(19	9
-----	---



(71) Applicant: JFE Steel Corporation Tokyo 100-0011 (JP)

METHOD FOR REFINING MOLTEN IRON (54)

(57) A method for refining molten iron that can stably produce low-nitrogen steel is proposed. In this method for refining molten iron, untreated molten iron with a carbon concentration [C]i between 0.5 mass% and 3.0 mass%, both inclusive, is placed into a vessel, and oxygen is blown onto the untreated molten iron under atmospheric pressure while a hydrogen gas, a hydrocarbon gas, or a mixture gas of these gases is blown in to perform a decarburization and denitrification treatment of the untreated molten iron. It is preferable, for example, that a nitrogen concentration [N]E in treated molten iron after being subjected to the decarburization and denitrification treatment be 30 mass ppm or lower; that treated molten iron after being subjected to the decarburization and denitrification treatment be further subjected to a vacuum degassing treatment; that the untreated molten iron include molten iron obtained by melting a cold iron source; that the untreated molten iron be a mixture of primary molten iron obtained by melting a cold iron source in a melting furnace and molten pig iron having a carbon concentration of 2.0 mass% or higher; that the cold iron source include reduced iron; and that the vessel be a converter.

Description

Technical Field

- ⁵ **[0001]** The present invention relates to a method that obtains molten steel by decarburizing untreated molten iron with a carbon concentration of 3.0 mass% or lower to reduce the nitrogen concentration in the decarburized molten iron, and thereby obtain low-nitrogen steel. In particular, this method is suitable for a case in which part or the whole of the untreated molten iron is obtained by melting a cold iron source.
- 10 Background Art

[0002] In recent years, from the viewpoint of preventing global warming, the steel industry has also been advancing the development of technology for cutting down on fossil fuel consumption and thereby reducing CO_2 gas generation. Conventional integrated ironworks produce molten pig iron by reducing iron ore with carbon. To produce molten pig iron,

- ¹⁵ about 500 kg of carbon source per ton of molten pig iron is required for reduction of iron ore etc. On the other hand, producing molten steel using a cold iron source, such as iron scrap, as the raw material does not require a carbon source needed to reduce iron ore, and requires only energy corresponding to an amount of heat enough to melt the cold iron source. Thus, CO₂ emissions can be drastically reduced.
- [0003] When obtaining molten steel by melting a cold iron source in a melting furnace, such as an electric furnace, the nitrogen concentration at the time of discharging the molten steel can be high compared with when refining molten pig iron discharged from a blast furnace, which is hereinafter referred to as "blast furnace molten pig iron", in a converter and discharging the molten steel. In the process of refining blast-furnace molten pig iron in a converter, nitrogen is removed mainly by having it adsorbed onto bubbles of carbon monoxide that are generated by decarburization, so that the nitrogen concentration at the time of discharging the molten steel is generally low. Specifically, blast-furnace molten
- pig iron contains about 4 mass% carbon, and the amount of carbon monoxide generated by decarburization refining is large enough to allow smelting of low-nitrogen steel with a nitrogen concentration of about 20 mass ppm. When using a cold iron source, however, the carbon concentration in molten iron resulting from melting the cold iron source is low and the amount of carbon monoxide to be generated is limited, which makes it difficult to remove nitrogen to a low concentration. It is possible to denitrify the molten iron resulting from melting a cold iron source to some extent by
- 30 subjecting it to a vacuum degassing treatment or the like. However, as the region where the denitrification reaction occurs is limited to a surface part of the molten steel that is in contact with a vacuum atmosphere inside a vacuum chamber, the upper limit of the nitrogen concentration at which stable smelting is possible is about 40 mass ppm.
 [0004] Generally produced through reduction with a natural gas etc., reduced iron contains 0.5 mass% to 2.0 mass%
- carbon. Therefore, molten iron obtained by melting such reduced iron requires decarburization refining, during which it
 can be denitrified to some extent. From the viewpoint of increasing the amount of nitrogen to be removed, it is conceivable to increase the carbon concentration in molten iron resulting from melting reduced iron in an electric furnace etc. by, for example, mixing this molten iron with blast-furnace molten pig iron, and then perform decarburization refining in a converter. In the future, however, to reduce CO₂ generation, the amount of blast-furnace molten pig iron produced is likely to decrease and the amount of cold iron source used is likely to increase. Then, the carbon concentration at the
- time of charging into a converter is expected to become lower, which would make it difficult to sufficiently reduce the nitrogen concentration at the time of discharging the molten steel.
 [0005] Based on this assumption, the following are disclosed as technologies for obtaining low-nitrogen steel. For example, Patent Literature 1 proposes a method in which molten steel discharged from a converter is recarburized and deoxidized with AI, and then oxygen is blown during a vacuum degassing treatment to perform decarburization refining.
- ⁴⁵ Thus, the N concentration [N] in the molten steel is reduced to 25 mass ppm or lower. [0006] Patent Literature 2 proposes a molten steel denitrification method in which CaO is fed onto a bath surface of molten steel without recarburization, then an Al-containing substance is added to remove nitrogen from the molten steel into slag as nitride, and further oxygen is blown to remove nitrogen into a gas phase as a nitrogen gas. Thus, the nitrogen concentration is reduced to 20 mass ppm or lower.
- ⁵⁰ **[0007]** Patent Literature 3 proposes a vacuum refining method in which, in an RH vacuum degassing treatment device, a hydrocarbon gas is supplied as a circulating gas to be supplied through an immersion pipe to thereby break up bubbles. Thus, the nitrogen concentration is reduced to 20 mass ppm or lower.

