purity steel manufacturing has been highly demanded for enhancing material characteristics along with adding high value to steel and an increase in use of steel materials, for example. Particularly, a demand has been highly increased for ultra low sulfur steel having a low content of sulfur, which is an element that reduces toughness of steel materials. In melting manufacturing processes of steel materials, desulfurization processing at a molten pig iron stage and desulfurization processing at a molten steel stage are available. Steel materials are typically subjected to only the desulfurization processing at the molten pig iron stage when manufactured by being melted. In the melting manufacturing processes of ultra low sulfur steel such as high-grade electromagnetic steel plates and line pipe steel materials, it is insufficient to perform only the desulfurization processing at the molten pig iron stage. It is, thus, necessary to perform the desulfurization processing at the molten steel stage in addition to the desulfurization processing at the molten pig iron stage.

20 **[0003]** The desulfurization processing at the molten steel stage is typically performed by a ladle refining method such as an ASEA-SKF method, a VAD method, or an LF method. The ladle refining method includes an arc heating means to heat molten steel and a stirring means to stir molten steel, and further includes a blowing means to blow powder such as flux or alloy powder to molten steel. In the ladle refining method, a desulfurization agent is added into a ladle holding molten steel manufactured by being melted by decarburization refining in a converter, the molten steel and the desulfurization agent are stirred and mixed with each other or subjected to arc heating, thereby causing the desulfurization agent to form slag, and a slag-metal reaction occurs between the slag formed by slag formation of the desulfurization agent and the molten steel to transfer sulfur in the molten steel to the slag.

25 **[0004]** The used desulfurization agent contains CaO (quicklime) as a major component and Al_2O_3 (alumina), CaF_2 (fluorite), and the like, which are added for the purpose of lowering a melting point of the desulfurization agent. For achieving effective desulfurization reaction in the desulfurization processing method by the ladle refining method, it is important to cause the added desulfurization agent to rapidly form slag and to increase a contact area between the slag formed by the slag formation of the desulfurization agent and the metal by increasing stirring strength. The desulfurization agent is typically added to molten steel in the ladle by being placed on the molten steel. It takes a long time that the desulfurization agent forms slag in any case where the desulfurization agent forms slag by arc heating or by being stirred and mixed with the molten steel after the desulfurization agent is added.

35 **[0005]** Patent Literature 1 discloses a method of desulfurizing molten steel in which flux, a mixture of quicklime, alumina, and fluorite, is added and bubbling processing is performed such that a slag composition after the desulfurization processing satisfies that $\text{CaO}/\text{Al}_2\text{O}_3 \geq 1.5$ mass% and $\text{CaF}_2 \geq 5$ mass%. Patent Literature 2 discloses a method in which pre-melt flux (preliminarily mixed or uniformly dissolved) of $\text{CaO}-\text{Al}_2\text{O}_3$ or pre-melt flux of $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ is used for promoting the slag formation of the desulfurization agent. As for enhancing stirring strength of molten steel, Patent Literatures 3, 4, and 5 disclose a method in which stirring gas mixed with flux is blown, as a means to enhance the stirring strength without increasing a stirring gas flow rate.

Citation List

45 Patent Literature

[0006]

50 Patent Literature 1: Japanese Patent Application Laid-open No. H08-260025
 Patent Literature 2: Japanese Patent Application Laid-open No. H09-217110
 Patent Literature 3: Japanese Patent Application Laid-open No. S61-91318
 Patent Literature 4: Japanese Patent Application Laid-open No. S61-281809
 Patent Literature 5: Japanese Patent Application Laid-open No. 2000-234119

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Summary

Technical Problem

[0007] The method described in Patent Literature 1, however, has a problem in that, when a desulfurization agent containing CaF_2 is used, refractory forming the ladle is heavily melted and eroded by CaF_2 in the produced slag, thereby significantly shortening a life-span of the ladle. The method described in Patent Literature 2 has a problem in that the pre-melt flux is very expensive, thereby increasing processing cost. The desulfurization agent containing CaF_2 has the same problem as described above.

[0008] The method described in Patent Literatures 3, 4, and 5, has a limit for a flux blowing amount with respect to a blowing gas rate (a solid-gas ratio has a limit ranging from 5 to 30 kg/kg). The method, thus, has a limit for increasing stirring strength. When a stirring gas flow rate is increased, a surface of molten steel in the ladle is heavily disturbed (waved). As a result, a problem arises in that splashes occur and metal sticks to a lid of the ladle, or another problem arises in that electrodes and molten steel are shorted, for example, to cause unstable arc, thereby making it difficult to perform arc heating.

[0009] The invention is made in view of above problems, and aims to provide a desulfurization processing method of molten steel and a desulfurization agent that can efficiently perform desulfurization processing without using CaF_2 and pre-melt flux.

Solution to Problem

[0010] To solve the problem and achieve the object, a desulfurization processing method of molten steel according to the present invention is a method including: adding a desulfurization agent containing quicklime into a ladle holding the molten steel; and stirring the molten steel in the ladle to reduce a sulfur concentration in the molten steel, wherein the desulfurization agent contains quicklime, where a sum of volumes of pores having a pore diameter ranging from 0.5 μm to 10 μm (inclusive of 0.5 μm and 10 μm) in the quicklime is equal to or larger than 0.1 mL/g.

[0011] Moreover, in the desulfurization processing method of molten steel according to the present invention, the quicklime contains particles, where 90% or more of the particles contained in the quicklime has a particle diameter ranging from 1 mm to 30 mm (inclusive of 1 mm and 30 mm).

[0012] Moreover, a desulfurization agent according to the present invention includes quicklime, where a sum of volumes of pores having a pore diameter ranging from 0.5 μm to 10 μm (inclusive of 0.5 μm and 10 μm) in the quicklime is equal to or larger than 0.1 mL/g, wherein the quicklime contains particles, where 90% or more of the particles contained in the quicklime has a particle diameter ranging from 1 mm to 30 mm (inclusive of 1 mm and 30 mm).

