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(54) METHOD FOR MANUFACTURING HIGH-PURITY STEEL

(57) Provided is a method of producing high-cleanliness steel that can both prevent clogging of an immersion nozzle in a continuous casting line and achieve superior sulfide stress corrosion cracking resistance (SSC resistance). The method comprises: adding Si and then adding Al to molten steel in a converter to perform deoxidation treatment; performing ladle refining using a ladle furnace; performing a vacuum degassing treatment; adding Ca-containing metal to the molten steel; and continuously casing the molten steel, wherein Si is not added to the molten steel in the ladle refining, or wherein in a case of adding additional Si for adjusting a chemical composition of the molten steel, the additional Si is added in a first half of a treatment period of the ladle refining and is not added in a latter half of the treatment period of the ladle refining and in a period of the vacuum degassing treatment.

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FIG. 1A

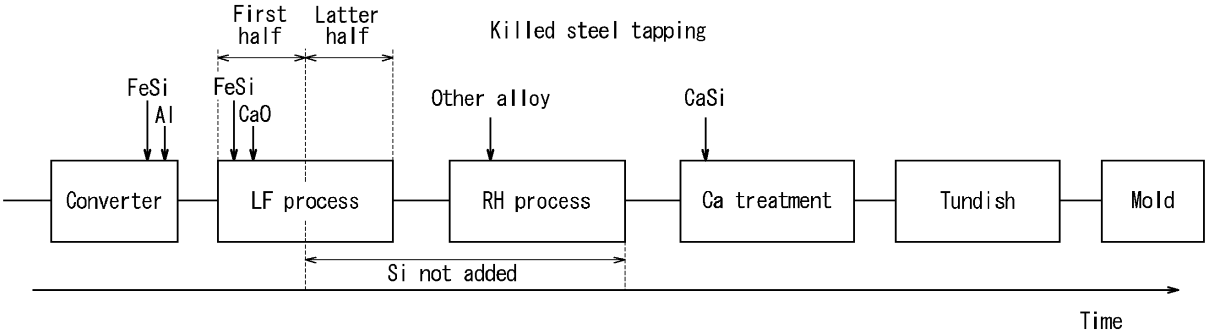
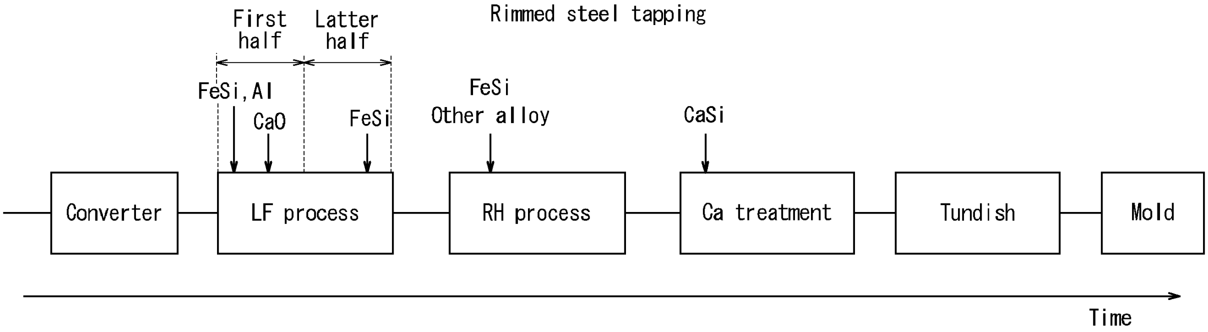

First half
Latter half
Killed steel tapping
FeSi
Al
FeSi
CaO
Other alloy
CaSi
Converter
LF process
RH process
Ca treatment
Tundish
Mold
Si not added
Time

FIG. 1B


First half
Latter half
Rimmed steel tapping
FeSi,Al
CaO
FeSi
FeSi
Other alloy
CaSi
Converter
LF process
RH process
Ca treatment
Tundish
Mold
Time

Description

TECHNICAL FIELD

[0001] The present disclosure relates to a method of producing steel with a low amount of oxide-based nonmetallic inclusions, namely, high-cleanliness steel, and particularly relates to a method of producing calcium-added steel.

BACKGROUND

[0002] Because of the need for stricter product characteristics and higher-performance materials, the demand for high-cleanliness steel with a reduced amount of oxide-based nonmetallic inclusions in steel material is increasing. Moreover, high-strength steel pipes or tubes for use in oil well pipes or tubes, etc. are used in acidified severe environments (sour environments) containing hydrogen sulfide of corrosive gas, and therefore are required to have excellent hydrogen-induced cracking resistance (HIC resistance) and sulfide stress corrosion cracking resistance (SSC resistance).

[0003] For improvement in HIC resistance and SSC resistance, it is necessary to not only reduce the amount of oxide-based nonmetallic inclusions in the molten steel stage, but also reduce sulfide, such as MnS, which precipitates and crystallizes during solidification of molten steel, and render it harmless. In particular, MnS is known to be harmful to HIC resistance and SSC resistance, because MnS has high stretching property and, in the subsequent rolling of the steel, stretches to become a hydrogen storage site.

[0004] A commonly known effective measure for this is to add Ca-containing metal in the molten steel stage to change MnS to CaS. Regarding methods of adding Ca-containing metal and its addition amounts, the following techniques are known.

[0005] JP 2002-60893 A (PTL 1) describes a production method for steel for an oil well having excellent sulfide stress corrosion cracking resistance, wherein Ca or a Ca-containing substance is added to molten steel after tapping of the molten steel from a converter and before casting so that the Ca content in the molten steel will be 0.0005 mass% to 0.005 mass%, and S, Al, Ca, and T.[O] (total oxygen) in the steel are controlled to satisfy the following formula:

$$-0.005 \leq (\mathrm{Ca}/40 - \mathrm{S}/32) \times \mathrm{sol.Al} \times \mathrm{T.[O]} \times 1000000 \leq 0.0042.$$

[0006] JP 2011-89180 A (PTL 2) describes a smelting method for steel material for a high-strength and high-corrosion-resistance oil well pipe or tube, wherein T.[O] in molten steel is measured after completion of secondary refining and, before starting pouring the molten steel into a tundish of a continuous caster, Ca is added in an addition amount calculated based on the measured value to control inclusions.

[0007] JP 2010-209372 A (PTL 3) describes the following production method for clean steel having excellent sulfide corrosion cracking resistance: In a process of adding Al to molten steel to deoxidize the molten steel during or after tapping of the molten steel from a converter to a ladle, first adding CaO-containing flux to the molten steel in the ladle to perform desulfurization treatment and adding Ca-containing metal during the desulfurization treatment, thereafter subjecting the molten steel in the ladle to vacuum degassing treatment and further adding Ca-containing metal to the molten steel in the ladle after the vacuum degassing treatment, and thereafter casting the molten steel, pure content of Ca in the Ca-containing metal in the desulfurization treatment is adjusted depending on the Al concentration and the total oxygen concentration in the molten steel.

CITATION LIST

Patent Literatures

[0008]

PTL 1: JP 2002-60893 A
PTL 2: JP 2011-89180 A
PTL 3: JP 2010-209372 A

SUMMARY

(Technical Problem)

[0009] By adding Ca-containing metal to molten steel, not only the formation of MnS can be suppressed as described above, but also Al_2O_3-based inclusions can be changed to CaO-Al_2O_3-based inclusions. The techniques described in PTL 1 to PTL 3 each define the addition amount of Ca-containing metal for the purpose of improving HIC resistance and SSC resistance from this perspective. In detail, the techniques described in PTL 1 to PTL 3 define the respective addition methods or addition amounts based on the concept that, assuming only Al_2O_3-based inclusions are present before Ca addition, the Al_2O_3-based inclusions react with Ca and as a result change to appropriate CaO-Al_2O_3-based inclusions.

[0010] However, our study revealed that, with Ca addition based on such a concept, there is a problem of nozzle clogging especially in an immersion nozzle of a small inner diameter in a continuous casting line, and, for steel types required to have a high strength of 110 psi (760 MPa) or more and strict SSC resistance, the formation of large inclusions exceeding 200 μm cannot be completely prevented and such strict SSC resistance requirement cannot be met.