Citation List

Patent Literature

[8000]

Patent Literature 1: JP-2004-211120A Patent Literature 2: JP-2007-211298A Patent Literature 3: JP-2000-45013A

5 Summary of Invention

Technical Problem

- [0009] However, the above-described conventional technologies have the following problems yet to be solved.
- ¹⁰ **[0010]** The method described in Patent Literature 1 has a problem in that the amount of CO_2 generated increases as an extra carbon source is added to generate bubbles of carbon monoxide, and another problem in that the productivity decreases as performing decarburization again during the vacuum degassing treatment prolongs the treatment time.
- [0011] It is mentioned that the method described in Patent Literature 2 requires adding at least 3 kg of metal Al per ton of molten steel, which leads to a significant cost increase. Moreover, after metal Al is added, Al in the molten steel needs to be removed again through oxidization. Thus, there are problems in that the productivity decreases due to the increased treatment time and that the amount of slag discharged increases.

[0012] In the method described in Patent Literature 3, the hydrogen concentration in molten iron has increased after the hydrocarbon gas is supplied, which necessitates a dehydrogenation treatment. Thus, there is a problem in that the treatment time increases, resulting in reduced productivity.

- 20 [0013] The present invention has been devised in view of these circumstances, and an object thereof is to propose a method for refining molten iron that stably produces low-nitrogen steel under the condition of an increased amount of cold iron source used, without causing a significant decrease in productivity or a cost increase, and without adding to the amount of slag generated or the amount of CO₂ generated.
- 25 Solution to Problem

40

55

[0014] In view of the above-described problems, the present inventors vigorously explored a method for promoting denitrification in a process of performing decarburization refining under atmospheric pressure in a converter or the like, and consequently completed the present invention.

- **[0015]** A method for refining molten iron according to the present invention that advantageously solves the abovedescribed problems is a method in which untreated molten iron with a carbon concentration [C]i between 0.5 mass% and 3.0 mass%, both inclusive, is placed into a vessel, and oxygen is blown onto the untreated molten iron under atmospheric pressure while a hydrogen gas, a hydrocarbon gas, or a mixture gas of these gases is blown in to perform a decarburization and denitrification treatment of the untreated molten iron.
- ³⁵ **[0016]** The Method for refining molten iron according to the present invention could have more preferable solutions:

(a) that a nitrogen concentration $[N]_{\epsilon}$ in treated molten iron after being subjected to the decarburization and denitrification treatment is 30 mass ppm or lower;

- (b) that treated molten iron after being subjected to the decarburization and denitrification treatment is further subjected to a vacuum degassing treatment;
 - (c) that the untreated molten iron includes molten iron obtained by melting a cold iron source;

(d) that the untreated molten iron is a mixture of primary molten iron obtained by melting the cold iron source in a melting furnace and molten pig iron having a carbon concentration of 2.0 mass% or higher;

- (e) that the cold iron source includes reduced iron; and
- 45 (f) that the vessel is a converter.

Advantageous Effects of Invention

[0017] The present invention makes it possible to stably produce low-nitrogen steel with a nitrogen concentration [N] ε in treated molten steel of 30 mass ppm or lower under the condition of an increased amount of cold iron source used, without causing a significant decrease in productivity or a cost increase, and without adding to the amount of slag generated or the amount of CO₂ generated.

Description of Embodiments

[0018] An embodiment of the present invention will be specifically described below.

[0019] As a first step, in a steelmaking melting furnace, an iron source is melted and heated using electric energy. Here, as the steelmaking melting furnace, an electric furnace, such as an arc furnace or an induction furnace, can be

used. In this case, as the iron source, not only a solid iron source, such as scrap or reduced iron, but also molten iron that has been melted by another process may be used. As the heat energy supplied to melt the solid iron source and heat the iron source, not only electric energy but also combustion heat of metal etc. may be supplementarily used. It is preferable that these energies be renewable energies from the viewpoint of cutting down on CO_2 emissions.