[0013] Moreover, in the desulfurization processing method of molten steel according to the present invention, the stirring is performed so as to satisfy a stirring power density represented by the following formula (1). In the present specification, " Nm^3 " means a volume of gas at an atmospheric pressure of 101325 Pa and a temperature of 273.15 K under standard conditions.

$$\varepsilon = 6.183 \times \frac{Q \times T_1}{W} \times \left(\ln \left(1 + \frac{h}{1.02 \times 10^{-4} \times P} \right) + \left(1 - \frac{T_g}{T_1} \right) \right) \geq 100$$

ε : stirring power density (W/t) of gas stirring molten steel,

Q : gas flow rate (Nm^3/min),

W : molten steel amount (t),

T_1 : molten steel temperature ($^{\circ}\text{C}$),

T_g : gas temperature ($^{\circ}\text{C}$),

h : bath depth (m), P : ambient pressure (Pa)

(1)

[0014] Moreover, in the desulfurization processing method of molten steel according to the present invention, an amount of aluminum supplied into the molten steel within 10 minutes after start of the desulfurization processing, the desulfurization processing starting after the molten steel is tapped from a converter, satisfies the following formula (2).

$$([sol.Al]_1 - [sol.Al]_2 + 0.05) \leq W_{Al} \leq ([sol.Al]_1 - [sol.Al]_2 + 0.1)$$

$[sol.Al]_1$: Al concentration standard upper limit (mass%)

in steel grade to be manufactured by being melted

$[sol.Al]_2$: Al concentration (mass%) in molten steel

after tapping from converter

W_{Al} : amount (kg/t) of Al supplied within 10 minutes

after start of ladle desulfurization processing (2)

[0015] Moreover, in the desulfurization processing method of molten steel according to the present invention, argon gas is blown into the ladle such that an oxygen concentration in the ladle is equal to or smaller than 15%. Advantageous Effects of Invention

[0016] The desulfurization processing method of molten steel and the desulfurization agent according to the invention can efficiently perform desulfurization processing without using CaF_2 and pre-melt flux.

Brief Description of Drawings

[0017]

FIG. 1 is a schematic diagram of a side surface of an LF facility used when the invention is implemented.

FIG. 2 is a diagram illustrating slagging ratios in invention examples and comparative examples.

Description of Embodiment

[0018] The inventors of the invention have earnestly studied for solving the problems described above by focusing attention on a particle size and a pore diameter of caustic lime and molten steel components. More specifically, the inventors of the invention have performed various experiments and researches for the purpose of causing flux added as a desulfurization agent to rapidly form slag to achieve efficient desulfurization processing without using CaF_2 as a part of the desulfurization agent when low sulfur steel having a sulfur concentration equal to or smaller than 0.0030 mass% is manufactured by being melted by desulfurization processing by a ladle refining method using a desulfurization agent having a CaO containing material as a major constituent material.

[0019] As a result, the inventors of the invention have found that the temperature of molten steel when flux is added, a sol. Al concentration, and the particle size and the pore diameter of caustic lime are important in order to promote flux added as a desulfurization agent to form slag. The temperature of molten steel is determined by the temperature of molten steel when the molten steel is tapped from a converter. As the temperature of the molten steel when the molten steel is tapped is increased, the refractory of the converter is increasingly melted and eroded, thereby causing processing cost to be increased. An immoderate increase in tapping temperature is, thus, inadvisable.

[0020] The inventors of the invention have found that the desulfurization processing can be performed highly efficiently using a powder desulfurization agent containing quicklime as a major component and the quicklime satisfies that a sum of volumes of pores having a pore diameter ranging from 0.5 to 10 μm in all of the pores included in the quicklime is equal to or larger than 0.1 mL/g. The inventors of the invention, thus, have conceived the invention. The pore diameter distribution of quicklime was measured by the following method.

[0021] As pretreatment, quicklime was dried at a constant temperature of 120 °C for 4 hours. Using Micromeritics autopore IV 9520, a pore diameter distribution of dried quicklime having a pore diameter ranging from approximately 0.0036 to 200 μm was obtained by a mercury intrusion method, and a cumulative pore volume curve was calculated. In addition, a sum of volumes of pores having a pore diameter ranging from 0.5 to 10 μm was obtained from the calculated cumulative pore volume curve.

[0022] The pore diameter was calculated using Washburn's equation represented in the following formula (3). In formula (3), P is the pressure, D is the pore diameter, σ is the surface tension (= 480 dynes/cm) of mercury, θ is the contact angle (= 140 degrees) between mercury and the specimen.

$$P \times D = -4 \times \sigma \times \cos \theta \quad (3)$$

[0023] Molten pig iron tapped from a blast furnace is received by a hot metal transfer vessel such as a hot metal ladle or a torpedo car, and transferred to a converter in which decarburization refining is performed as the next process. Typically, during the transportation, hot metal pretreatment such as desulfurization processing and dephosphorization processing are performed on molten pig iron. The invention is the technique to manufacture low sulfur steel. The desulfurization processing is, thus, performed. Even when the dephosphorization processing is not required in accordance with the compositional standard of the low sulfur steel, the dephosphorization processing is performed to prevent rephosphorization from converter slag in desulfurization processing after tapping from the converter.