[0011] It could therefore be helpful to provide a method of producing high-cleanliness steel that can both prevent clogging of an immersion nozzle in a continuous casting line and achieve superior sulfide stress corrosion cracking resistance (SSC resistance).

(Solution to Problem)

[0012] We closely studied an inclusion composition in steel for a high-strength seamless pipe or the like used in a sour environment. Since such steel is typically required to have extremely low S component and P component and low O component, the steel is usually produced by the following process: First, Si and Al are added to molten steel in a converter or a ladle subsequent to the converter, to perform deoxidation treatment. Following this, CaO-containing flux is added to the molten steel in the ladle, to perform ladle refining (desulfurization treatment) using a ladle furnace (LF). Next, vacuum degassing treatment by an RH vacuum degasser is performed. Next, Ca treatment of adding Ca-containing metal to the molten steel (hereafter also simply referred to as "Ca addition") is performed. After this, the molten steel is transferred from the ladle to a tundish, and continuously cast to form cast steel.

[0013] Regarding inclusions in the molten steel, Al_2O_3-based inclusions are predominant immediately after the deoxidation treatment. Steel for a high-strength seamless pipe, a line pipe, etc. used in a sour environment is required to have high strength, and thus typically has a composition having a Si content of 0.1 % or more. In the case of producing such steel, for Si component, it is common to add a large amount of a FeSi alloy simultaneously with Al as a deoxidizer and then add, in the ladle that receives the molten steel tapped from the converter or in the subsequent LF treatment and vacuum degassing, the FeSi alloy to the molten steel several times so as to achieve the target Si content. About 1 % of Ca component is inevitably contained in the FeSi alloy. Moreover, in the ladle refining, a reaction between CaO-Al_2O_3-SiO_2-based flux added for desulfurization and a refractory of MgO-C composition causes Mg to enter into the molten steel. Thus, the inclusion composition at the end of the ladle refining tends to be not Al_2O_3-based inclusions alone but have changed to CaO-MgO-Al_2O_3-based inclusions containing CaO and MgO.

[0014] Our study further revealed that, in the case where the CaO concentration varies among a plurality of inclusions in the molten steel before Ca addition within one charge, even when a predetermined amount of Ca-containing metal is added in the subsequent Ca treatment, the composition of oxide inclusions in the molten steel in the tundish stage varies. If there are variations in inclusion composition, nozzle clogging occurs or a stricter SSC resistance requirement cannot be met.

[0015] As a result of conducting close research, we learned that, when the Ca concentration in the molten steel after the vacuum degassing treatment and before the Ca treatment is higher, the final inclusion composition is more likely to vary even though the Ca addition amount in the subsequent Ca treatment is adjusted, and the probability that giant inclusions of 200 μm or more are observed in cast steel is higher.

[0016] Regarding the production process, we learned the following: The foregoing problem is more likely to occur in a rimmed steel tapping process of adding deoxidizers such as Si and Al in the ladle subsequent to the converter (i.e. tapping without killing a converter) than in a killed steel tapping process of adding deoxidizers such as Si and Al in the converter (i.e. tapping with killing). Moreover, the foregoing problem is particularly noticeable in the case where the FeSi alloy for Si component adjustment is added in the latter half of the ladle refining (LF) or in the vacuum degassing treatment. Analysis results in these cases indicate that the Ca concentration in the molten steel after the vacuum degassing treatment and before the Ca treatment increased to about 5 ppm to 10 ppm.

[0017] In view of this, we discovered the following: By satisfying all of: (1) performing the deoxidation treatment not by rimmed steel tapping but by killed steel tapping; (2) in the deoxidation treatment, adding the deoxidizers in the order of Si and Al; and (3) in the case of additionally adding Si for chemical composition adjustment, adding Si before or in the first half of the ladle refining and not in the latter half of the ladle refining or in the vacuum degassing, the following effects (A) to (C) can be achieved: (A) the Ca concentration in the molten steel from the converter treatment to the vacuum degassing can be continuously maintained at a low concentration of 4 ppm or less; (B) variations in the inclusion composition after the Ca addition can be suppressed and the inclusion composition can be controlled within a 1600 °C liquid phase composition range; and (C) the molten steel after the Ca addition contains few large inclusions of 5 μm or more in diameter. Consequently, high-cleanliness steel having superior SSC resistance can be produced while preventing clogging of an immersion nozzle in a continuous casting line.

[0018] The present disclosure is based on these discoveries. We thus provide:

[1] A method of producing high-cleanliness steel, the method comprising: adding Si and then adding Al to molten steel in a converter to subject the molten steel to deoxidation treatment; performing ladle refining of adding CaO-containing flux to the molten steel and of subjecting the molten steel to desulfurization treatment using a ladle furnace; thereafter subjecting the molten steel to vacuum degassing treatment using a vacuum degasser; thereafter adding Ca-containing metal to the molten steel; and thereafter continuously casting the molten steel, wherein Si is not added to the molten steel in the ladle refining, or wherein in a case of adding additional Si for adjusting a chemical composition of the molten steel, the additional Si is added in a first half of a treatment period of the ladle refining and is not added in a latter half of the treatment period of the ladle refining and in a period of the vacuum degassing treatment.

[2] The method of producing high-cleanliness steel according to [1], wherein the additional Si is added within 10 minutes from a treatment start of the ladle refining.

[3] The method of producing high-cleanliness steel according to [1] or [2], wherein an interval between the addition of Si and the addition of Al in the deoxidation treatment is 1 minute or more and 10 minutes or less.

[4] The method of producing high-cleanliness steel according to any one of [1] to [3], wherein a Ca concentration in the molten steel after the vacuum degassing treatment and before the addition of the Ca-containing metal is 0.0004 mass% or less, and an addition amount of the Ca-containing metal is set to satisfy the following Formula (1):

$$1.00 \leq \{[\%\mathrm{Ca}] - (0.18 + 130 \times [\%\mathrm{Ca}]) \times [\%\mathrm{O}]\}/1.25/[\%\mathrm{S}] \leq 2.00 \quad \dots (1)$$

where [%Ca], [%O], and [%S] are respective concentrations of elements Ca, O, and S in the molten steel in a tundish, in mass%.

(Advantageous Effect)

[0019] It is thus possible to produce high-cleanliness steel having superior sulfide stress corrosion cracking resistance (SSC resistance) while preventing clogging of an immersion nozzle in a continuous casting line.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] In the accompanying drawings:

FIG. 1A is a production process flowchart of a method of producing high-cleanliness steel according to one of the disclosed embodiments;

FIG. 1B is a production process flowchart of a method of producing high-cleanliness steel according to a comparative example;

FIG. 2 is a diagram illustrating an example of changes in Ca concentration in molten steel in each of the production processes of comparative methods 1 and 2 and a disclosed method;

FIG. 3A is a diagram illustrating results of studying, in a plurality of charges, the average composition of CaO-MgO-Al_2O_3-based inclusions in molten steel samples collected after RH treatment and before Ca addition in each of the comparative methods 1 and 2 and the disclosed method;

FIG. 3B is a diagram illustrating results of studying, in each charge in FIG. 3A, the average composition of CaO-MgO-Al_2O_3-based inclusions in molten steel samples collected after Ca addition;

FIG. 4 is a diagram illustrating results of studying the number of CaO-MgO-Al_2O_3-based inclusions of 5 μm or more in diameter in molten steel samples collected after Ca addition in each of the comparative methods 1 and 2 and the disclosed method; and

FIG. 5 is a graph illustrating the relationship between the atomic concentration ratio (ACR) index and the stress corrosion cracking (SSC) test fail rate.

DETAILED DESCRIPTION

[0021] A method of producing high-cleanliness steel according to one of the disclosed embodiments comprises: adding deoxidizers to molten steel in a converter to subject the molten steel to deoxidation treatment; performing ladle refining of adding CaO-containing flux to the molten steel and of subjecting the molten steel to desulfurization treatment using a ladle furnace; thereafter subjecting the molten steel to vacuum degassing treatment using a vacuum degasser; thereafter adding Ca-containing metal to the molten steel; and thereafter continuously casting the molten steel.