- ⁵ **[0020]** As a second step, the molten iron is discharged into a vessel, such as a ladle. When reduced iron is used as the cold iron source, a large amount of slag attributable to gangue contained in the reduced iron is generated. Therefore, performing slag removal as necessary is desirable. Slag removal may be performed using a slag dragger or the like. When the height of the freeboard in the ladle (the height from the upper end of the ladle to the surface of the molten iron) is insufficient, before the molten iron is discharged from the electric furnace, the furnace body may be tilted to flow
- ¹⁰ out the slag. Alternatively, before the molten iron is discharged from the electric furnace, the furnace body may be tilted to flow out the slag, and then the slag flown into a vessel, such as a ladle, along with the molten iron may be further removed. [0021] As a third step, the molten iron is mixed with molten pig iron, such as blast-furnace molten pig iron, as necessary to adjust the carbon concentration [C]i in the molten iron to between 0.5 mass% and 3.0 mass%, both inclusive. Then, this molten iron is charged into a reaction vessel, and decarburization refining is performed by supplying an oxygen gas.
- ¹⁵ through a top-blowing lance etc. When the carbon concentration [C]i in the untreated molten iron is lower than 0.5 mass%, denitrification may become insufficient due to the small amount of CO gas generated during decarburization. On the other hand, when the carbon concentration exceeds 3.0 mass%, the reducing effect on CO₂ generation lessens. In the case where molten metals are mixed, the molten pig iron to be mixed is preferable to have a carbon concentration of 2.0 mass% or higher, and may be molten pig iron as discharged from a blast furnace, or may be molten pig iron that
- ²⁰ has undergone one of desiliconization, dephosphorization, and desulfurization or a combination of two or more of these treatments after being discharged from a blast furnace. As the reaction vessel, a converter is preferable in terms of the height of the freeboard (the height from the upper end of the reaction vessel to the surface of the molten iron). The reaction vessel should be a vessel in which oxygen blowing is possible, and may also be a ladle or the like. Oxygen blowing is not limited to a method of supplying oxygen through a top-blowing lance, and oxygen may instead be supplied
- through a bottom-blowing tuyere. A combination of supplying oxygen through a top-blowing lance and supplying oxygen through a bottom-blowing tuyere may be adopted.
 [0022] Next, at the same time as supply of an oxygen gas for decarburization is started, a gas containing hydrogen atoms formed by a hydrogen gas or a hydrocarbon gas or a mixture gas of these gases is supplied through a porous
- plug etc. installed at the bottom of the furnace. It is believed that when a gas containing hydrogen atoms is supplied into molten iron, after a dissociation reaction of gas molecules occurs, hydrogen atoms dissolve temporarily into the molten iron and are then generated as fine hydrogen gas bubbles again. The denitrification reaction is believed to progress between the fine bubbles generated here and the molten iron interface. Therefore, when performing decarburization refining using molten iron obtained by melting a cold iron source, even when the amount of bubbles of carbon monoxide generated is insufficient, the nitrogen concentration after decarburization refining can be reduced. Thus, decarburization
- ³⁵ and denitrification can be simultaneously performed. As a result of vigorously conducting studies, the present inventors have found that, for the amount to be supplied of the gas containing hydrogen atoms, a flow rate of about 0.1 to 0.3 Nm³/min per ton of molten iron is appropriate. Here, "Nm³" means a volume of a gas in a normal state. In this Description, the normal state of a gas is 0°C and 1 atm (101325 Pa). Upon completion of decarburization refining, supply of the oxygen gas is stopped and, at the same time, supply of the gas containing hydrogen atoms is stopped. To prevent
- 40 clogging of the bottom-blowing plug, it is preferable that supply of the gas containing hydrogen atoms, after it is stopped, be switched to supply of an inert gas, such as an argon gas. The gas containing hydrogen atoms is not limited to being supplied through a porous plug and may instead be supplied using an injection lance (immersion lance), a single pipe, or a double pipe.
- [0023] Performing a treatment such that the nitrogen concentration [N]ε in the treated molten iron becomes 30 mass ppm or lower is preferable, because then low-nitrogen steel with a nitrogen concentration N in the product at the stage of crude steel, such as a steel slab, of 30 mass ppm or lower can be produced. Performing a treatment such that the nitrogen concentration [N]ε in the treated molten iron becomes 20 mass ppm or lower through adjustment of the treatment conditions so as to increase the amount of hydrogen atoms supplied, for example, by increasing the flow rate of the hydrogen gas or by using a hydrocarbon-based gas containing a large amount of hydrogen per gas volume is further preferable, because this results in extremely low-nitrogen steel.
- [0024] As a fourth step, upon completion of the decarburization refining, a vacuum degassing treatment is performed, and casting is performed preferably after being otherwise adjusted to a predetermined composition. By performing a vacuum degassing treatment after decarburization refining, hydrogen can be removed. This embodiment can prevent a decrease in productivity compared with the technology described in Patent Literature 3 in which a gas containing
- ⁵⁵ hydrogen atoms is supplied in a vacuum degassing treatment. For the vacuum degassing treatment, an RH vacuum treatment device, a DH vacuum treatment device, a facility with a ladle installed inside a vacuum chamber, etc. can be used.