[0024] The decarburization refining is performed on the molten pig iron on which the desulfurization processing and the dephosphorization processing are performed, and resulting molten steel is tapped to the ladle. In the decarburization refining in the converter, a little amount of quicklime (CaO) and a little amount of dolomite ($\text{MgCO}_3\text{-CaCO}_3$), or calcined dolomite (MgO-CaO) is used as flux, and the flux forms slag in the converter (hereinafter described as the "converter slag"), because the desulfurization processing and the dephosphorization processing are already performed on the molten pig iron. The converter slag has a role to promote dephosphorization reaction of the molten pig iron. The dephosphorization processing is, however, already performed on the molten pig iron. The main role of converter slag is, thus, prevention of occurrence of iron splashes in blowing refining and melting and erosion of the lining refractory of the converter.

[0025] At the last stage of tapping, the converter slag is mixed into the molten steel and flows into the ladle. Slag flow-out prevention measures, which are typically taken, are performed to prevent the flow out of the converter slag. It is, however, difficult to perfectly prevent the converter slag from being flowed out even when the slag flow-out prevention measures are taken. Some amount of converter slag is mixed into the molten steel in the ladle and flows out from the converter. After tapping, the converter slag that is mixed into the molten steel and flows into the ladle may be removed from the ladle. The converter slag may, however, not be removed because SiO_2 component in the converter slag contributes to the slag formation of a CaO containing material added later as the desulfurization agent.

[0026] In order to form CaO-MgO- Al_2O_3 - SiO_2 desulfurization slag having a certain composition in the ladle, a CaO containing material, a MgO containing material, an Al_2O_3 containing material, and a SiO_2 containing material are added into the ladle as flux. As described above, MgO has a lower desulfurization ability than that of CaO, the MgO containing material may not be added. Metallic Al is added into the ladle for deoxidation of the molten steel and reduction of the slag (reduction of Fe oxides and Mn oxides in the slag).

[0027] Those materials may be added into a facility in later process that performs desulfurization processing by any of an ASEA-SKF method, a VAD method, and an LF method. From a point of view of promoting the slag formation of CaO, those materials are preferably added into the ladle at tapping from the converter to the ladle or just after the tapping. It is preferable for quicklime added just after the tapping that a sum of volumes of pores having a pore diameter ranging from 0.5 to 10 μm in all of the pores included in the quicklime is equal to or larger than 0.1 mL/g, and the quicklime contains particles 90% or more of which have a particle diameter ranging from 1 to 30 mm.

[0028] Respective additive amounts of the CaO containing material, the MgO containing material, metallic Al, the Al_2O_3 containing material, and the SiO_2 containing material are determined, by considering a mass and a component composition of converter slag flowed into the ladle, such that the composition of the slag produced in the ladle after the slag formation of the added flux, i.e., the slag formed from the flux and the converter slag, satisfies that the SiO_2 content is in a range from 5 to 15 mass% and a value of $[(\text{mass}\% \text{ CaO}) + (\text{mass}\% \text{ MgO})]/(\text{mass}\% \text{ Al}_2\text{O}_3)$ is in a range from 1.5 to 3.0, and, preferably, the value of $[(\text{mass}\% \text{ CaO}) + (\text{mass}\% \text{ MgO})]/(\text{mass}\% \text{ Al}_2\text{O}_3)$ is in a range from 1.8 to 2.5.

[0029] In this case, the respective additive amounts are more preferably determined such that a value of $(\text{mass}\% \text{ MgO})/(\text{mass}\% \text{ CaO})$ of the produced slag is equal to or smaller than 0.10. Those materials are added into the ladle by the determined additive amounts. All of the additive amount of metallic Al does not become Al_2O_3 . Some amount of metallic Al is dissolved and remains in the molten steel. A ratio of Al_2O_3 in slag to Al dissolved in molten steel is obtained preliminarily by an experiment. The additive amount of metallic Al is set on the basis of the ratio. No CaF_2 is added.

[0030] In the invention, "the composition of the slag in the ladle after the desulfurization processing is adjusted to the composition that does not substantially contain CaF_2 " means that the slag composition of after the desulfurization processing is adjusted without using a fluorine compound such as CaF_2 as a slag formation accelerator of CaO, and even when fluorine that is unavoidably mixed into the used CaO containing material and Al_2O_3 containing material, for example, and brought into the ladle is present in the slag after the desulfurization processing, the slag in the ladle is defined that the slag substantially does not contain CaF_2 .

[0031] As for the CaO containing material to be added, quicklime (CaO), limestone (CaCO_3), slaked lime (Ca(OH)_2), dolomite ($\text{MgCO}_3\text{-CaCO}_3$), and calcined dolomite (MgO-CaO) are used, for example. As for the MgO containing material to be added, magnesia clinker (MgO), dolomite ($\text{MgCO}_3\text{-CaCO}_3$), and calcined dolomite (MgO-CaO) are used, for example.

[0032] It is preferable for a particle size of caustic lime that an average particle diameter of the caustic lime is in a range from 1 to 30 mm from a point of view of a reaction efficiency and an addition yield. From a point of view of reducing an amount sucked in an exhaust system, an amount of fine powder is preferably small. An amount of caustic lime having

an average particle diameter equal to or larger than 30 mm is, thus, preferably small. The measuring method of the average particle diameter is as follows. One kilogram of a desulfurization agent was collected. The collected desulfurization agent was sieved into nine classes, i.e., equal to or smaller than 500 μm , 500 μm to 1 mm, 1 to 5 mm, 5 to 10 mm, 10 to 15 mm, 15 to 20 mm, 20 to 25 mm, 25 to 30 mm, and equal to or larger than 30 mm. The average particle diameter was obtained by calculating the weight ratio represented in the following formula (4).

$$D_a = \frac{\sum_i (w_i)}{\sum_i (w_i / d_i)}$$

D_a : average particle diameter (mm)

d_i : average particle diameter (sieve mesh median) (mm)
in each particle diameter range

w_i : slag weight (kg) on each sieve

(4)

[0033] As for the Al_2O_3 containing material, aluminum dross (contains 20 to 70 mass% metallic Al and main component of the balance is Al_2O_3), bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), and calcined alumina (Al_2O_3) are used, for example. Aluminum dross can be used as alternative of metallic Al. As for the SiO_2 containing material, silica sand (SiO_2) and wollastonite ($\text{CaO} \cdot \text{SiO}_2$) are used, for example. When the mass of the converter slag flowed in the ladle is large, the SiO_2 containing material may not be required to be added. The MgO containing material may not be required to be added when the slag composition satisfies that a value of $[(\text{mass}\% \text{ CaO}) + (\text{mass}\% \text{ MgO})] / (\text{mass}\% \text{ Al}_2\text{O}_3)$ is in a range from 1.5 to 3.0, preferably in a range 1.8 to 2.5 without addition of the MgO containing material.

