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(54) STEEL PLATE HAVING EXCELLENT HYDROGEN-INDUCED CRACKING RESISTANCE AND STEEL PIPE FOR LINE PIPE

(57) A steel plate and a steel pipe with excellent hydrogen-induced cracking resistance are achieved. Further, the steel plate and steel pipe are achieved that can evaluate the hydrogen-induced cracking resistance based on the quality of an internal structure of a cast strip without executing a hydrogen-induced cracking test after rolling. The steel plate having the excellent hydrogen-induced cracking resistance satisfies the specified contents of C, Si, Mn, P, S, Al, Ca, N, and O, and further contains the specified content of one or more elements selected from the group consisting of REM and Zr, with the balance being iron and inevitable impurities. The steel plate is further characterized by that the ratio (Ca/S) of the Ca to the S is 2.0 or more, the Ca, the S, and the O satisfies the relationship of $(\mathrm{Ca} - 1.25\mathrm{S})/\mathrm{O} \leq 1.80$, and a decrease in an amount of Ca obtained by subtracting a Ca concentration in a slab from a Ca concentration in a molten steel in a tundish is a threshold value $\mathrm{Ca}_{\mathrm{drop}\theta}$ or less, the threshold value $\mathrm{Ca}_{\mathrm{drop}\theta}$ being a maximum decrease in an amount of Ca that avoids the occurrence of hydrogen-induced cracking in the steel plate obtained by rolling the slab.

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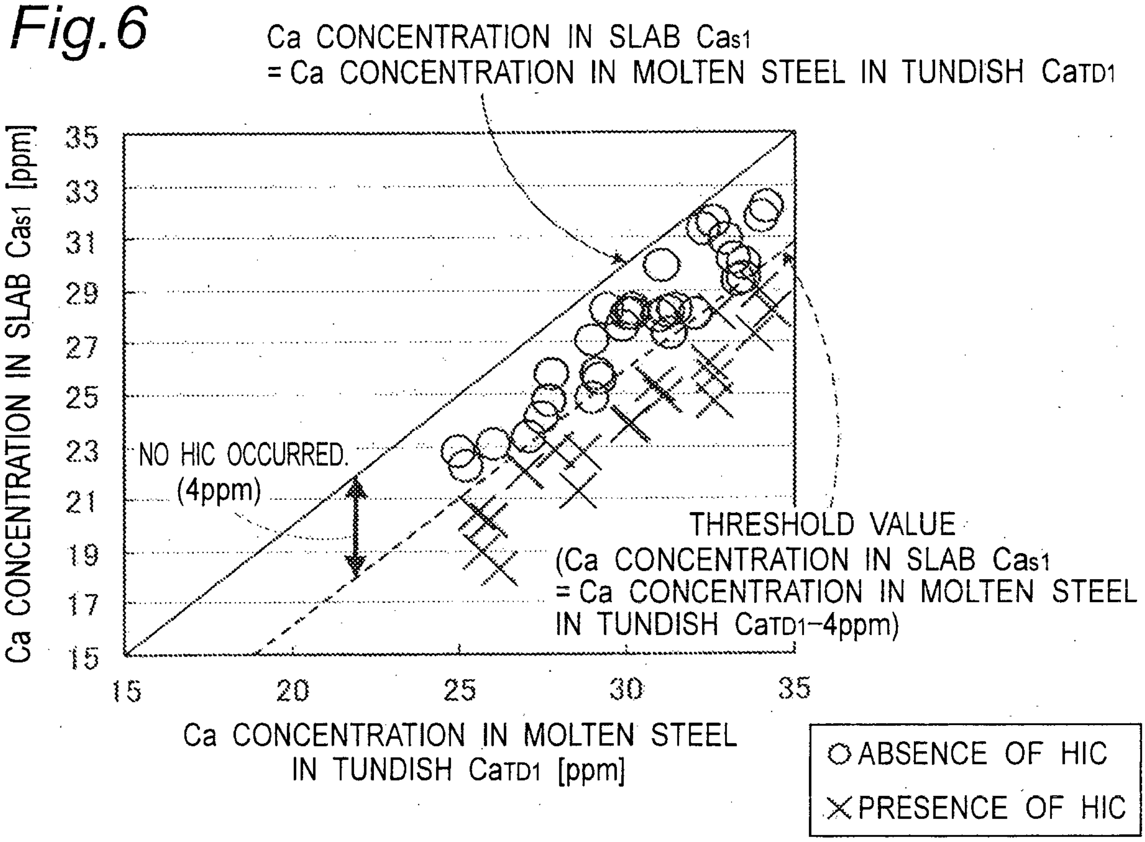
(Cont. next page)