Examples

[0025] Scrap or reduced iron as a cold iron source was charged into a 150 t-scale electric furnace and melted. After the molten iron was discharged into a ladle, slag removal was performed. The reduced iron used in the test was reduced

- ⁵ iron produced through reduction with a natural gas, and the carbon concentration was analyzed to be 1.0 mass%. The discharged molten iron inside the ladle and blast-furnace molten pig iron were mixed in a converter-charging pot so as to adjust the amount of molten iron to 300 t. After the components of the molten iron were analyzed, the molten iron was charged into a converter and subjected to decarburization blowing. The amount of carbon contained in the blast-furnace molten pig iron used as the molten metal to be mixed was 4.3 mass%. The mixing ratio between the molten iron obtained
- ¹⁰ by melting a cold iron source and the blast-furnace molten pig iron were changed to various ratios, and the carbon concentration [C]i (mass%) at the time of charging into the converter was also changed to various concentrations. An oxygen gas needed for decarburization was supplied through a top-blowing lance, and the amount of oxygen gas to be supplied was determined based on analytical values (represented with a suffix "i") of carbon and others in the molten iron before being charged into the converter. At the same time as supply of the oxygen gas was started, a hydrogen
- gas, a propane gas, or a mixture gas of 50 vol% hydrogen and 50 vol% propane was supplied through a porous plug installed at the bottom of the converter.
 [0026] After the predetermined amount of oxygen was supplied, supply of a hydrogen gas, a propane gas, or a mixture gas of hydrogen and propane was stopped, and the bottom-blown gas was switched to an argon gas. The molten steel
- was discharged into a ladle, and the components of the molten steel were analyzed (represented with a suffix "f").
 Thereafter, the ladle was subjected to a vacuum treatment in a vacuum degassing device, and the molten steel was cast after being adjusted to a predetermined composition.

[0027] A test was conducted under, as comparative conditions, conditions where an argon gas was supplied as a bottom-blown gas during decarburization refining in a converter. Further, a test was conducted under conditions where only an argon gas was supplied by being bottom-blown during decarburization refining in a converter, and after the

²⁵ molten steel was discharged into a ladle, a hydrogen gas or a hydrocarbon gas was supplied as a circulating gas during a vacuum degassing treatment.

(Tests 1 to 3)

- ³⁰ **[0028]** Molten iron obtained by melting scrap in an electric furnace and blast-furnace molten pig iron were mixed in a converter-charging pot so as to adjust the amount of the mixed molten iron to 300 t. The carbon concentration [C]_e of the molten iron at the time of discharging from the electric furnace was 0.2 to 0.3 mass%. When the mixing ratio between the blast-furnace molten pig iron and the electric-furnace molten iron was changed, the carbon concentration [C]i after the mixing was 2.5 to 3.5 mass%. The molten iron thus mixed was charged into a converter and subjected to decarbu-
- ³⁵ rization refining. While an oxygen gas for decarburization was being supplied, an argon gas was supplied at 40 Nm³/min through a porous plug installed at the bottom of the converter. After the molten steel was discharged from the converter, the components were analyzed, and further a vacuum degassing treatment was performed. As the circulating gas in this case, an argon gas was used. Upon completion of the degassing treatment, casting was performed using a continuous casting machine.
- 40 [0029] As a result, under a condition where the carbon concentration [C]i at the time of charging into the converter exceeded 3.0 mass%, both the nitrogen concentration [N]_f (mass ppm) at the time of discharging from the converter and the crude steel nitrogen concentration N (mass ppm) were low. However, when the carbon concentration [C]i at the time of charging into the converter is at a level below 3.0 mass%, both the nitrogen concentration [N]_ε at the time of discharging from the converter is at a level below 3.0 mass%, both the nitrogen concentration [N]_ε at the time of discharging from the converter and the crude steel nitrogen concentration N were high.
- 45

(Tests 4 to 7)

50

[0030] Molten iron obtained by melting scrap in an electric furnace and blast-furnace molten pig iron were mixed in a converter-charging pot so as to adjust the amount of the mixed molten iron to 300 t. The carbon concentration $[C]_e$ of the molten iron at the time of discharging from the electric furnace was 0.2 to 0.3 mass%. When the mixing ratio between the blast-furnace molten pig iron and the electric-furnace molten iron was changed, the carbon concentration $[C]_i$ after the mixing was 2.5 to 2.8 mass%. The molten iron thus mixed was charged into a converter and subjected to decarburization refining. While an oxygen gas for decarburization was being supplied, an argon gas was supplied at 40 Nm³/min through a porous plug installed at the bottom of the converter. After the molten steel was discharged from the converter,

⁵⁵ the components were analyzed, and further a vacuum degassing treatment was performed. As the circulating gas in this case, a hydrogen gas or a propane gas was used. Upon completion of the degassing treatment, casting was performed using a continuous casting machine.