[0022] Types of deoxidation treatment include killed steel tapping treatment of adding deoxidizers such as Si and Al in a converter (i.e. tapping with killing) as illustrated in FIG. 1A as an example and rimmed steel tapping treatment of adding deoxidizers such as Si and Al in ladle refining or vacuum degassing treatment after converter refining (i.e. tapping without killing a converter) as illustrated in FIG. 1B as an example. In this embodiment, the killed steel tapping treatment is used as the deoxidation treatment. With the rimmed steel tapping treatment, the Ca concentration in the molten steel cannot be limited to 0.0004 % or less between the converter treatment and the vacuum degassing treatment, the inclusion composition after Ca addition cannot be controlled within a 1600 °C liquid phase composition range, and many large inclusions of 5 μm or more in diameter form, as described later. This causes nozzle clogging and insufficient SSC resistance. The deoxidation treatment can be performed by a typical method of adding deoxidizers such as Si and Al to molten steel. A deoxidation product formed as a result of the deoxidation treatment is Al_2O_3 (alumina).

[0023] In this embodiment, it is important to add Si and then add Al as the order of addition of the deoxidizers in the deoxidation treatment. If Si is added after Al or Al and Si are simultaneously added, the Ca concentration in the molten steel cannot be limited to 0.0004 % or less between the converter treatment and the vacuum degassing treatment, the inclusion composition after Ca addition cannot be stably controlled within the 1600 °C liquid phase composition range, and many large inclusions of 5 μm or more in diameter form. This causes nozzle clogging and insufficient SSC resistance.

[0024] The interval between the Si addition and the Al addition in the deoxidation treatment is not limited, but is preferably 1 minute or more and 10 minutes or less. If the interval is less than 1 minute, the effects according to the present disclosure may not be achieved sufficiently. If the interval is more than 10 minutes, giant SiO_2-MnO(-CaO) oxide may grow.

[0025] The ladle refining includes heating stirring treatment of introducing gas into the molten steel while heating the molten steel by arc discharge using a ladle furnace (LF). CaO-containing flux is added to the molten steel, and desulfurization treatment is performed. Examples of the flux include quicklime (CaO) alone and a mixture of quicklime and Al_2O_3 or SiO_2 as a slag formation accelerator for CaO. The vacuum degassing treatment can be performed, for example, using a typical device such as a RH vacuum degasser. The treatment time of the ladle refining and the treatment time of the vacuum degassing treatment are not limited, and may be set as appropriate depending on the contents of O and S before the treatment with respect to the target contents of O and S. Typically, the treatment time of the ladle refining is about 30 minutes to 60 minutes, and the treatment time of the vacuum degassing treatment is about 10 minutes to 40 minutes.

[0026] The chemical composition of the molten steel is eventually adjusted to the target chemical composition as a result of adding an alloy in the vacuum degassing treatment. Regarding Mn and Si components, typically the elements are added in large amounts simultaneously with Al as a deoxidizer and then added several times until the ladle refining or the vacuum degassing treatment ends to achieve the target content. In this embodiment, on the other hand, it is important to, in the case of additionally adding Si for chemical composition adjustment, add Si until the end of the first half of the ladle refining and not in the latter half of the ladle refining and in the vacuum degassing. It is also preferable to achieve the target Si content only by the Si addition performed before the Al addition in the converter, without adding additional Si from the ladle refining onward. Thus, the Ca concentration in the molten steel from the converter treatment to the vacuum degassing can be continuously maintained at a low concentration of 4 ppm or less, and high-cleanliness steel having superior SSC resistance can be produced.

[0027] To further ensure the effects according to the present disclosure, in the case of adding additional Si, the additional Si is preferably added within 10 minutes from the treatment start of the ladle refining.

[0028] After the vacuum degassing treatment, Ca-containing metal is added to the molten steel. The method of adding Ca is not limited. A commonly used method involves adding, to the molten steel, a massive alloy containing Ca: 70 mass% and Si: 30 mass% or a wire obtained by wrapping it in a Fe hoop. A Ca alloy reacts vigorously with the molten steel and thus tends to form a molten steel reoxidation product when added. It is therefore preferable to ensure perfect argon sealing upon the addition.

[0029] The Ca addition after the vacuum degassing treatment may be performed in a ladle of the RH vacuum degasser, following the vacuum degassing treatment. However, it is preferable to transfer the molten steel to a ladle dedicated to Ca treatment and then add Ca to the molten steel in the ladle.

[0030] Experimental examples that led to the completion of the presently disclosed technique will be described below.

(Disclosed method (method according to one of the disclosed embodiments))

[0031] In the process illustrated in FIG. 1A, steel having a chemical composition containing C: 0.2 % to 0.3 %, Si: 0.22 % to 0.27 %, Mn: 0.4 % to 0.6 %, P: 0.005 % to 0.009 %, S: 0.0005 % to 0.002 %, sol.Al: 0.03 % to 0.1 %, Ca: 0 % to 0.003 %, and O: 0.0010 % to 0.0020 % with the balance being Fe and inevitable impurities as molten steel in the tundish was obtained by steelmaking. The converter treatment time was 60 minutes, and a FeSi alloy of 2.2 kg/ton-steel was added 50 minutes after the treatment start and then Al of 3.5 kg/ton-steel was added 5 minutes later. The treatment time of the LF process was 30 minutes, and a FeSi alloy of 1.8 kg/ton-steel was added 10 minutes after the treatment start as additional Si for chemical composition adjustment. Si was not added in the latter half of the LF process and in the RH process. After the RH process, Ca was added to the molten steel.

(Comparative method 1)

[0032] Steel was obtained by steelmaking in the same way as in the disclosed method, except that the order of Al addition and Si addition in the converter was reversed. In detail, in the comparative method 1, the converter treatment time was 60 minutes, and Al of 3.7 kg/ton-steel was added 50 minutes after the treatment start and then a FeSi alloy of 2.2 kg/ton-steel was added 3 minutes later.

(Comparative method 2)

[0033] In the process of rimmed steel tapping illustrated in FIG. 1B, steel having a chemical composition containing C: 0.2 % to 0.3 %, Si: 0.22 % to 0.27 %, Mn: 0.4 % to 0.6 %, P: 0.005 % to 0.009 %, S: 0.0005 % to 0.002 %, sol.Al: 0.03 % to 0.1 %, Ca: 0 % to 0.003 %, and O: 0.0010 % to 0.0020 % with the balance being Fe and inevitable impurities as molten steel in the tundish was obtained by steelmaking. In detail, Si and Al as deoxidizers were not added in the converter. The treatment time of the subsequent LF process was 45 minutes, and a FeSi alloy of 2.2 kg/ton-steel as deoxidizer Si was added simultaneously with Al of 3.5 kg/ton-steel 5 minutes after the treatment start. Further, an additional FeSi alloy was added for chemical composition adjustment 2 minutes after the start of the RH treatment. After the RH process, Ca was added to the molten steel.

[0034] We collected molten steel samples for each of these production processes, and studied the molten steel components, the amount of inclusions, and the inclusion composition. The molten steel components were analyzed by Quantovac rapid analysis. The inclusions were studied using a PSEM device produced by Aspex Corporation. Specifically, first, a molten steel sample was collected from a depth position of 2 m or more from the bath surface, and subjected to resin embedding and polishing to produce a sample for SEM observation. SEM observation was performed on the sample, and the compositions of all inclusions of 5 μm or more in inclusion diameter in an observation field of 15 mm × 15 mm were determined using an EDX and their average was calculated. In the case where the inclusion cross-sectional shape was anisotropic, the square root of the product of the major axis and the minor axis of an ellipse enclosing the cross-section was taken to be the inclusion diameter.

[0035] Composition of inclusions are influenced by reactions among oxides produced by deoxidizer (Al, Si, Mn, etc.) and elements entering from slag, and strongly deoxidizier (Ca, Mg, Ti, etc.) contained in alloyes. Lastly, Ca treatment is performed in order to suppress MnS inclusions which form during solidification, as a result of which an oxide with high CaO content or a CaS-based sulfide is formed.