Fig.6


Ca CONCENTRATION IN SLAB Cas1
= Ca CONCENTRATION IN MOLTEN STEEL IN TUNDISH CaTD1
Ca CONCENTRATION IN SLAB Cas1 [ppm]
35
33
31
29
27
25
23
21
19
17
15
NO HIC OCCURRED.
(4ppm)
THRESHOLD VALUE
(Ca CONCENTRATION IN SLAB Cas1
= Ca CONCENTRATION IN MOLTEN STEEL
IN TUNDISH CaTD1−4ppm)
15
20
25
30
35
Ca CONCENTRATION IN MOLTEN STEEL
IN TUNDISH CaTD1 [ppm]
○ ABSENCE OF HIC
× PRESENCE OF HIC

Description

Technical Field

[0001] The present invention relates to a steel plate that has excellent hydrogen-induced cracking resistance and is suitable for use in line pipes for transportation and tanks for storage of natural gas, crude oil, and the like. The present invention also relates to a steel pipe for line pipes with excellent hydrogen-induced cracking resistance, obtained by using the steel plate.

Background Art

[0002] With the development of degradation resources containing hydrogen sulfide, mainly, line pipes for transportation and tanks for storage of oil, gas, etc., require so-called sour resistance, such as hydrogen-induced cracking resistance or stress-corrosion cracking resistance. Hereinafter, a steel plate that exhibits the adequate sour resistance is sometimes referred to as a "sour-resistant steel plate". Hydrogen-induced cracking (hereinafter sometimes referred to as "HIC") is known as a crack caused by the penetration of hydrogen thereinto due to a corrosion reaction with the hydrogen sulfide or the like, and the collection and gasification of the hydrogen at non-metallic inclusions, such as MnS or Nb(C, N).

[0003] HIC is also known to have a tendency to occur in segregation zones, including a center segregation of a cast strip and internal cracks, particularly, at an inclusion, such as MnS, as a starting point. For this reason, some techniques for enhancing HIC resistance have been hitherto proposed. For example, Patent Document 1 discloses that a steel material has improved HIC resistance by suppressing segregation degrees of Mn, Nb, and Ti at the center in the thickness direction of a steel plate. Patent Document 2 discloses a method for suppressing HIC that would occur in MnS or a Ca-based acid sulfide as a starting point, by using a parameter formula that includes the contents-of Ca, O, and S.

[0004] These methods suppress the occurrence of a large amount of HIC, but in some cases, fine HIC can occur locally at a number of sites.

[0005] Meanwhile, a steel plate is subjected to melting, casting, and hot-rolling, and then it undergoes an HIC test before being dispatched as a product. However, it takes several weeks to obtain the result of the HIC test. Once the HIC occurs during the HIC test, the above-mentioned steel plate cannot be dispatched as a product with excellent hydrogen-induced cracking resistance. Because of this, the steel plate needs to be manufactured again, that is, melted again to produce a product, and then the product needs to undergo the HIC test again. This increases the manufacturing time period and might possibly result in missing the deadline or the like.