[0034] The ladle holding the molten steel is transferred to the facility that performs the desulfurization processing by any of the ASEA-SKF method, the VAD method, and the LF method, and the desulfurization processing is performed on the molten steel by the facility. In the invention, the desulfurization processing is performed by an LF facility as an example. FIG. 1 is a schematic diagram of a side view of the LF facility used when the invention is implemented. FIG. 1 illustrates an LF facility 1, a ladle 2, an elevating lid 3, arc heating electrodes 4, submerged lances 5 and 6, bottom-blowing porous bricks 7 and 8, molten steel 9, slag 10, a row material supply chute 11, and an Ar gas introduction pipe 12.

[0035] In the LF facility 1, the ladle 2 that contains the molten steel 9 and is mounted on a traveling carriage (not illustrated) is disposed at a certain position just under the lid 3. The lid 3 is moved downward to be tightly in contact with the upper end of the ladle 2. While the contact is kept, Ar gas is supplied from the Ar gas introduction pipe 12, resulting in a space surrounded by the ladle 2 and the lid 3 becoming Ar gas atmosphere. Ar gas is preferably blown from piping provided on the periphery of the furnace lid such that an oxygen concentration in the ladle 2 is equal to or smaller than 15%. The reduction of the oxygen concentration in the ladle 2 makes it possible to reduce an amount of Al lost by reaction with oxygen in the air in the LF processing. The flow rate of Ar gas blown from the ladle 2 preferably satisfies that a value of $\pi L^2/4Q$ is in a range from 50 to 150 (m/min) and more preferably 70 to 100 (m/min). L is the diameter (m) of the ladle and Q is the flow rate of Ar gas (Nm^3/min). When the flow rate of Ar gas is small, the oxygen concentration is not sufficiently reduced. In contrast, when the flow rate of Ar gas is too large, the molten steel temperature is caused to be reduced.

[0036] When the CaO containing material, the MgO containing material, metallic Al, the Al_2O_3 containing material, and the SiO_2 containing material are not preliminarily added into the ladle 2, and when the additive amounts of those materials are insufficient, the flux containing those materials and metallic Al are supplied into the ladle 2 via the row material supply chute 11. Metallic Al is preferably added within 10 minutes after start of the desulfurization processing such that the following formula (5) is satisfied. It is, thus, preferable for promoting the desulfurization processing that metallic Al is added in accordance with the Al concentration after tapping from the converter to increase the Al concentration in molten steel.

$$([sol.Al]_1 - [sol.Al]_2 + 0.05) \leq W_{Al} \leq ([sol.Al]_1 - [sol.Al]_2 + 0.1)$$

$[sol.Al]_1$: Al concentration standard upper limit (mass%)

in steel grade to be manufactured by being melted

$[sol.Al]_2$: Al concentration (mass%) in molten steel

after tapping from converter

W_{Al} : amount (kg/t) of Al supplied within 10 minutes

after start of ladle desulfurization processing

(5)

[0037] Then, the electrodes 4 are energized to generate arc, if necessary, to heat the molten steel 9 and to cause the added flux to form slag. Thereafter, the submerged lance 5 or 6 is immersed into the molten steel 9 and then Ar gas serving as a stirring gas is blown into the molten steel 9 from at least one of the submerged lances 5 and 6, or the bottom-blowing porous bricks 7 and 8 to stir the molten steel 9. As a result of stirring the molten steel 9, the flux is mixed with the molten steel 9, thereby causing the flux to form slag. As a result, slag 10 is produced.

[0038] The produced slag 10 is stirred and mixed with the molten steel 9 as a result of stirring of the molten steel 9. As a result, a slag-metal reaction occurs between the molten steel 9 and the slag 10 and, thus, a desulfurization reaction occurs in which sulfur in the molten steel 9 transfers into the slag. From a point of view of promoting the desulfurization reaction, as described above, one or more kinds of Ca alloy powder, metallic Mg powder, and Mg alloy powder are preferably blown into the molten steel 9 together with Ar gas from the submerged lances 5 and 6, or, at least one period in the desulfurization processing, blowing of the stirring gas from the submerged lances 5 and 6 and blowing of the stirring gas from the bottom-blowing porous bricks 7 and 8 are preferably performed simultaneously.

[0039] As for the Ca alloy powder, Ca-Si alloy powder and Ca-Al alloy powder are used, for example. As for the Mg alloy powder, Mg-Al-Zn alloy powder and Mg-Si-Fe alloy powder are used, for example. The particle diameters of those metallic powder are not limited to specific diameters as long as those metallic powder can be added by being blown. From a point of view of keeping a reaction interfacial area, the maximum particle diameter is preferably equal to or smaller than 1 mm. When the sulfur concentration in the molten steel 9 becomes equal to or smaller than 0.0010 mass%, blowing Ar gas into the molten steel 9 stops to end the desulfurization processing. When the temperature of the molten steel 9 is lower than a target temperature at the end of the desulfurization processing, arc heating is performed. When the composition of the molten steel 9 is not in a target range, an alloy iron and metals for composition adjustment are supplied via the row material supply chute 11. After the completion of the desulfurization processing, degassing refining is performed by an RH vacuum degassing apparatus, for example. Thereafter, a strip cast slab is casted by a continuous casting machine.