[0036] Our study has demonstrated that the inclusion composition mainly changes as follows:

(1) before Al addition: Fe_2O_3 (+ MnO + SiO_2 + CaO ...)
(2) after Al addition: Al_2O_3 inclusions
(3) during desulfurization treatment by CaO flux addition: MgO-Al_2O_3-based inclusions
(4) Si addition: CaO-Al_2O_3-based inclusions increase
(5) after ladle refining (LF), after vacuum degassing (RH): CaO-MgO-Al_2O_3-based inclusions
(6) after Ca treatment: CaO-Al_2O_3-based inclusions + CaS.

[0037] Regarding the foregoing inclusion compositions, it is known that during desulfurization treatment by CaO-based flux addition (3), Mg molten from a refractory or the like into slag reacts with inclusions to form $MgO{\cdot}Al_2O_3$ inclusions.

[0038] Si addition (4) is typically performed by adding a FeSi alloy for Si component adjustment. Atypical FeSi alloy inevitably contains about 0.3 % to 1.5 % of Ca component, and a slight amount of Ca component is added to the molten steel as a result of the Si addition, so that CaO-Al_2O_3-based inclusions form. Another method for Si addition that can be used is to add an alloy such as a SiMn alloy or Si scrap within a range in which the permissible amounts of other components such as Mn are not exceeded.

[0039] In production of high-tensile-strength steel that involves an LF process for lowering S while no Ca addition process is needed, for example, a refining process of "converter → LF process → RH process → tundish → mold" is performed. By controlling the timing of adding a FeSi alloy in the same way as in the present disclosure, formation of giant $CaO \cdot Al_2O_3$-based inclusions in steel after continuous casting can be prevented.

[0040] Inclusions after each of ladle refining (LF) and vacuum degassing (RH) (5) are a mixture of the foregoing $MgO \cdot Al_2O_3$ inclusions and $CaO \cdot Al_2O_3$ inclusions and exist as CaO-MgO-Al_2O_3-based inclusions. Considerable variations in composition were recognized, as described later.

[0041] Ca treatment (6) is performed by charging the ladle after the vacuum degassing mainly with a CaSi alloy. Typically, Ca is added to the molten steel so as to be 10 ppm or more. The foregoing CaO-MgO-Al_2O_3-based inclusions become CaS sulfide or CaO-Al_2O_3-based inclusions with little MgO content.

[0042] The use of an alloy having a low Ca content of 0.1 % to 0.2 %, called high-purity FeSi, is also effective in avoiding the above-mentioned entrance of Ca during FeSi alloy addition. However, such an alloy is very expensive, and alloy types that can be used in production are restricted. According to the present disclosure, an effective method can be provided without using high-purity FeSi.

[0043] FIG. 2 illustrates changes in Ca concentration in molten steel in each of the comparative methods 1 and 2 and the disclosed method. For the comparative method 1, the average value of 22 charges is plotted. For the disclosed method and the comparative method 2, the average value of five charges is plotted. As is clear from FIG. 2, the Ca analysis value before Ca addition is a low value of 4 ppm or less in the disclosed method, whereas the Ca analysis value varies greatly from 5 ppm to 15 ppm in the comparative methods 1 and 2.

[0044] The reason that the Ca concentration is low in the case of adding the deoxidizers in the order of Si and Al in killed steel tapping is not clear, but is considered to be as follows: In the case where FeSi is added in a high oxygen concentration state with little deoxidation, Ca which has high oxidizability and easily evaporates oxidizes instantaneously on the molten steel surface upon the addition, and either stays on the molten steel surface or evaporates and discharges out of the system. In the case where FeSi is added after or simultaneously with Al, on the other hand, in a state in which oxygen in the steel decreases rapidly due to Al deoxidation and Al_2O_3 inclusions are formed, Ca reacts with Al_2O_3 inclusions and exists stably as $CaO \cdot Al_2O_3$-based inclusions. In rimmed steel tapping, FeSi tends to be added several times in ladle refining (LF) and vacuum degassing (RH) for chemical composition adjustment, and, at each addition, a slight amount of Ca component enters the molten steel.

[0045] We further compared the average composition of all inclusions of 5 μm or more in diameter between molten steel after RH treatment and before Ca addition and molten steel after Ca addition. FIG. 3A illustrates results of studying, in a plurality of charges, the average composition of CaO-MgO-Al_2O_3-based inclusions in each molten steel sample collected after RH treatment and before Ca addition. FIG. 3B illustrates results of studying, in each charge in FIG. 3A, the average composition of CaO-MgO-Al_2O_3-based inclusions in each molten steel sample collected in the tundish after Ca addition.

[0046] In all charges, Ca addition was performed with the Ca addition amount being determined so that the inclusion composition after the Ca addition would be within the 1600 °C liquid phase range in the tundish stage. As illustrated in FIG. 3A and FIG. 3B, however, in the case of rimmed steel tapping (comparative method 1), the average composition of inclusions before Ca treatment was already an inclusion composition containing many CaO-Al_2O_3 inclusions, due to Ca which appeared to have derived from the FeSi alloy. In the case of adding Si after Al in killed steel tapping (comparative method 2), too, the change to CaO-Al_2O_3 inclusions progressed before Ca treatment, and the inclusion composition varied greatly.

[0047] In the case of killed steel tapping whereby Al addition was performed after Si addition in the disclosed method, the inclusion composition before Ca addition was a uniform composition with very little variations, containing MgO-$\cdot Al_2O_3$ component as a main component and containing 10 wt% to 20 wt% of CaO. Consequently, the inclusion composition of the tundish-collected sample after Ca treatment was able to be controlled within the 1600 °C liquid phase range. With the comparative methods 1 and 2, on the other hand, the composition varied greatly and CaO-Al_2O_3 inclusions of a high CaO composition with a high melting point formed.

[0048] The following are the reasons for limiting the average composition of inclusions in the tundish stage to the 1600 °C liquid phase range:

(1) In the case where the average composition of inclusions in the molten steel stage in the process is CaO-Al_2O_3 inclusion composition ($3CaO \cdot Al_2O_3$ to $CaO + CaS$) of high CaO concentration associated with CaS precipitation, nozzle clogging caused by CaS tends to occur in an immersion nozzle in the subsequent tundish to mold stages upon a temperature decrease. Besides, large inclusions resulting from coagulation drop from the nozzle adhesion site and are incorporated into the cast steel. This causes significant degradation in HIC resistance and SSC resistance.

(2) In the case where the average composition of inclusions in the molten steel stage is a CaO-Al_2O_3 inclusion composition (especially, $CaO \cdot 6Al_2O_3$ to $CaO \cdot 2Al_2O_3$) of lower CaO concentration than the liquid phase inclusion composition (1600 °C liquid phase range), too, nozzle clogging tends to occur. Moreover, harmful MnS is likely to

precipitate during solidification. This causes significant degradation in HIC resistance and SSC resistance.

[0049] It is therefore important to control the inclusion composition to be an inclusion composition of $CaO{\cdot}Al_2O_3$ to $3CaO{\cdot}Al_2O_3$ and preferably an inclusion composition of $12CaO{\cdot}7Al_2O_3$.

[0050] FIG. 4 illustrates results of studying the inclusion cleanliness of each tundish-collected sample used in FIG. 3B. The number of inclusions of 5 μm or more in diameter was considerably improved by the disclosed method as compared with the comparative methods 1 and 2. It seems that, with the disclosed method, the average composition of inclusions after Ca addition was able to be controlled within the 1600 °C liquid phase range, so that flotation and removal of inclusions were facilitated.

[0051] Next, the appropriate range of the Ca addition amount in the Ca treatment was determined by studying Ca addition conditions and sulfide stress corrosion cracking (SSC) test results beforehand.