[0006] For this reason, it is considered that if the HIC resistance can be evaluated at the stage of a cast strip after the casting without performing the HIC test after hot rolling, the manufacturing time period can be significantly shortened. As mentioned above, HIC occurs at segregation zones (center segregation, internal cracks) or inclusions, such as MnS, as a starting point. Thus, if these can be evaluated at the stage of the cast strip, the evaluation of the HIC resistance is considered to be possible based on the evaluation results.

[0007] For example, in a conventional method that involves executing an HIC test after rolling, a long procedure A-1 from casting to dispatching is carried out in the following way. In contrast, when the HIC resistance can be evaluated at the stage of the cast strip, the steps of "Sample Preparation (for HIC test) → HIC Test" in performing the HIC test can be omitted as illustrated in a procedure B-1, so that products can be dispatched at an early stage.

Procedure A-1 : Casting → Rolling → Sample Preparation (for HIC test) → HIC Test → Dispatching
Procedure B-1 : Casting → Evaluation of HIC Resistance → Rolling → Dispatching

[0008] If the result of the HIC test is no good (NG), the conventional method will perform the following procedure A-2, where it takes a long time to perform steps from the casting to re-melting. In contrast, as long as the HIC resistance can be evaluated at the stage of the cast strip as illustrated in the following procedure B-2, even if the evaluation result is NG, the steps of "Rolling → Sample Preparation (for the HIC Test) → HIC Test" in the procedure A-2 below can be omitted, which enables a quick start of re-melting.

Procedure A-2 : Casting → Rolling → Sample Preparation (for HIC test) → HIC Test → Re-Melting
Procedure B-2: Casting → Evaluation of HIC Resistance → Re-Melting

[0009] As such a method, Patent Document 3 discloses a method in which internal cracks are evaluated at the stage of the cast strip. In this method, the possibility of a hot charge rolling (HCR) operation is determined based on the assessment result on internal cracks.

[0010] Patent Documents 4 to 8 disclose a method for evaluating the quality of a cast strip before rolling, which is not performed to evaluate CaO inclusions. For example, the techniques mentioned in Patent Documents 4 to 7 evaluate the quality of a cast strip, which is based on the content of inclusions or the content of elements in the cast strip or a molten steel in a tundish or-the like. In the technique mentioned in Patent Document 8, the quality of the cast strip is evaluated (primary determination) from an analytical result of the molten steel in the tundish. If the determination accuracy does not meet the desired accuracy, the quality of the cast strip is evaluated from an analytical result of a cast-strip sample (secondary determination).

Prior Art Document

Patent Document

[0011]

Patent Document 1: JP 2010-209461 A
Patent Document 2: JP H6-136440 A
Patent Document 3: JP 2006-198649 A
Patent Document 4: JP S62-277539 A
Patent Document 5: JP 2002-214222 A
Patent Document 6: JP H10-122854 A
Patent Document 7: JP H10-249505 A
Patent Document 8: JP 2000-292418 A

Disclosure of the Invention

Problems to be solved by the Invention

[0012] Although the techniques mentioned in Patent Documents 3 to 8 are not intended to evaluate CaO inclusions as mentioned above, an evaluation method for CaO inclusions is considered to include evaluation of the content of inclusions or elements and the like in the cast strip or the molten steel in the tundish, like Patent Documents 3 to 8.

[0013] To evaluate the CaO inclusions at the stage of the cast strip, it is necessary to analyze the CaO content or the Ca concentration in a position where a CaO accumulation zone is generated. However, there are variations of the position where the CaO accumulation zone is generated, in the dimensions of a cast strip in the width direction, thickness direction, and casting direction, which makes it difficult to predict the position. Furthermore, even the analysis of a predetermined part of the cast strip does not necessarily lead to the analysis result that shows the CaO content in the CaO accumulation zone. Thus, the analysis result of the steel strip cannot be used to evaluate the CaO inclusions.