[0040] As described above, in the invention, the slag composition after the desulfurization processing is adjusted such that the SiO_2 content is in a range from 5 to 15 mass% in the desulfurization processing of the molten steel 9 by the ladle refining method using the desulfurization agent containing the CaO containing material as the major constituent material. SiO_2 , thus, functions as the slagging accelerator to promote the slag formation of CaO. In addition, the slag composition after the desulfurization processing is adjusted such that a value of $[(\text{mass}\% \text{CaO}) + (\text{mass}\% \text{MgO})]/(\text{mass}\% \text{Al}_2\text{O}_3)$ is in a range from 1.5 to 3.0, thereby causing the slag 10 to have high desulfurization ability. As a result, the desulfurization processing can be efficiently performed on the molten steel 9 without using CaF_2 as a part of the desulfurization agent and pre-melt flux as the desulfurization agent. The above description is an example where the invention is implemented using the LF facility. The invention can also be applied to an ASEA-SKF facility and a VAD facility according to the manner as described above.

[First example]

[0041] Molten pig iron tapped from a blast furnace was subjected to the desiliconization processing, the desulfurization processing, and the dephosphorization processing. The processed molten pig iron was, then, charged into a converter to be subjected to the decarburization refining. As a result, obtained was approximately 250 tons of molten steel having a carbon concentration ranging from 0.05 to 0.09 mass%, a sulfur concentration ranging from 0.0041 to 0.0043 mass%, and a phosphorous concentration ranging from 0.004 to 0.010 mass%. After tapping, the converter slag flowed in a ladle was not discharged. Metallic Al, quicklime, lightly calcined dolomite, and aluminum dross were added into the ladle, and the ladle was transferred to the LF facility illustrated in FIG. 1. The desulfurization processing was performed for approximately 30 minutes in such a manner that the molten steel was stirred by blowing Ar gas at 2000 NL/min from the submerged lances into the molten steel while the arc heating was performed by the electrodes immersed in the slag so as to achieve a target sulfur concentration equal to or smaller than 0.0024%.

[0042] Table 1 illustrates the sulfur concentrations (chemical analysis values) before and after the desulfurization processing and the desulfurization ratios in respective desulfurization tests. The remarks column in Table 1 illustrates "invention examples", which are the tests according to the invention, and "comparative examples", which are the tests other than those according to the invention. The desulfurization ratio is the value of a ratio of a difference in sulfur concentration in the molten steel before and after the desulfurization processing to a sulfur concentration in the molten steel before the desulfurization processing and the value is expressed by percentage. The desulfurization evaluation "Good" means that the sulfur concentration in the molten steel after the desulfurization processing was equal to or smaller than 0.0024% while the desulfurization evaluation "Poor" means that the sulfur concentration in the molten steel after the desulfurization processing exceeded 0.0024%.

Table 1

Test No.	Sum of volumes of pores 0.5-10 μm	Average particle diameter	[S] Component change			Desulfurization evaluation	Remarks
			Before processing [S]	After processing [S]	Desulfurization ratio		
			Mass [%]	Mass [%]	[%]	-	
1	0.03	10	0.0042	0.0028	33.3	Poor	Comparative example
2	0.06	10	0.0043	0.0027	37.2	Poor	Comparative example
3	0.09	10	0.0041	0.0025	39.0	Poor	Comparative example
4	0.15	10	0.0042	0.0021	50.0	Good	Example
5	0.2	10	0.0042	0.0019	54.8	Good	Example
6	0.2	0.5	0.0044	0.0022	50.0	Good	Example
7	0.2	0.8	0.0041	0.0020	51.2	Good	Example
8	0.2	1.5	0.0043	0.0018	58.1	Good	Example
9	0.2	3	0.0043	0.0016	62.8	Good	Example
10	0.2	5	0.0042	0.0016	61.9	Good	Example
11	0.2	15	0.0041	0.0015	63.4	Good	Example
12	0.2	25	0.0043	0.0014	67.4	Good	Example
13	0.2	28	0.0042	0.0016	61.9	Good	Example
14	0.2	32	0.0043	0.0017	60.5	Good	Example
15	0.2	40	0.0042	0.0019	54.8	Good	Example

[0043] Table 1 also illustrates the test levels and the results. In the comparative examples (test numbers 1 to 3), in which the sum of volumes of pores having a pore diameter ranging from 0.5 to 10 μm is inadequate, the desulfurization ratios were lower than those in the invention examples (test numbers 4 to 15). In the invention examples having test levels in each of which the average particle diameter of quicklime is in a range from 1 to 30 mm, slag formation was promoted and the desulfurization ratio of molten steel were higher.

[Second example]

[0044] Molten pig iron tapped from a blast furnace was subjected to the desiliconization processing, the desulfurization processing, and the dephosphorization processing. The processed molten pig iron was, then, charged into a converter to be subjected to the decarburization refining. As a result, obtained was approximately 250 tons of molten steel having a carbon concentration ranging from 0.05 to 0.09 mass%, a sulfur concentration ranging from 0.0041 to 0.0043 mass%, and a phosphorous concentration ranging from 0.004 to 0.010 mass%. After tapping, the converter slag flowed in a ladle was not discharged. Metallic Al, quicklime, lightly calcined dolomite, and aluminum dross were added into the ladle, and

the ladle was transferred to the LF facility illustrated in FIG. 1. The desulfurization processing was performed for approximately 30 minutes in such a manner that the molten steel was stirred by blowing Ar gas at 500 to 2000 NL/min from the submerged lances into the molten steel while the arc heating was performed by the electrodes immersed in the slag so as to achieve a target sulfur concentration equal to or smaller than 0.0024%.