[0031] As a result, while the nitrogen concentration $[N]_{\epsilon}$ of the molten steel at the time of discharging from the converter

was high, the crude steel nitrogen concentration N was low owing to the denitrification reaction being promoted during the vacuum degassing treatment. However, the crude steel hydrogen concentration H (mass ppm) was high.

(Tests 8 to 11)

5

[0032] Molten iron obtained by melting scrap in an electric furnace and blast-furnace molten pig iron were mixed in a converter-charging pot so as to adjust the amount of the mixed molten iron to 300 t. The carbon concentration $[C]_e$ of the molten iron at the time of discharging from the electric furnace was 0.2 to 0.3 mass%. When the mixing ratio between the blast-furnace molten pig iron and the electric-furnace molten iron was changed, the carbon concentration $[C]_i$ after

- the mixing was 2.5 to 2.8 mass%. The molten iron thus mixed was charged into a converter and subjected to decarburization refining. While an oxygen gas for decarburization was being supplied, an argon gas was supplied at 40 Nm³/min through a porous plug installed at the bottom of the converter. After the molten steel was discharged from the converter, the components were analyzed, and further a vacuum degassing treatment was performed. As the circulating gas in this case, a hydrogen gas or a propane gas was used. The components were analyzed during the vacuum degassing
- ¹⁵ treatment, and the vacuum treatment was continued until the hydrogen concentration became equal to or lower than a predetermined concentration. Upon completion of the degassing treatment, casting was performed using a continuous casting machine.

[0033] As a result, while the nitrogen concentration $[N]_{\epsilon}$ of the molten steel at the time of discharging from the converter was high, the crude steel nitrogen concentration N was low owing to the denitrification reaction being promoted during

20 the vacuum degassing treatment. Further, the crude steel hydrogen concentration H was also low. However, the vacuum degassing treatment time increased significantly.

(Tests 12 to 26)

- ²⁵ **[0034]** Molten iron obtained by melting scrap in an electric furnace and blast-furnace molten pig iron were mixed in a converter-charging pot so as to adjust the amount of the mixed molten iron to 300 t. The carbon concentration [C]_e of the molten iron at the time of discharging from the electric furnace was 0.2 to 0.3 mass%. When the mixing ratio between the blast-furnace molten pig iron and the electric-furnace molten iron was changed, the carbon concentration [C]i after the mixing was 0.6 to 2.8 mass%. The molten iron thus mixed was charged into a converter and subjected to decarbu-
- 30 rization refining. While an oxygen gas for decarburization was being supplied, a hydrogen gas or a propane gas or a mixture gas of these gases was supplied at 40 Nm³/min through a porous plug installed at the bottom of the converter. After the molten steel was discharged from the converter, the components were analyzed, and further a vacuum degassing treatment was performed. As the circulating gas in this case, an argon gas was used. Upon completion of the degassing treatment, casting was performed using a continuous casting machine.
- ³⁵ **[0035]** As a result, both the nitrogen concentration $[N]_{\epsilon}$ of the molten steel at the time of discharging from the converter and the crude steel nitrogen concentration N were low. While the hydrogen concentration $[H]_{f}$ of the molten steel at the time of discharging from the converter was high, the crude steel hydrogen concentration H was low as a result of performing the vacuum degassing treatment. The vacuum degassing treatment time was found not to be prolonged.
- 40 (Tests 27 to 41)

[0036] Molten iron obtained by melting reduced iron in an electric furnace and blast-furnace molten pig iron were mixed in a converter-charging pot so as to adjust the amount of the mixed molten iron to 300 t. The carbon concentration [C] $_{e}$ of the molten iron at the time of discharging from the electric furnace was 1.0 to 1.1 mass%. When the mixing ratio

- ⁴⁵ between the blast-furnace molten pig iron and the electric-furnace molten iron was changed, the carbon concentrations [C]i in tests No. 31, 36, and 41 in which unmixed molten iron was used were 0.9 mass%, while the carbon concentrations [C]i of other mixed molten irons were 1.4 to 2.9 mass%. Thus, unmixed molten iron or mixed molten iron was charged into a converter and subjected to decarburization refining. While an oxygen gas for decarburization was being supplied, a hydrogen gas or a propane gas or a mixture gas of these gases was supplied at 40 Nm³/min through a porous plug
- installed at the bottom of the converter. After the molten steel was discharged from the converter, the components were analyzed, and further a vacuum degassing treatment was performed. As the circulating gas in this case, an argon gas was used. Upon completion of the degassing treatment, casting was performed using a continuous casting machine.
 [0037] As a result, both the nitrogen concentration [N]ε of the molten steel at the time of discharging from the converter and the crude steel nitrogen concentration N were low. While the hydrogen concentration [H]_f of the molten steel at the
- time of discharging from the converter was high, the crude steel hydrogen concentration H was low as a result of performing the vacuum degassing treatment. The vacuum degassing treatment time was found not to be prolonged. [0038] The test conditions and results having been described above are collectively shown in Tables 1-1 to 1-3. The product components in these tables represent values obtained by analyzing the components sampled from a cast steel slab as crude steel components.