[0052] FIG. 5 illustrates the relationship between the atomic concentration ratio (ACR value) in the tundish when performing Ca addition after vacuum degassing treatment (RH) and the fail rate in an SSC test in the disclosed method. In the SSC test, a uniaxial tensile test was conducted for 720 hours by applying, to each test piece with the same hardness of HRC = 27, stress of 85 % of the minimum yield point in a NACE test liquid in which hydrogen sulfide of 1 atm had been saturated. In the SSC test, each test piece fractured in an intermediate stage before the end of 720 hours was determined as "fail". In the case of "fail", a fracture occurred mainly in a relatively short time, i.e. within several tens of hours, from the test start (short-time fracture type), and observation of the fractured surface revealed giant $CaO\text{-}Al_2O_3$ inclusions or CaS inclusions stretched to several hundred μm. The atomic concentration ratio (ACR) is defined by the following formula:

$$ACR = \{[\%Ca] - (0.18 + 130 \times [\%Ca]) \times [\%O]\}/1.25/[\%S]$$

where [%Ca], [%O], and [%S] are the respective concentrations (mass%) of elements Ca, O, and S in the molten steel in the tundish.

[0053] The ACR value is an index used to control MnS sulfide which crystallizes during solidification and CaS sulfide, CaO oxide, and calcium aluminate inclusion ($CaO\text{-}Al_2O_3$) composition which form during excessive Ca addition. It is commonly known that the formation of MnS sulfide can be effectively suppressed when $ACR \geq 1.0$, and the formation of CaO-CaS inclusions caused by excessive Ca addition can be suppressed when $ACR \leq 3.0$.

[0054] However, our detailed evaluation using a pipe having a strength of 110 psi (760 MPa) or more revealed that the SSC test fail rate sharply increases when $ACR > 2.00$, as illustrated in FIG. 5. This result was obtained along with recognition that stress corrosion cracking (SSC) is caused by CaS or $CaO\text{-}Al_2O_3$ inclusions having a higher melting point than the liquid phase state in the 1600 °C molten steel stage described above. Thus, the effectiveness of limiting the Ca treatment condition to ACR = 1.00 to 2.00 was able to be confirmed.

[0055] According to the present disclosure, the composition of $MgO\text{-}CaO\text{-}Al_2O_3$-based inclusions before Ca addition is controlled to be in a less varying state, to enable more accurate control of the subsequent oxide composition and sulfide composition. Moreover, clogging of a tundish immersion nozzle caused by inclusions can be prevented, and the formation of inclusions, such as oxide and sulfide, harmful to SSC resistance can be sufficiently suppressed. The use of the presently disclosed technique makes it possible to produce a steel pipe or tube having excellent SSC resistance without clogging of an immersion nozzle caused by inclusions, and achieves production cost reduction and yield rate stabilization.

EXAMPLES

[0056] Steel having a chemical composition containing C: 0.2 % to 0.3 %, Si: 0.22 % to 0.27 %, Mn: 0.4 % to 0.6 %, P: 0.005 % to 0.009 %, S: 0.0005 % to 0.002 %, sol.Al: 0.03 % to 0.1 %, Ca: 0 % to 0.003 %, and O: 0.0010 % to 0.0020 % with the balance being Fe and inevitable impurities as molten steel in the tundish was obtained by steelmaking, and cast using a round billet continuous casting machine of cast steel size 210Φ.

[0057] Table 1 lists the steel tapping form (killed steel tapping or rimmed steel tapping) in the production, the FeSi alloy addition timing, the Ca concentration in the molten steel before Ca treatment, the molten steel components in the tundish after Ca treatment, and the ACR value. The converter treatment time was 60 minutes. In the case of killed steel tapping, Si and Al were added to the molten steel in the converter, to perform deoxidation treatment. The addition order is shown in Table 1. In the case of adding Al after adding FeSi, a FeSi alloy of 2.2 kg/ton-steel was added 50 minutes after the start of converter treatment, and then Al of 3.5 kg/ton-steel was added 5 minutes later. In the case of adding FeSi after adding Al, Al of 3.7 kg/ton-steel was added 50 minutes after the start of converter treatment, and then a FeSi alloy of 2.2 kg/ton-steel was added 3 minutes later. In the case of rimmed steel tapping, deoxidizers were not added in the converter, and Si and Al were added 5 minutes after the start of LF treatment to perform deoxidation treatment.

[0058] Next, $CaO-Al_2O_3-SiO_2$-based flux was added to the molten steel to perform ladle refining (desulfurization treatment) using an LF. The treatment time of the LF process was 45 minutes. In FIG. 1, in each example in which Si was added in the LF first half, Si was added 5 minutes after the start of LF treatment. In each example in which Si was added in the LF latter half, Si was added 30 minutes after the start of LF treatment.

[0059] Next, vacuum degassing treatment using an RH vacuum degasser was performed. The molten steel was then transferred to another ladle, and Ca was added to the molten steel. The molten steel was then transferred from the ladle to the tundish, and continuously cast to form cast steel.

<SSC resistance evaluation>

[0060] In a test of SSC resistance, a uniaxial tensile test was conducted for 720 hours by applying, to each sample, stress of 85 % of the minimum yield point in a NACE test liquid in which hydrogen sulfide of 1 atm had been saturated. Each sample used in the SSC test had the same hardness of HRC = 27 as a result of heat treatment. The SSC test was conducted on six samples for each condition, and the rate of the number of samples that successfully passed the test without fracturing until the end of 720 hours is shown in Table 1 as the pass rate. A pass rate of 100 % is evaluated as good SSC resistance.

<Nozzle clogging determination>

[0061] As a nozzle clogging determination method, the state of clogging was determined from the opening degree (hereafter referred to as "SN opening") of a sliding nozzle in an upper part of an immersion nozzle for pouring molten steel from the tundish into the mold. In detail, in the case where the cross-sectional area of the flow passage of the immersion nozzle decreases due to clogging, the SN opening approaches 100 % by an inner-mold bath surface level automatic control function. With the present casting conditions, operation with an SN opening of 60 % to 70 % corresponds to a stable casting state, but the SN opening sharply increases to 80 % to 100 % if nozzle clogging occurs. Hence, in the case where the SN opening was 80 % or more, it was determined that nozzle clogging occurred.

Table 1

ID	Category	Steel tapping category	FeSi alloy addition				Before Ca treatment	After Ca treatment (tundish)				SSC test result	SN opening (nozzle clogging degree evaluation)
			Converter (order of deoxidizers)	LF first half	LF latter half	RH	Ca amount (%)	Ca (%)	0 (%)	S (%)	ACR		
A	Example	Killed	Added (FeSi, Al)	Not added	Not added	Not added	0.0001	0.0020	0.0010	0.0008	1.82	100%	62%
B	Example	Killed	Added (FeSi, Al)	Added	Not added	Not added	0.0004	0.0021	0.0009	0.0008	1.94	100%	65%
C	Example	Killed	Added (FeSi, Al)	Added	Not added	Not added	0.0004	0.0015	0.0010	0.0009	1.17	100%	64%
D	Example	Killed	Added (FeSi, Al)	Not added	Not added	Not added	0.0002	0.0012	0.0012	0.0009	0.87	84%	80%
E	Example	Killed	Added (FeSi, Al)	Added	Not added	Not added	0.0003	0.0025	0.0010	0.0008	2.32	50%	98%
F	Comparative Example	Killed	Added (FeSi, Al)	Added	Added	Added	0.0006	0.0015	0.0010	0.0008	1.32	33%	66%
G	Comparative Example	Killed	Added (Al, FeSi)	Added	Not added	Added	0.0005	0.0022	0.0010	0.0009	1.80	33%	62%
H	Comparative Example	Rimmed	Not added	Added	Added	Added	0.0006	0.0021	0.0010	0.0008	1.92	17%	62%
I	Comparative Example	Rimmed	Not added	Added	Added	Added	0.0008	0.0020	0.0010	0.0008	1.82	17%	62%
J	Comparative Example	Rimmed	Not added	Added	Added	Not added	0.0005	0.0015	0.0010	0.0007	1.51	33%	63%
K	Comparative Example	Rimmed	Not added	Added	Added	Not added	0.0004	0.0022	0.0012	0.0008	1.98	0%	60%
L	Comparative Example	Rimmed	Not added	Added	Added	Added	0.0007	0.0011	0.0010	0.0007	1.05	33%	96%
M	Comparative Example	Killed	Added (Al, FeSi)	Added	Not added	Not added	0.0006	0.0023	0.0010	0.0009	1.88	67%	65%

[0062] Steel sample IDs A, B, and C satisfied all conditions according to the present disclosure, and were good in both SSC resistance and immersion nozzle clogging degree. Steel sample ID D is an example in which the ACR value was less than the lower limit of the preferred range, and clogging of the immersion nozzle caused by inclusions of $CaO \cdot 6Al_2O_3$ to $CaO \cdot 2Al_2O_3$ composition of a high melting point with a low CaO weight ratio increased and the SSC test result worsened a little. Steel sample ID E is an example in which the ACR value was more than the upper limit of the preferred range, and the SSC test result decreased to 50 % (three out of six samples fractured) due to an increase of CaO-CaS-based inclusions.