[0045] Table 2 illustrates the sulfur concentrations (chemical analysis values) before and after the desulfurization processing and the desulfurization ratios in respective desulfurization tests. The desulfurization evaluation "Good" means that the sulfur concentration in the molten steel after the desulfurization processing was equal to or smaller than 0.0024%.

Table 2

Test No.	Stirring power density	Slagging ratio 5 min. after start of LF processing	[S] Component change			Desulfurization evaluation	Remarks
			Before processing [S]	After processing [S]	Desulfurization ratio		
	[W/t]	[%]	Mass [%]	Mass [%]	[%]	-	-
16	10	35	0.0042	0.0019	54.8	Good	Example
17	15	50	0.0042	0.0018	57.1	Good	Example
18	27	57	0.0041	0.0018	56.1	Good	Example
19	35	68	0.0042	0.0018	57.1	Good	Example
20	45	85	0.0042	0.0017	59.5	Good	Example
21	55	94	0.0042	0.0017	59.5	Good	Example
22	74	100	0.0042	0.0017	59.5	Good	Example
23	100	100	0.0043	0.0015	65.1	Good	Example
24	135	100	0.0041	0.0014	65.9	Good	Example
25	158	100	0.0042	0.0013	69.0	Good	Example
26	167	100	0.0042	0.0012	71.4	Good	Example
27	185	100	0.0044	0.0011	75.0	Good	Example

[0046] Table 2 also illustrates the test levels and the results. It was found that with an increase in stirring power, the slagging ratio after 5 minutes from start of the LF processing and the desulfurization ratio were increased. It was found that high slagging ratio and desulfurization ratio were obtained because the stirring power density satisfies the following formula (6).

$$\varepsilon = 6.183 \times \frac{Q \times T_1}{W} \times \left(\ln \left(1 + \frac{h}{1.02 \times 10^{-4} \times P} \right) + \left(1 - \frac{T_g}{T_1} \right) \right) \geq 100$$

ε : stirring power density (W/t) of gas stirring molten steel,

Q : gas flow rate (Nm³/min),

W : molten steel amount (t),

T_1 : molten steel temperature (°C),

T_g : gas temperature (°C),

h : bath depth (m), P : ambient pressure (Pa)

(6)

[Third example]

[0047] FIG. 2 is a diagram illustrating the slagging ratios of the invention examples and the comparative examples. The invention examples used quicklime satisfying that the quicklime has a particle diameter equal to or smaller than 20 μm and the sum of the volumes of pores having a pore diameter ranging from 0.5 to 10 μm is 0.2 mL/g. The comparative

examples used quicklime satisfying that the quicklime has a particle diameter equal to or smaller than 20 mm and the sum of the volumes of pores having a pore diameter ranging from 0.5 to 10 μm is 0.03 mL/g. As illustrated in FIG. 2, it was found that slagging was more promoted in the invention examples than that in the comparative examples even at the identical stirring power density (135 W/t).

[Fourth example]

[0048] Molten pig iron tapped from a blast furnace was subjected to the desiliconization processing, the desulfurization processing, and the dephosphorization processing. The processed molten pig iron was, then, charged into a converter to be subjected to the decarburization refining. As a result, obtained was approximately 250 tons of molten steel having a carbon concentration ranging from 0.05 to 0.09 mass%, a sulfur concentration ranging from 0.0041 to 0.0044 mass%, and a phosphorous concentration ranging from 0.004 to 0.010 mass%. After tapping, the converter slag flowed in a ladle was not discharged. Metallic Al, quicklime, lightly calcined dolomite, and aluminum dross were added into the ladle, and the ladle was transferred to the LF facility illustrated in FIG. 1. The LF processing used quicklime satisfying that the quicklime has a particle diameter equal to or smaller than 20 mm and the sum of the volumes of pores having a pore diameter ranging from 0.5 to 10 μm is 0.2 mL/g.

[0049] Table 3 illustrates the sulfur concentrations (chemical analysis values) before and after the desulfurization processing and the desulfurization ratios in respective desulfurization tests. $[\text{sol.Al}]_1$ is the upper limit value (mass%) of an Al concentration standard of a steel grade to be manufactured by being melted and $[\text{sol.Al}]_2$ is the Al concentration (mass%) in the molten steel after tapping from the converter. The desulfurization evaluation "Good" means that the sulfur concentration in the molten steel after the desulfurization processing was equal to or smaller than 0.0024%.

Table 3

Test No.	[sol.Al] ₁	[sol.Al] ₂	Left side of Formula (5)	Right side of Formula (5)	W _{Al}	[sol.Al] ₃	RH processing time	[S] Component change			Desulfurization evaluation	Remarks
								Before processing [S]	After processing [S]	Desulfurization ratio		
	%	%	kg/t	kg/t	kg/t	%	min	Mass [%]	Mass [%]	[%]	-	
28	0.050	0.023	0.77	1.27	1	0.039	30	0.0042	0.0011	73.8	Good	Example
29	0.050	0.025	0.75	1.25	1.1	0.043	29	0.0043	0.0011	74.4	Good	Example
30	0.050	0.026	0.74	1.24	1.2	0.047	31	0.0041	0.0010	75.6	Good	Example
31	0.050	0.024	0.76	1.26	1.3	0.051	36	0.0042	0.0009	78.6	Good	Example
32	0.050	0.025	0.75	1.25	1.4	0.055	39	0.0042	0.0008	81.0	Good	Example
33	0.050	0.024	0.76	1.26	1.5	0.059	42	0.0044	0.0008	81.8	Good	Example

[0050] As illustrated in Table 3, in the test levels in which the amount of Al supplied within 10 minutes after start of the LF processing is in the range represented by formula (5), the value of $[\text{sol. Al}]_3$ at the end of the LF processing was within the standard and the desulfurization ratio was higher. In the test levels in which the amount of Al supplied within 10 minutes after start of the LF processing was larger than the range represented by formula (5), the value of $[\text{sol. Al}]_3$ at the end of the LF processing exceeded the upper limit value of the standard. Dealuminization was, thus, necessary in the next process RH and the processing time in the RH was, thus, extended.