Comparative Example Comparative Comparative Comparative Comparative Remarks Invention Example Example Example Example Example 5 mass bpm components Т 2 2 2 ດ თ o თ ~ 2 ~ ~ ~ Product 10 mass bpm 43 3 19 3 z 25 38 26 24 17 23 24 27 Treatment Vacuum degassing time 15 25 25 25 25 25 25 25 40 25 40 40 40 treatment circulating I Type of Hydrogen Hydrogen Hydrogen Propane Hydrogen Propane Propane Propane gas 20 Argon Argon Argon Argon mass bpm from converter Ξf ო ო 4 ო ო ო ω discharged 4 4 4 4 4 When 25 mass ppm Ĩ 33 35 39 34 34 34 22 34 37 37 37 37 [Table 1-1] blown gas during decarburizat ion Type of bottom-30 Hydrogen Argon 35 charged converter mass% When into 3.5 <u>[</u>] 2.8 2.5 2.00 2.5 2.8 2.5 2.8 2.5 2.8 2.5 2.0 40 blast-furnace molten pig Mixed with iron Mixed 45 from electric discharged mass% fumace When [C]e 0.2 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 50 Type of cold iron source Scrap 55 °. 9 7 42 . 2 ო 4 ß ശ ~ ω ი

	Remarks			Invention Example	Invention Example	Invention Example
	Product components	н	mass ppm	2	2	-
	Product componen	z	mass ppm	23	26	23
	Vacuum degassing treatment	Treatment	time	25	25	25
	Vacuum o treat	I Type of	circulating gas	Argon	Argon	Argon
	When discharged from converter	[H]f	mass ppm	8	8	6
ed)	WF dischi from co	[N]f	mass ppm	21	24	21
(continued)	Type of bottom- blown gas during	decarburizat ion		Hydrogen	Hydrogen	Hydrogen
	When charged into converter	[C]i	mass%	2.5	1.7	1.2
	Mixed with blast-furnace	molten pig iron		Mixed	Mixed	Mixed
	When discharged from electric furnace	[C]e	mass%	0.3	0.3	0.2
	Type of cold iron	source		Scrap	Scrap	Scrap
	Ö		13	14	15	

5		Remarks			Invention Example	Invention Example	Invention Example	Invention Example						
Ū		duct onents	т	mass ppm	2	1	2	2	1	2	~	L.	2	٢
10		Product components	z	mass ppm	25	18	18	19	20	18	18	19	19	20
15		Vacuum degassing treatment	Traatment	time	25	25	25	25	25	25	25	25	25	25
20		Vacuum . treat	Type of	circulating gas	Argon	Argon	Argon	Argon						
		When discharged from converter	[H]f	mass ppm	2	8	8	8	6	2	8	7	8	6
25		Wh disch from co	[N]f	mass ppm	23	16	17	18	18	17	17	18	18	19
30	[Table 1-2]	Type of bottom- blown gas during	decarburization		Hydrogen	Propane	Propane	Propane	Propane	Propane	Mixture of 50% hydrogen and 50% propane			
35		When charged into converter	[C]i	mass%	0.6	2.8	2.5	1.7	1.2	0.6	2.8	2.5	1.7	1.2
40		Mixed with blast-furnace	molten pig iron		Mixed	Mixed	Mixed	Mixed						
45 50		When discharged from electric furnace	[C]e	mass%	0.3	0.2	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2
55		Type of cold iron	source	1	Scrap	Scrap	Scrap	Scrap						
		No			16	17	18	19	20	21	22	23	24	25

	Remarks			Invention Example	Invention Example	Invention Example	Invention Example	Invention Example
	Product components	Н	mass ppm	2	L	2	2	4
	Proc	Ν	mass ppm	20	24	27	28	25
	Vacuum degassing treatment	triante arT	time	25	25	25	25	25
	Vacuum c treat	Type of	circulating gas	Argon	Argon	Argon	Argon	Argon
	When discharged from converter][H]	mass ppm	8	8	8	8	6
	WF discha	[N]f	mass ppm	19	23	25	25	24
(continued)	Type of bottom- blown gas during	decarburization		Mixture of 50% hydrogen and 50% propane	Hydrogen	Hydrogen	Hydrogen	Hydrogen
	When charged into converter	[C]i	mass%	9.0	5.9	2.4	1.7	1.4
	Mixed with blast-fumace	molten pig iron		Mixed	Mixed	Mixed	Mixed	Mixed
	When discharged from electric furnace	[C]e	mass%	0.3	1.1	1.0	1.1	1.1
	Type of cold iron	source		Scrap	Reduced iron	Reduced iron	Reduced iron	Reduced iron
	No.			26	27	28	29	30