[0063] Steel sample ID F is a comparative example in which the FeSi addition timing did not satisfy the conditions according to the present disclosure, and also the Ca concentration before Ca treatment was more than the upper limit of the preferred range, so that the SSC test result decreased to 33 % (four out of six samples fractured). Steel sample ID G had the same results as steel sample ID F. Steel sample IDs H to L are comparative examples in which rimmed steel tapping (non-deoxidized steel tapping) was used and the FeSi addition timing did not satisfy the conditions according to the present disclosure, and also the Ca concentration before Ca treatment was high, so that the SSC test result was low. Steel sample ID M is a comparative example in which the addition order of FeSi and Al did not satisfy the conditions according to the present disclosure, and also the Ca concentration before Ca treatment was high, so that the SSC test result was below the levels of steel sample IDs A, B, and C.

INDUSTRIAL APPLICABILITY

[0064] It is therefore possible to produce high-cleanliness steel having superior SSC resistance while preventing clogging of an immersion nozzle in a continuous casting line.

Claims

1. A method of producing high-cleanliness steel, the method comprising:

adding Si and then adding Al to molten steel in a converter to subject the molten steel to deoxidation treatment;
performing ladle refining of adding CaO-containing flux to the molten steel and of subjecting the molten steel to desulfurization treatment using a ladle furnace;
thereafter subjecting the molten steel to vacuum degassing treatment using a vacuum degasser;
thereafter adding Ca-containing metal to the molten steel; and
thereafter continuously casting the molten steel,
wherein Si is not added to the molten steel in the ladle refining, or
wherein in a case of adding additional Si for adjusting a chemical composition of the molten steel, the additional Si is added in a first half of a treatment period of the ladle refining and is not added in a latter half of the treatment period of the ladle refining and in a period of the vacuum degassing treatment.

2. The method of producing high-cleanliness steel according to claim 1, wherein the additional Si is added within 10 minutes from a treatment start of the ladle refining.

3. The method of producing high-cleanliness steel according to claim 1 or 2, wherein an interval between the addition of Si and the addition of Al in the deoxidation treatment is 1 minute or more and 10 minutes or less.

4. The method of producing high-cleanliness steel according to any one of claims 1 to 3, wherein a Ca concentration in the molten steel after the vacuum degassing treatment and before the addition of the Ca-containing metal is 0.0004 mass% or less, and
an addition amount of the Ca-containing metal is set to satisfy the following Formula (1):

$$1.00 \leq \{[\%Ca] - (0.18 + 130 \times [\%Ca]) \times [\%O]\}/1.25/[\%S] \leq 2.00 \quad \ldots (1)$$

where [%Ca], [%O], and [%S] are respective concentrations of elements Ca, O, and S in the molten steel in a tundish, in mass%.