[Fifth example]

[0051] Molten pig iron tapped from a blast furnace was subjected to the desiliconization processing, the desulfurization processing, and the dephosphorization processing. The processed molten pig iron was, then, charged into a converter to be subjected to the decarburization refining. As a result, obtained was approximately 250 tons of molten steel having a carbon concentration ranging from 0.05 to 0.09 mass%, a sulfur concentration ranging from 0.0041 to 0.0044 mass%, and a phosphorous concentration ranging from 0.004 to 0.010 mass%. After tapping, the converter slag flowed in a ladle was not discharged. Metallic Al, quicklime, lightly calcined dolomite, and aluminum dross were added into the ladle, and the ladle was transferred to the LF facility illustrated in FIG. 1. The LF processing used quicklime satisfying that the quicklime has a particle diameter equal to or smaller than 20 mm and the sum of the volumes of pores having a pore diameter ranging from 0.5 to 10 μm is 0.2 mL/g. Metallic Al was added so as to satisfy formula (5) within 10 minutes after start of the LF processing.

[0052] Table 4 illustrates the sulfur concentrations (chemical analysis values) before and after the desulfurization processing and the desulfurization ratios in respective desulfurization tests. The desulfurization evaluation "Good" means that the sulfur concentration in molten steel after the desulfurization processing was equal to or smaller than 0.0024%.

Table 4

Test No.	Oxygen concentration	Al loss in processing (Air entrainment)	[S] Component change			Desulfurization evaluation	Remarks
			Before Processing [S]	After Processing [S]	Desulfurization ratio		
-	%	kg/t	Mass [%]	Mass [%]	[%]	-	
34	20	0.50	0.0042	0.0014	66.7	Good	Example
35	18	0.47	0.0043	0.0014	67.4	Good	Example
36	16	0.45	0.0041	0.0013	68.3	Good	Example
37	14	0.37	0.0042	0.0012	71.4	Good	Example
38	12	0.32	0.0042	0.0011	73.8	Good	Example
39	10	0.30	0.0044	0.0010	77.3	Good	Example

[0053] As illustrated in Table 4, in the test levels (test numbers 37 to 39) in which the oxygen concentration in ladle is equal to or smaller than 15%, it was found that the Al loss in processing was reduced. The Al loss in processing (air entrainment) was obtained by using the following formula (7).

$$X_{Al-loss} = ([sol.Al]_2 - [sol.Al]_3) \times 10 + W_{Al-all} - X_{Al-loss-De-S} - X_{Al-loss-slag}$$

$[sol.Al]_2$: Al concentration (mass%) in molten steel after tapping from converter,

$[sol.Al]_3$: Al concentration (mass%) in molten steel after completion of ladle desulfurization processing,

W_{Al-all} : amount (kg/t) of Al supplied in ladle desulfurization processing,

$X_{Al-loss-De-S}$: amount (kg/t) of Al lost by desulfurization reaction ($3CaO + 3S + 2Al \rightarrow 3CaS + Al_2O_3$),

$X_{Al-loss-slag}$: amount (kg/t) of Al lost by reduction reaction ($6MnO + 4Al \rightarrow 2Al_2O_3 + 6Mn$, for example) of oxide in slag,

$X_{Al-loss}$: amount (kg/t) of Al lost by air entrainment (7)

Industrial Applicability

[0054] The invention can provide the desulfurization processing method of molten steel and the desulfurization agent that can efficiently perform the desulfurization processing without using CaF_2 and pre-melt flux. Reference Signs List

[0055]

- 1 LF facility
- 2 ladle
- 3 lid
- 4 electrode
- 5, 6 submerged lance
- 7, 8 bottom-blowing porous brick
- 9 molten steel
- 10 slag
- 11 row material supply chute
- 12 Ar gas introduction pipe

Claims

1. A desulfurization processing method of molten steel, comprising:

adding a desulfurization agent containing quicklime into a ladle holding the molten steel; and stirring the molten steel in the ladle to reduce a sulfur concentration in the molten steel, wherein the desulfurization agent contains quicklime, where a sum of volumes of pores having a pore diameter ranging from 0.5 μm to 10 μm (inclusive of 0.5 μm and 10 μm) in the quicklime is equal to or larger than 0.1 mL/g.

2. The desulfurization processing method of molten steel according to claim 1, wherein the quicklime contains particles, where 90% or more of the particles contained in the quicklime has a particle diameter ranging from 1 mm to 30 mm (inclusive of 1 mm and 30 mm).
3. A desulfurization agent comprising quicklime, where a sum of volumes of pores having a pore diameter ranging from 0.5 μm to 10 μm (inclusive of 0.5 μm and 10 μm) in the quicklime is equal to or larger than 0.1 mL/g, wherein the quicklime contains particles, where 90% or more of the particles contained in the quicklime has a particle diameter ranging from 1 mm to 30 mm (inclusive of 1 mm and 30 mm).