EP 4 328 330 A1

Invention Example Remarks Invention Example 5 mass ppm components Т 2 2 2 2 2 ~ ~ <u>-</u> <u>_</u> <u>-</u> Product mass bpm 10 8 19 19 19 19 19 19 19 z 19 27 Treatment Vacuum degassing time 25 25 25 25 25 25 25 25 25 25 15 treatment circulating Type of Argon gas 20 mass bpm from converter Ē discharged ~ ω ω ω ი თ ω თ ω ი When 25 mass ppm Ĩ 25 16 7 <u>∞</u> <u>∞</u> 3 3 3 7 1 [Table 1-3] hydrogen and 50% hydrogen and 50% hydrogen and 50% hydrogen and 50% blown gas during Type of bottomdecarburization Mixture of 50% Mixture of 50% Mixture of 50% Mixture of 50% 30 Hydrogen Propane Propane propane propane Propane propane propane Propane Propane 35 converter charged mass% When into <u>[</u>] 0.9 2.9 2.4 4. 4 0.9 2.9 2.4 1.7 4. 4 1.7 40 blast-furnace Mixed with molten pig Not mixed Not mixed iron Mixed Mixed Mixed Mixed Mixed Mixed Mixed Mixed 45 discharged from electric furnace mass% When [C]e 1.0 1.0 1.0 1.0 :-:-50 Type of cold iron Reduced iron Reduced iron Reduced Reduced Reduced Reduced Reduced Reduced Reduced Reduced source iron iron iron iron iron iron iron iron 55 ġ 33 35 38 æ ဓိ 3 8 8 37 4

5	Remarks	Invention Example		
	luct nents	т	mass ppm	-
10	Product components	z	mass ppm	20
15	Vacuum degassing treatment	Trontont	time	25
20	Vacuum o treat	Type of	circulating gas	Argon
	When discharged from converter	lΗ]f	mass ppm	თ
25	WI disch from co	[N]f	mass ppm	19
30 (continued)	Type of bottom- blown gas during	Mixture of 50% hydrogen and 50% propane		
	When charged into converter	[C]i	mass%	6.0
40	Mixed with blast-furnace	Not mixed		
45 50	When discharged from electric furnace	[C]e	mass%	1.0
55	Type of cold iron		Reduced iron	
	N N			41

Industrial Applicability

[0039] The method for refining molten iron according to the present invention can stably produce low-nitrogen steel with a nitrogen concentration of 30 mass ppm or lower under the condition of an increased amount of cold iron source used, without a significant decrease in productivity or cost increase, and without adding to the amount of slag generated or the amount of CO_2 generated. This method is industrially useful in that it allows existing integrated ironworks to reduce CO_2 emissions and produce high-grade steels at the same time while using blast-furnace molten pig iron and a cold iron source in combination.

10

5

Claims

- 1. A method for refining molten iron, characterized in that
- 15

untreated molten iron with a carbon concentration [C]i between 0.5 mass% and 3.0 mass%, both inclusive, is placed into a vessel, and

oxygen is blown onto the untreated molten iron under atmospheric pressure while a hydrogen gas, a hydrocarbon gas, or a mixture gas of these gases is blown in to perform a decarburization and denitrification treatment of the untreated molten iron.

20

- 2. The method for refining molten iron according to claim 1, wherein a nitrogen concentration [N]ε in treated molten iron after being subjected to the decarburization and denitrification treatment is 30 mass ppm or lower.
- The method for refining molten iron according to claim 1 or 2, wherein treated molten iron after being subjected to the decarburization and denitrification treatment is further subjected to a vacuum degassing treatment.
 - **4.** The method for refining molten iron according to any one of claims 1 to 3, wherein the untreated molten iron includes molten iron obtained by melting a cold iron source.
 - **5.** The method for refining molten iron according to any one of claims 1 to 3, wherein the untreated molten iron is a mixture of primary molten iron obtained by melting a cold iron source in a melting furnace and molten pig iron having a carbon concentration of 2.0 mass% or higher.
- 35

30

- **6.** The method for refining molten iron according to claim 4 or 5, wherein the cold iron source includes reduced iron.
- **7.** The method for refining molten iron according to any one of claims 1 to 6, wherein the vessel is a converter.