FIG. 1A

Killed steel tapping

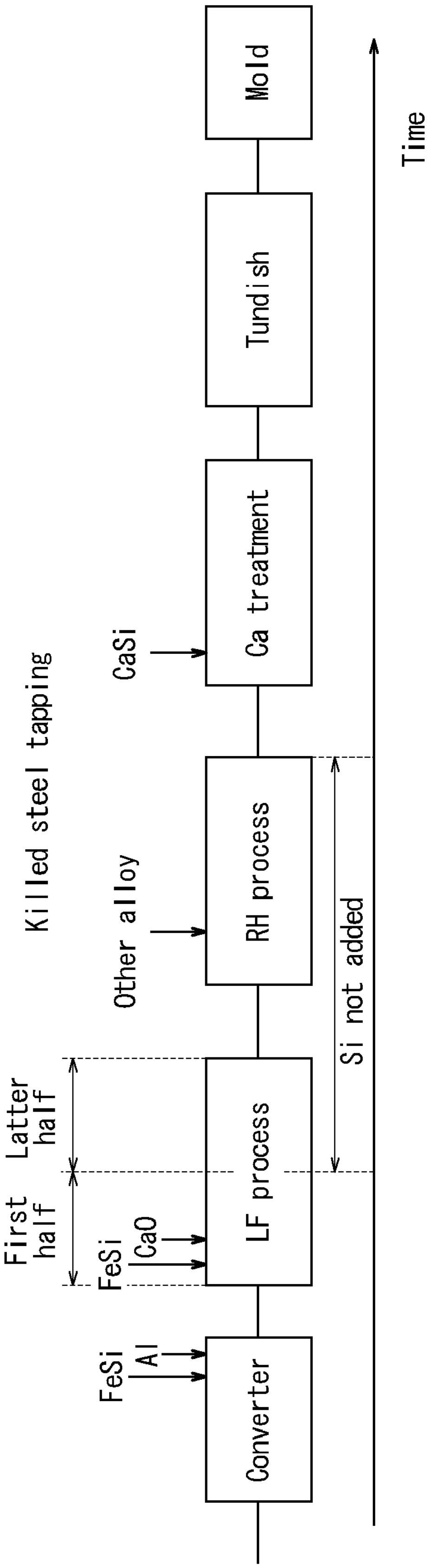


FIG. 1B

Rimmed steel tapping

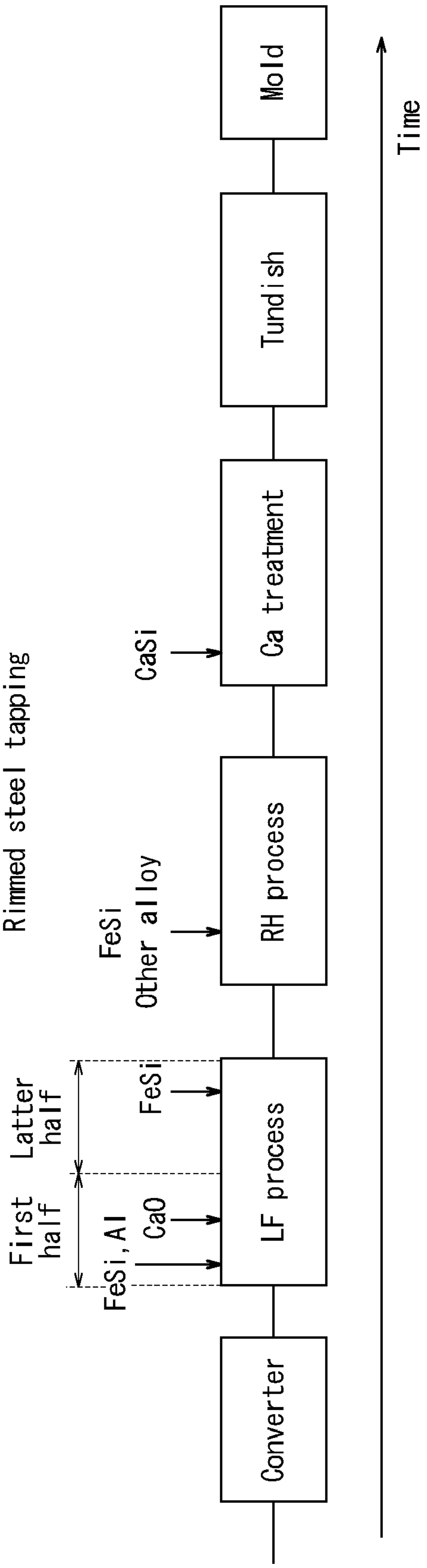


FIG. 2

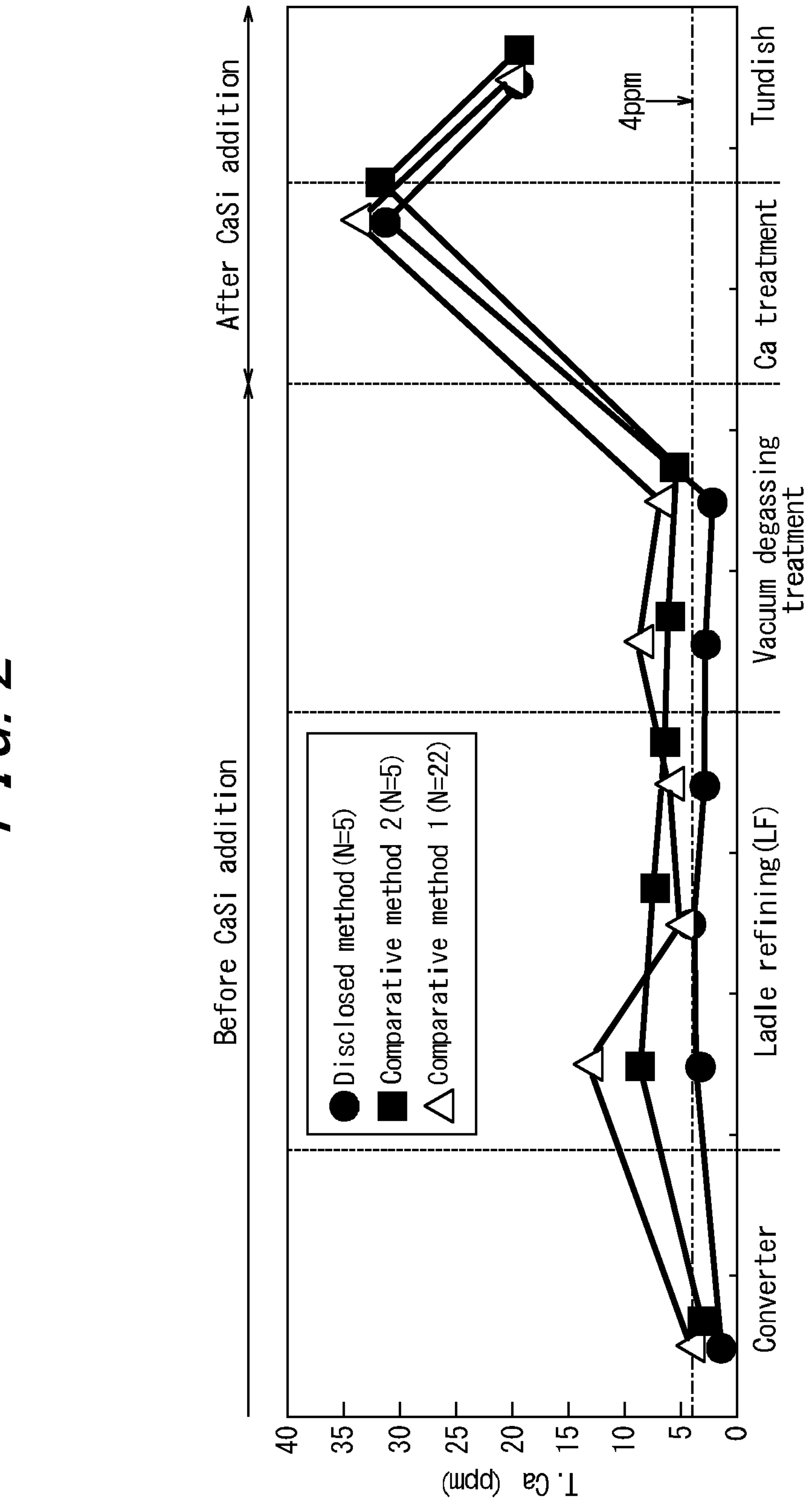

T. Ca (ppm)
0
5
10
15
20
25
30
35
40
Converter
Ladle refining (LF)
Vacuum degassing treatment
Ca treatment
Tundish
Before CaSi addition
After CaSi addition
4ppm
● Disclosed method (N=5)
■ Comparative method 2 (N=5)
△ Comparative method 1 (N=22)

FIG. 3A

After RH treatment
(Before Ca addition)

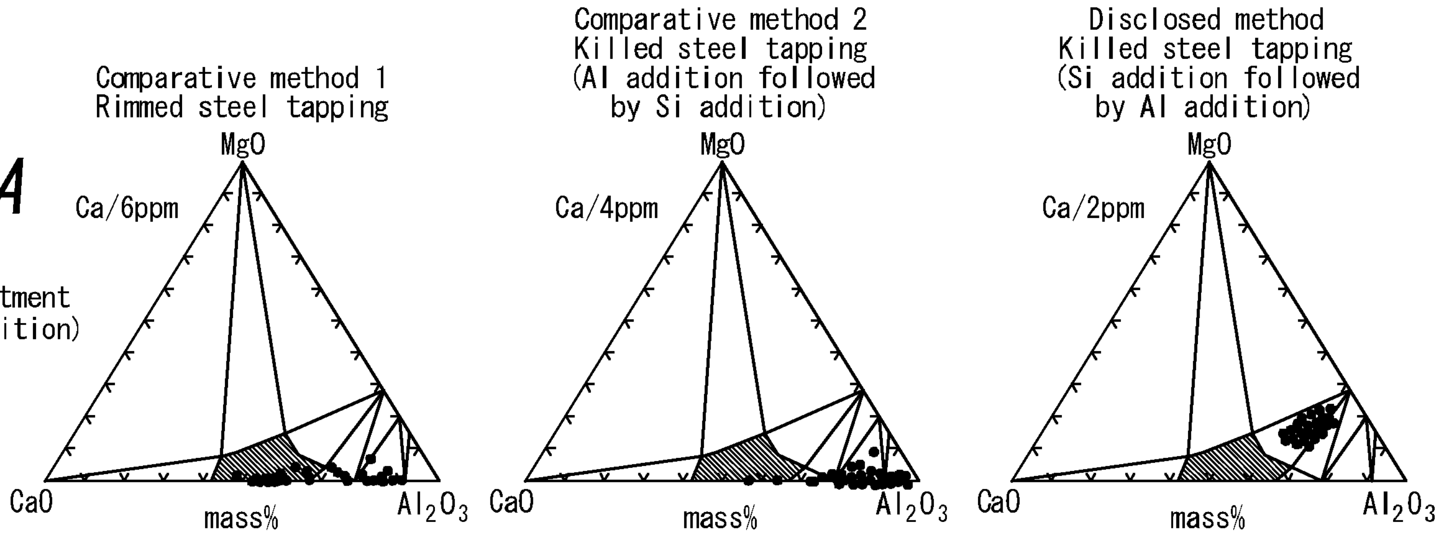


FIG. 3B

Tundish
(After Ca addition)