[0014] It is also considered that the CaO inclusions are evaluated from the amount of inclusions or elements in the molten steel in the tundish. However, CaO inclusions are aggregated and accumulated after being charged into a mold. Thus, even though no CaO accumulation zone is evaluated to be present based on the CaO content or Ca concentration in the molten steel in the tundish, CaO inclusions can be aggregated thereafter, causing the HIC.

[0015] The present invention has been made in view of the foregoing circumstance, and it is an object of the present invention to achieve a steel plate and a steel pipe that have excellent hydrogen-induced cracking resistance, and further to achieve a steel plate and a steel pipe with HIC resistance that can be evaluated by the quality of an internal structure of a cast strip without executing an HIC test.

Means for Solving the Problems

[0016] A steel plate having excellent hydrogen-induced cracking resistance according to the present invention that can solve the above-mentioned problem includes, in percent by mass:

0.02 to 0.15% of C;
0.02 to 0.50% of Si;
0.6 to 2.0% of Mn;
more than 0% and 0.030% or less of P;
more than 0% and 0.003% or less of S;
0.010 to 0.08% of Al;
0.0003 to 0.0060% of Ca;
0.001 to 0.01% of N;
more than 0% and 0.0045% or less of O; and
one or more elements selected from more than 0% and 0.02% or less of REM and more than 0% and 0.010% or

less of Zr, with the balance being iron and inevitable impurities, wherein
a ratio (Ca/S) of the Ca to the S is 2.0 or more,
the Ca, the S, and the O satisfy the formula below: $(Ca - 1.255)/O \leq 1.80$, and
a decrease in an amount of Ca obtained by subtracting a Ca concentration in a slab from a Ca concentration in a molten steel in a tundish is a threshold value $Ca_{drop\theta}$ or less, the threshold value $Ca_{drop\theta}$ being a maximum decrease in an amount of Ca that avoids occurrence of hydrogen-induced cracking in the steel plate obtained by rolling the slab.

[0017] The threshold value $Ca_{drop\theta}$ may be a value previously determined by a method including following (i) to (iii):

(i) the Ca concentration in the molten steel in the tundish and the Ca concentration in the slab are measured, and the decrease in the amount of Ca is calculated by subtracting the Ca concentration in the slab from the Ca concentration in the molten steel in the tundish;
(ii) a hydrogen-induced cracking test is performed on a steel plate that is obtained by rolling a slab, which has been casted on the same casting conditions as the above-mentioned slab; and
(iii) a maximum decrease in an amount of Ca that avoids the occurrence of hydrogen-induced cracking is determined from the decrease in the amount of Ca measured by the step (i) and a result of the hydrogen-induced cracking test shown in the step (ii).

[0018] The slab casted on the same casting conditions as the above-mentioned slab may be the slab in which the decrease in the amount of Ca is measured.
[0019] The Ca concentration in the slab may be a minimum one of two or more Ca concentrations obtained by examining the Ca concentration at two or more different sites in the thickness direction of the slab.
[0020] The threshold value $Ca_{drop\theta}$ may be 4 ppm (ppm by mass).
[0021] The steel plate may further include one or more of the elements (A) and (B) below, as another element:

(A) in percent by mass, one or more elements selected from the group consisting of more than 0% to 0.005% or less of B, more than 0% and 0.1% or less of V, more than 0% and 1.5% or less of Cu, more than 0% and 1.5% or less of Ni, more than 0% to 1.5% or less of Cr, more than 0% and 1.5% or less of Mo, and more than 0% and 0.06% or less of Nb; and
(B) in percent by mass, one or more elements selected from the group consisting of more than 0% and 0.03% or less of Ti and more than 0% and 0.01% or less of Mg.

[0022] The steel plate is suitable use in line pipes and pressure containers. The invention also includes a steel pipe for a line pipe formed of the steel plate.

Effects of the Invention

[0023] The invention can provide the steel plate and steel pipe that surely have the excellent hydrogen-induced cracking resistance. Further, the present invention can provide the steel plate and steel pipe in-which the HIC resistance can be evaluated by the quality of the internal structure of the cast strip without executing an HIC test. These steel plates are suitable for use in line pipes for transportation of natural gas and crude oil, pressure containers, such as the storage tank, and the like.