45

40

50

	INTERNATIONAL SEARCH REPORT	International appl	ication No.		
		PCT/,	JP2022/018168		
A. CLA	SSIFICATION OF SUBJECT MATTER	I			
	* <i>5/28</i> (2006.01)i; <i>C21C 7/00</i> (2006.01)i; <i>C21C 7/068</i> (2 C21C5/28 Z; C21C7/10 Z; C21C7/00 N; C21C7/068; C				
According to	D International Patent Classification (IPC) or to both na	tional classification and IPC			
B. FIEI	DS SEARCHED				
	ocumentation searched (classification system followed 5/28; C21C7/00; C21C7/068; C21C7/10	by classification symbols)			
Publis Publis Regis Publis	ion searched other than minimum documentation to the hed examined utility model applications of Japan 1922 hed unexamined utility model applications of Japan 19 tered utility model specifications of Japan 1996-2022 hed registered utility model applications of Japan 1994 ata base consulted during the international search (nam	1996 71-2022 2022			
		e of data base and, where practicable, se			
C. DOC	UMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where a	ppropriate, of the relevant passages	Relevant to claim No.		
X	JP 5-78726 A (SUMITOMO METAL IND LTD) 30	March 1993 (1993-03-30)	1, 2, 4, 6, 7		
Y	paragraphs [0045]-[0047], table 4 paragraphs [0045]-[0047], table 4	3, 5			
Х		JP 4-224612 A (SUMITOMO METAL IND LTD) 13 August 1992 (1992-08-13)			
Y	paragraphs [0026]-[0027] paragraphs [0026]-[0027]	3, 5			
Х	JP 61-223117 A (KAWASAKI STEEL CORP) 03 O claims, example 1, table 4	ctober 1986 (1986-10-03)	1, 2, 4, 6, 7		
Y	claims, example 1, table 4		3, 5		
X	JP 60-194009 A (KAWASAKI STEEL CORP) 02 O claims, examples, table 1		1, 2, 4, 6, 7		
Y	claims, examples, table 1		3, 5		
	documents are listed in the continuation of Box C.	See patent family annex.	ernational filing date or priori		
"A" documer to be of "E" earlier a filing da "L" documer	nt defining the general state of the art which is not considered particular relevance oplication or patent but published on or after the international	date and not in conflict with the applic principle or theory underlying the inv "X" document of particular relevance; th considered novel or cannot be conside when the document is taken alone "Y" document of particular relevance; th	ation but cited to understand th ention e claimed invention cannot b rred to involve an inventive ste e claimed invention cannot b		
special r "O" documer means "P" documer	eason (as specified) at referring to an oral disclosure, use, exhibition or other at published prior to the international filing date but later than ity date claimed	considered to involve an inventive combined with one or more other suc- being obvious to a person skilled in th "&" document member of the same patent	h documents, such combinatione art		
Date of the ac	tual completion of the international search	Date of mailing of the international sear	rch report		
	20 May 2022	07 June 202	2		
Japan Pa	iling address of the ISA/JP tent Office (ISA/JP) sumigaseki, Chiyoda-ku, Tokyo 100-8915	Authorized officer			

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.

0

		INTERNATIONAL SEARCH REPORT	International appl PCT/,	ication No. JP2022/018168
5	C. DOC	CUMENTS CONSIDERED TO BE RELEVANT	•	
	Category*	Citation of document, with indication, where appropriate, of the rel	evant passages	Relevant to claim No.
	Х	JP 59-25916 A (KAWASAKI STEEL CORP) 10 February 1984 (1984-0. claims, table 2	2-10)	1, 2, 4, 6, 7
10	Y	3, 5		
	X	JP 58-147509 A (KAWASAKI STEEL CORP) 02 September 1983 (1983) claims, table 3	3-09-02)	1, 2, 4, 6, 7
	Y	claims, table 3		3, 5
15	Y	JP 2015-30868 A (JFE STEEL CORP) 16 February 2015 (2015-02-16) claims, paragraph [0001]		3-7
	Y	JP 2009-263783 A (JFE STEEL CORP) 12 November 2009 (2009-11-12 paragraph [0019])	3-7
	Y	JP 2010-209383 A (JFE STEEL CORP) 24 September 2010 (2010-09-24 paragraph [0001], claims		5-7
20	Y	JP 2011-80143 A (JFE STEEL CORP) 21 April 2011 (2011-04-21) paragraphs [0072]-[0073], [0077]-[0078]		5-7
25 30				
35				
40				
45				
50				
55				

Form PCT/ISA/210 (second sheet) (January 2015)

International application No.

INTERNATIONAL SEARCH REPORT Information on patent family members

	Informati	on on p	Р	CT/JP2022/018168		
	ent document in search report		Publication date (day/month/year)	Patent family me	mber(s)	Publication date (day/month/year)
JP	5-78726	Α	30 March 1993	(Family: none)		
JP	4-224612	А	13 August 1992	(Family: none)		
JP	61-223117	А	03 October 1986	(Family: none)		
JP	60-194009	А	02 October 1985	(Family: none)		
JP	59-25916	А	10 February 1984	(Family: none)		
JP	58-147509	А	02 September 1983	(Family: none)		
JP	2015-30868	А	16 February 2015	(Family: none)		
JP	2009-263783	А	12 November 2009	(Family: none)		
JP	2010-209383	А	24 September 2010	(Family: none)		
JP	2011-80143	А	21 April 2011	(Family: none)		

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2004211120 A [0008]
- JP 2007211298 A [0008]

• JP 2000045013 A [0008]