4. The desulfurization processing method of molten steel according to claim 1 or 2, wherein the stirring is performed so as to satisfy a stirring power density represented by the following formula (1):

$$\varepsilon = 6.183 \times \frac{Q \times T_1}{W} \times \left(\ln \left(1 + \frac{h}{1.02 \times 10^{-4} \times P} \right) + \left(1 - \frac{T_g}{T_1} \right) \right) \geq 100$$

ε : stirring power density (W/t) of gas stirring molten steel,

Q : gas flow rate (Nm³/min),

W : molten steel amount (t),

T_1 : molten steel temperature (°C),

T_g : gas temperature (°C),

h : bath depth (m), P : ambient pressure (Pa)

(1)

5. The desulfurization processing method of molten steel according to any one of claims 1, 2, and 4, wherein an amount of aluminum supplied into the molten steel within 10 minutes after start of the desulfurization processing, the desulfurization processing starting after the molten steel is tapped from a converter, satisfies the following formula (2) :

$$([sol.Al]_1 - [sol.Al]_2 + 0.05) \leq W_{Al} \leq ([sol.Al]_1 - [sol.Al]_2 + 0.1)$$

$[sol.Al]_1$: Al concentration standard upper limit (mass%)

in steel grade to be manufactured by being melted

$[sol.Al]_2$: Al concentration (mass%) in molten steel

after tapping from converter

W_{Al} : amount (kg/t) of Al supplied within 10 minutes

after start of ladle desulfurization processing

(2)

6. The desulfurization processing method of molten steel according to any one of claims 1, 2, 4, and 5, wherein argon gas is blown into the ladle such that an oxygen concentration in the ladle is equal to or smaller than 15%.

FIG.1

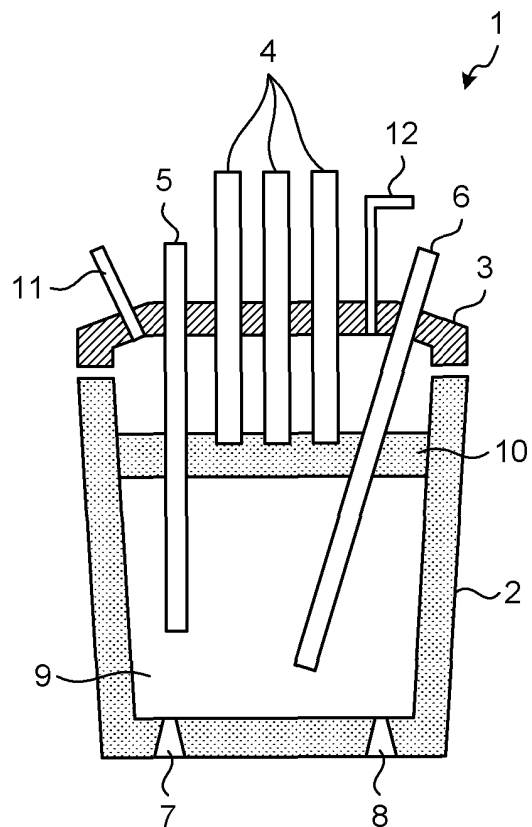
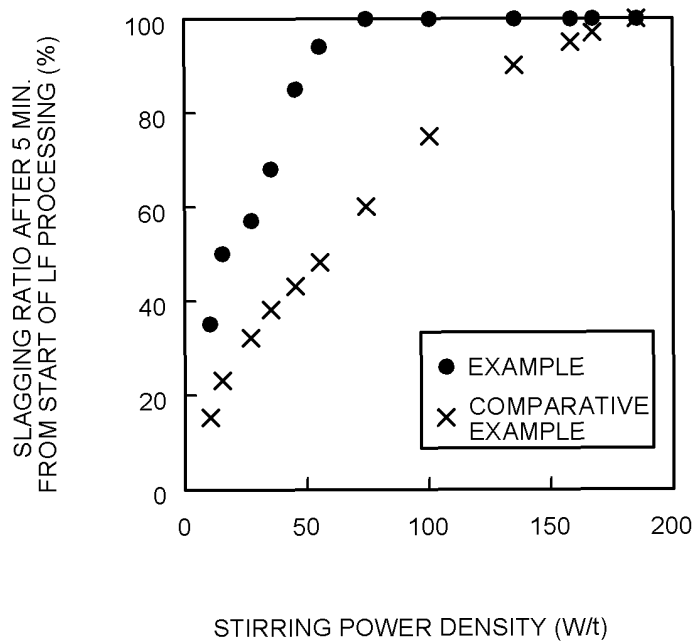


FIG.2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/000280

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C21C7/064(2006.01)i, C21C7/04(2006.01)i, C21C7/072(2006.01)i,
C21C7/076(2006.01)i

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. C21C7/064, C21C7/04, C21C7/072, C21C7/076

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 62-56509 A (KAWASAKI STEEL CORP.) 12 March 1987, examples (Family: none)	1-6
A	JP 62-283847 A (KAWASAKI STEEL CORP.) 09 December 1987, examples (Family: none)	1-6
A	JP 11-221432 A (NITTETSU MINING CO., LTD.) 17 August 1999, paragraphs [0008]-[0028] (Family: none)	1-6

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search
22.03.2018

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/000280

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-108344 A (NIPPON STEEL CORPORATION) 21 May 2009, paragraphs [0010]-[0041], fig. 1-4 (Family: none)	1-6
A	JP 2004-225059 A (NIPPON STEEL CORPORATION) 12 August 2004, paragraphs [0013]-[0039], fig. 2 (Family: none)	1-6
P, X	JP 2017-71854 A (JFE STEEL CORPORATION) 13 April 2017, paragraphs [0015]-[0044], fig. 2 (Family: none)	1-3
P, X	JP 2017-71853 A (JFE STEEL CORPORATION) 13 April 2017, paragraphs [0012]-[0041], fig. 2 (Family: none)	1-3
P, X	WO 2017/018263 A1 (JFE STEEL CORPORATION) 02 February 2017, paragraphs [0013]-[0050], fig. 2 & TW 201714828 A	1-3

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP H08260025 B [0006]
- JP H09217110 B [0006]
- JP S6191318 B [0006]
- JP S61281809 B [0006]
- JP 2000234119 A [0006]