Brief Description of the Drawings

[0024]

Fig. 1 is a schematic diagram for explaining the flow of CaO inclusions.
Fig. 2 is a diagram showing Ca concentration distribution in various slabs.
Fig. 3 (a) is a cross-sectional view of a slab, and Fig. 3 (b) is a cross-sectional view of a product.
Fig. 4 is a cross-sectional view of a slab.
Fig. 5 is a diagram for explaining an examined surface of the slab.
Fig. 6 shows the result of determination of a threshold value in an example according to a first embodiment, specifically, showing the relationship among a Ca concentration Ca_{TD1} in a molten steel in a tundish, a Ca concentration Ca_{s1} in a slab, and HIC test results thereof.
Fig. 7 shows the result of determination of a threshold value in an example according to a second embodiment, specifically, showing the relationship among a Ca concentration Ca_{TD1} of the molten steel in the tundish, a minimum value Ca_{min1} of the Ca concentration in the slab, and HIC test results thereof.

Mode for Carrying Out the Invention

[0025] The inventors have intensively studied to solve the foregoing problems. First, the inventors have focused on the tendency for HIC to occur at a MnS inclusion as a starting point. As a result, it is conceived that by causing a steel to contain a rare earth element or Zr, which has a desulfurization effect, the formation of MnS can be suppressed, and the hydrogen-induced cracking resistance can be improved. Furthermore, an appropriate content in such an element is found to efficiently exhibit the desulfurization effect as mentioned later.

[0026] Next, the inventors have focused on the tendency for HIC to occur at a CaO accumulation zone generated during producing a cast strip. Consequently, attention is paid to the "decrease in the amount of Ca obtained by subtracting the Ca concentration in the slab from the Ca concentration in the molten steel in the tundish" that can evaluate the presence or absence of the CaO accumulation zone. It is found that if the decrease in the amount of Ca at the stage of the slab is restricted to a predetermined threshold value or less, a steel plate with higher hydrogen-induced cracking resistance can be obtained, so that products can be dispatched at an early stage. This matter will be described below.

[0027] The component composition of a steel will be described below. Note that "%" for each component is "% by mass" and "ppm" is "ppm by mass".

[0028] To ensure the excellent HIC resistance, the component composition of the steel needs to be controlled. Furthermore, to ensure the high strength, excellent weldability, and the like, which are other properties required as, for example, the steel for line pipes, the component composition of the steel plate needs to be as follows. The reasons for specifying the contents of the respective components, including the aforesaid rare earth elements and Zr, will be described below.

[Component Composition]

[C: 0.02 to 0.15%]

[0029] Carbon (C) is an element essential to ensure the strength of a base metal and a weld bead. Thus, the C content needs to be 0.02% or more. The C content is preferably 0.03% or more, and more preferably 0.05% or more. On the other hand, an extremely high C content degrades the heat-affected zone (HAZ) toughness and the weldability of the steel plate. Any excessive C content is more likely to form NbC or island-shaped martensite, which possibly becomes as the starting point of HIC or a fracture propagation route. Thus, the C content needs to be 0.15% or less. The C content is preferably 0.12% or less, and more preferably 0.10% or less.

[Si: 0.02 to 0.50%]

[0030] Silicon (Si) has a deoxidation function and is effective in improving the strength of a base metal and a weld bead. To exhibit these effects, the Si content is set at 0.02% or more. The Si content is preferably 0.05% or more, and more preferably 0.15% or more. However, an extremely high Si content degrades the weldability and toughness of the steel. Any excessive Si content forms island-shaped martensite to generate and propagate HIC. Accordingly, the Si content needs to be suppressed to 0.50% or less. The Si content is preferably 0.45% or less, and more preferably 0.35% or less.