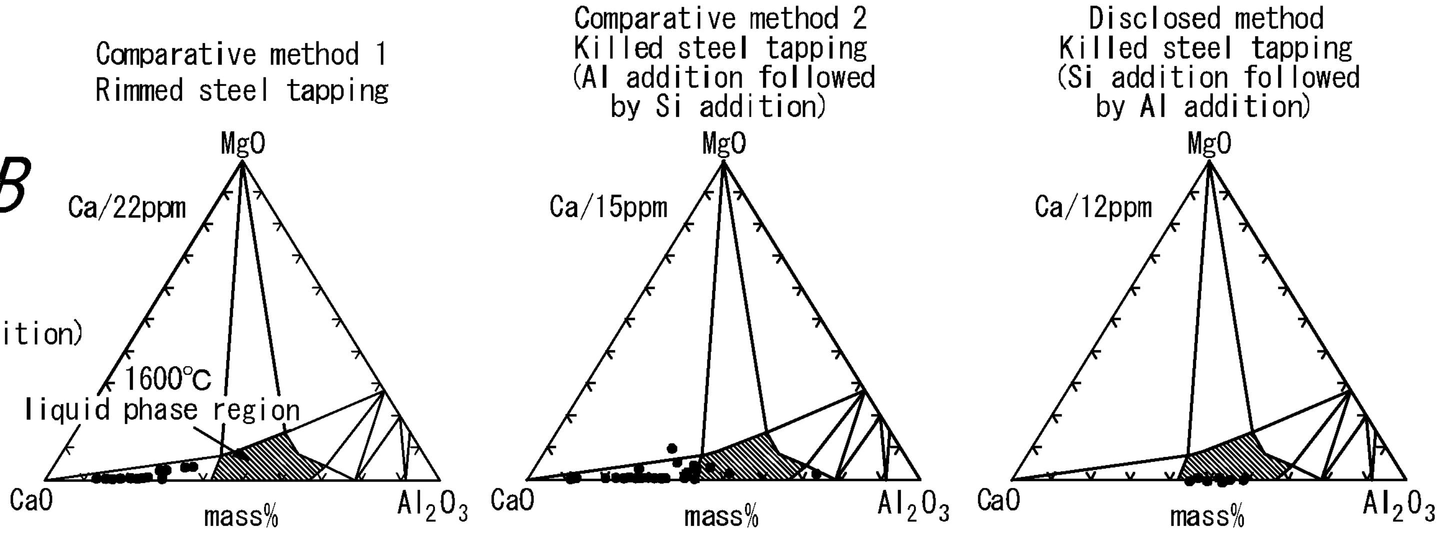


FIG. 4

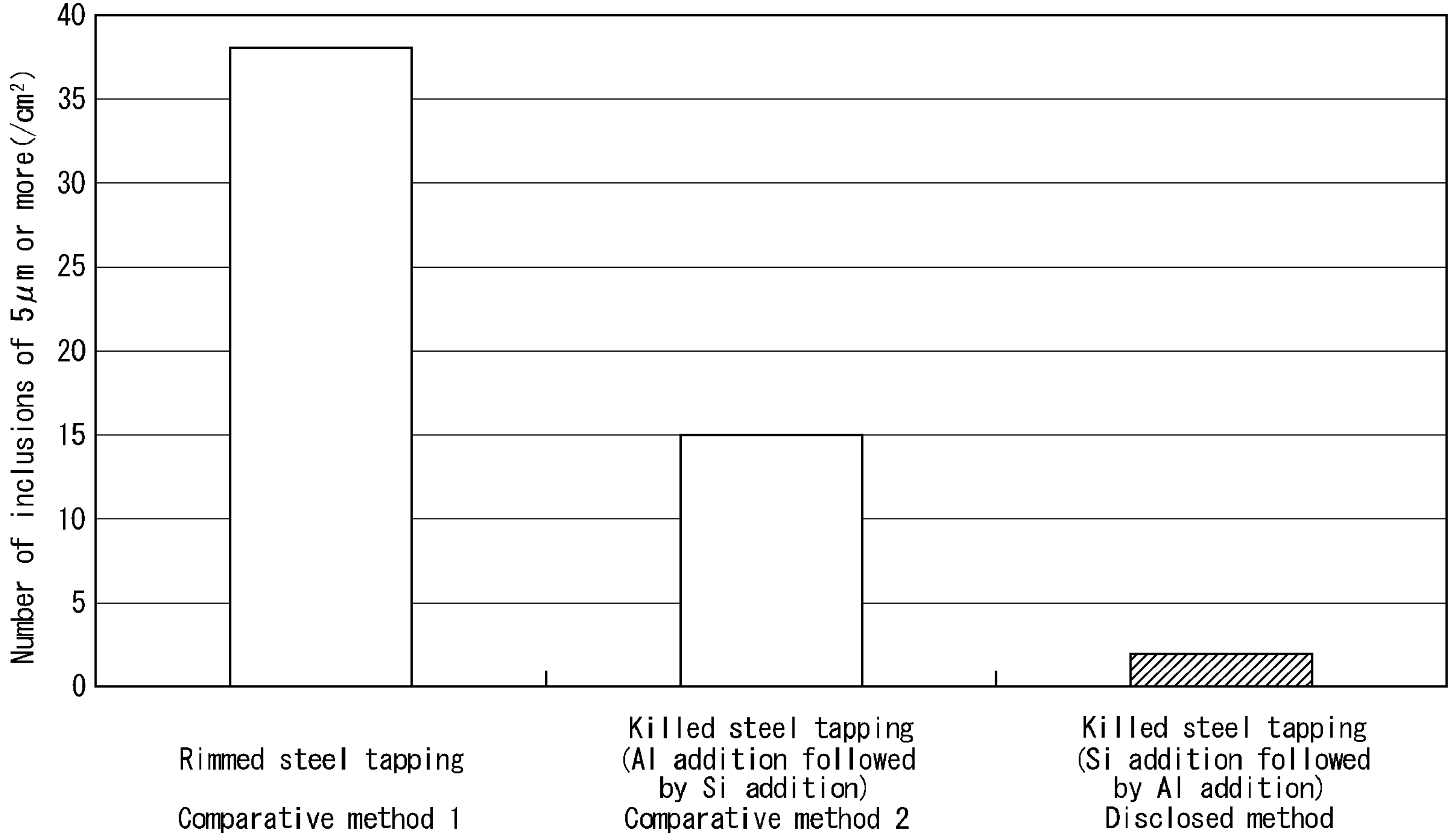
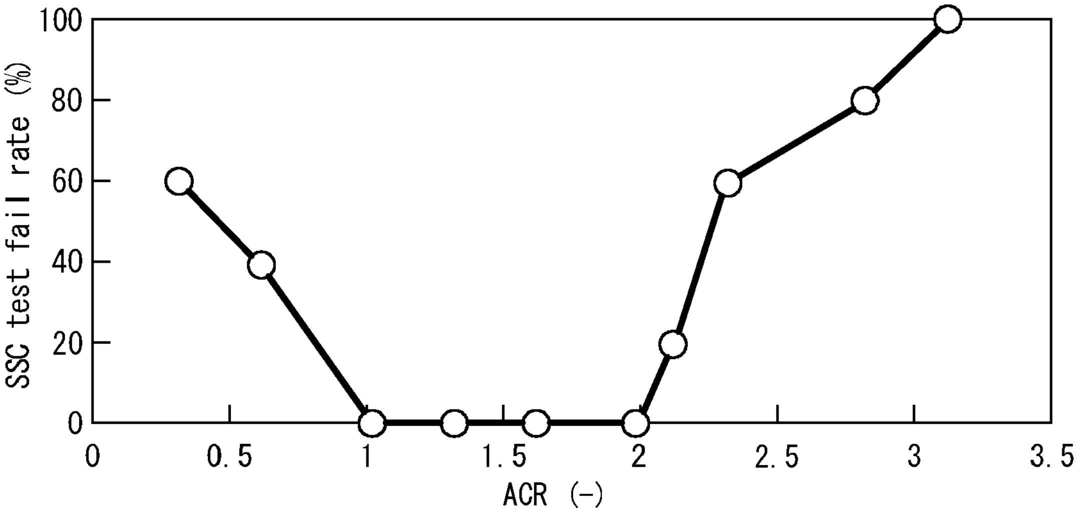

Number of inclusions of 5μm or more(/cm²)
40
35
30
25
20
15
10
5
0
Rimmed steel tapping
Comparative method 1
Killed steel tapping
(Al addition followed
by Si addition)
Comparative method 2
Killed steel tapping
(Si addition followed
by Al addition)
Disclosed method

FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/011852

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C21C7/06(2006.01)i, C21C7/04(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. C21C7/06, C21C7/04

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	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

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.
A	JP 2017-170487 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 28 September 2017, entire text (Family: none)	1-4
A	JP 2010-209372 A (JFE STEEL CORPORATION) 24 September 2010, entire text (Family: none)	1-4

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search 23 May 2019 (23.05.2019)	Date of mailing of the international search report 04 June 2019 (04.06.2019)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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

REFERENCES CITED IN THE DESCRIPTION

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- JP 2011089180 A **[0006] [0008]**
- JP 2010209372 A **[0007] [0008]**