[Mn: 0.6 to 2.0%]

[0031] Manganese (Mn) is an element that is effective in improving the strength of a base metal and a weld bead. In the present invention, the Mn content is set at 0.6% or more. The Mn content is preferably 0.8% or more, and more preferably 1.0% or more. However, an extremely high Mn content forms MnS, degrading not only the hydrogen-induced cracking resistance, but also the HAZ toughness and weldability. Thus, the upper limit of Mn content is set at 2.0%. The Mn content is preferably 1.8% or less, more preferably 1.5% or less, and still more preferably 1.2% or less.

[P: more than 0% and 0.030% or less]

[0032] Phosphorus (P) is an element inevitably contained in steel. When the P content exceeds 0.030%, the roughness of a base metal and a HAZ are significantly degraded, and the hydrogen-induced cracking resistance of the steel is also degraded. Thus, in the present invention, the P content is restricted to 0.030% or less. The P content is preferably 0.020% or less, and more preferably 0.010% or less.

[S: more than 0% and 0.003% or less]

[0033] Sulfur (S) is an element that forms a large amount of MnS to significantly degrade the hydrogen-induced cracking resistance.when contained in a large amount. Thus, in the present invention, the upper limit of S content is 0.003%. The S content is preferably 0.002% or less, more preferably 0.0015% or less, and still more preferably 0.0010% or less. Thus, the S content is desirable low from the viewpoint of improving the hydrogen-induced cracking resistance.

[Al: 0.010 to 0.08%]

[0034] Aluminum (Al) is a strong deoxidizing element. When the Al content is low, the Ca concentration in the oxide tends to increase, that is, the Ca-based inclusions are more likely to be formed at a superficial layer of a steel plate, causing fine HIC. Thus, in the present invention, the Al content needs to be 0.010% or more. The Al content is preferably 0.020% or more, and more preferably 0.030% or more. On the other hand, when the Al content is extremely high, an Al oxide is formed in a cluster shape and becomes a starting point of hydrogen-induced cracking. Thus, the Al content needs to be 0.08% or less. The Al content is preferably 0.06% or less, and more preferably 0.05% or less.

[Ca: 0.0003 to 0.0060%]

[0035] Calcium (Ca) serves to control the form of a sulfide and has an effect of suppressing the formation of MnS by forming CaS. To obtain this effect, the Ca content needs to be 0.0003% or more. The Ca content is preferably 0.0005% or more, and more preferably 0.0010% or more. On the other hand, when the Ca content exceeds 0.0060%, HIC occurs at many sites from the Ca-based inclusions as the starting point. Thus, in the present invention, the upper limit of Ca content is set at 0.0060%. The Ca content is preferably 0.005% or less, more preferably 0.0035% or less, and still more preferably 0.0025% or less.

[N: 0.001 to 0.01%]

[0036] Nitrogen (N) precipitates as TiN in a steel microstructure, preventing austenite grains in a HAZ zone from being coarsened and further promoting ferrite transformation to thereby improve the toughness of the HAZ zone. To obtain these effects, the N content needs to bye 0.001% or more. The N content is preferably 0.003% or more, and more preferably 0.0040% or more. An extremely high N content, however, degrades the toughness of the HAZ by the presence of the solid-solute N. The N content needs to be 0.01% or less. The N content is preferably 0.008% or less, and more preferably 0.0060% or less.

[O: more than 0% and 0.0045% or less]

[0037] An oxygen (O) content is desirably low from the viewpoint of improving the cleanliness of a steel. An extremely high O content degrades the toughness of the steel, and additionally causes HIC at an oxide as a starting point, thereby degrading the hydrogen-induced cracking resistance. In this regard, the O content needs to be 0.0045% or less, preferably 0.0030% or less, and more preferably 0.0020% or less.

[Ca/S (mass ratio): 2.0 or more]

[0038] As mentioned above, S forms MnS as a sulfide-based inclusion, and HIC might occur at the MnS as a starting point. Thus, the sulfide-based inclusion in the steel has its form controlled as CaS by adding Ca, thereby rendering S harmless for the HIC resistance. To sufficiently exhibit these effects, the Ca/S needs to be set at 2.0 or more. The Ca/S is preferably 2.5 or more, and more preferably 3.0 or more. Note that the upper limit of Ca/S is approximately 17 based on the Ca content and S content specified by the present invention.

[$(Ca - 1.25S)/O \leq 1.80$]

[0039] To avoid the occurrence of HIC due to a Ca-based oxysulfide, it is effective to suppress, especially, CaO that is the most likely to form aggregates among Ca-based inclusions. For this reason, a Ca content (Ca-1.25S) that is obtained by subtracting a content in Ca present as a sulfide (CaS) in the steel from the total Ca content in the steel must not be excessive relative to the O content. When the Ca content (Ca-1.25S) is excessive relative to the O content, CaO is more likely to be formed as an oxide-based inclusion, which makes it easier for aggregates of the CaO (coarse Ca-based inclusions) to be formed in a larger amount at a superficial layer of a steel plate. Since these coarse Ca-based inclusions each serves as the starting point of HIC, the (Ca - 1.25S)/O needs to be 1.80 or less in order to obtain the excellent HIC resistance. (Ca - 1.25S)/O is preferably 1.40 or less, more preferably 1.30 or less, still more preferably 1.20 or less, and particularly preferably 1.00 or less. Like CaO, to suppress Al_2O_3 that tends to form aggregates, the lower limit of (Ca - 1.25S)/O is approximately 0.1.

[REM: more than 0% and 0.02% or less]

[0040] A rare earth metal (REM) is an element that is effective in enhancing the hydrogen-induced cracking resistance by suppressing the formation of MnS through the desulfurization effect as mentioned above. To exhibit such effects, the REM content is preferably 0.0002% or more. The REM content is more preferably 0.0005% or more, and still more preferably 0.0010% or more. On the other hand, if REM is contained in a large amount, the effect is saturated. Thus, the upper limit of the REM content needs to be 0.02%. From the viewpoint of preventing the clogging of an immersion nozzle during casting to enhance the productivity, the REM content is preferably 0.015% or less, more preferably 0.010% or less, and even more preferably 0.0050% or less. Note that in the present invention, REM means lanthanoid elements (15 elements from La to Lu), scandium (Sc), and yttrium (Y).

[Zr: more than 0% and 0.010% or less]

[0041] Zirconium (Zr) serves to form an oxide and disperse it finely in steel, while improving the HIC resistance by the desulfurization effect, thereby contributing to improving the HAZ toughness. To exhibit these effects, the Zr content is preferably set at 0.0003% or more, more preferably 0.0005% or more, still more preferably 0.0010% or more, and still more preferably 0.0015% or more. On the other hand, any excessive Zr content forms coarse inclusions to degrade the hydrogen-induced cracking resistance and the toughness of the base metal. Thus, the Zr content needs to be 0.010% or less. The Zr content is preferably 0.0070% or less, more preferably 0.0050% or less, and still more preferably 0.0030% or less.

[0042] The components of the steel (steel plate, steel pipe) in the present invention have been mentioned above, with the balance being iron and inevitable impurities. In addition to the elements mentioned above, the steel further includes:

(a) one or more elements selected from the group consisting of B, V, Cu, Ni, Cr, Mo, and Nb in the following contents, thereby making it possible to enhance the strength and toughness; and/or
(b) one or more elements selected from the group consisting of Ti and Mg in the following contents, thereby making it possible to improve the HAZ toughness and to promote the desulfurization, thus further improving the HIC resistance. These elements will be described in detail below.

[B: more than 0% and 0.005% or less]

[0043] Boron (B) enhances the hardenability of a steel and the strength of a base metal and a weld bead. Furthermore, B is bonded to N to precipitate BN while the heated HAZ zone is cooled in welding, thus promoting ferrite transformation from the inside of an austenite grain. In this way, B improves the HAZ toughness. To obtain these effects, the B content is preferably 0.0002% or more. The B content is more preferably 0.0005% or more, and still more preferably 0.0010% or more. However, any excessive B content degrades the toughness of a base metal and a HAZ zone, thus leading to degradation in the weldability. Thus, the B content is preferably 0.005% or less. The B content is more preferably 0.004% or less, and still more preferably 0.0030% or less.

[V: more than 0% and 0.1% or less]

[0044] Vanadium (V) is an element effective in improving the strength of steel. To obtain this effect, the V content is preferably 0.003% or more, and more preferably 0.010% or more. On the other hand, when the V content exceeds 0.1%, the weldability and the toughness of a base metal would be degraded. Thus, the V content is preferably 0.1% or less, and more preferably 0.08% or less.

[Cu: more than 0% and 1.5% or less]

[0045] Copper (Cu) is an element effective in improving the hardenability of steel. To obtain this effect, the Cu content is preferably 0.01% or more. The Cu content is more preferably 0.05% or more, and still more preferably 0.10% or more. However, when the Cu content exceeds 1.5%, the toughness of steel is degraded. Thus, the Cu content is preferably 1.5% or less. The Cu content is more preferably 1.0% or less, and still more preferably 0.50% or less.

[Ni: more than 0% and 1.5% or less]

[0046] Nickel (Ni) is an element effective in improving the strength and toughness of a base metal and a weld bead. To obtain these effects, the Ni content needs to be 0.01% or more. The Ni content is more preferably 0.05% or more, and still more preferably 0.10% or more. However, an extremely high Ni content leads to an excessively expensive steel for a structure. From the economical aspect, the Ni content is preferably 1.5% or less. The Ni content is more preferably 1.0% or less, and still more preferably 0.50% or less.

[Cr: more than 0% and 1.5% or less]

[0047] Chromium (Cr) is an element effective in improving the strength of steel. To obtain such an effect, the Cr content is preferably 0.01% or more. The Cr content is more preferably 0.05% or more, and further preferably 0.10% or more. On the other hand, when the Cr content exceeds 1.5%, the HAZ toughness of the steel is degraded. Thus, the Cr content is preferably 1.5% or less. The Cr content is more preferably 1.0% or less, and still more preferably 0.50% or less.

[Mo: more than 0% and 1.5% or less]

[0048] Molybdenum (Mo) is an element effective in improving the strength and toughness of a base metal. To exhibit this effect, the Mo content is preferably 0.01% or more. The Mo content is more preferably 0.05% or more, and still more preferably 0.10% or more. However, when the Mo content exceeds 1.5%, the HAZ toughness and weldability of the steel are degraded. Thus, the Mo content is preferably 1.5% or less, more preferably 1.0% or less, and still more preferably 0.50% or less.

[Nb: more than 0% and 0.06% or less]

[0049] Niobium (Nb) is an element effective in enhancing the strength of steel and the toughness of a base metal without degrading its weldability. To obtain this effect, the Nb content is preferably 0.002% or more. The Nb content is more preferably 0.010% or more, and still more preferably 0.020% or more. However, when the Nb content exceeds 0.06%, the toughness of the base metal and HAZ is degraded. Thus, in the present invention, the upper limit of Nb content is preferably set at 0.06%. The Nb content is more preferably 0.050% or less, still more preferably 0.040% or less, and still more preferably 0.030% or less.

[Ti: more than 0% and 0.03% or less]

[0050] Titanium (Ti) precipitates as TiN in steel, thereby preventing austenite grains in a HAZ zone from being coarsened during welding and thereby promoting the ferrite transformation. Thus, Ti is an element that is effective in improving the toughness of the HAZ zone. Furthermore, Ti exhibits the desulfurization effect, and thus is an element that is effective in improving the HIC resistance. To obtain these effects, the Ti content is preferably 0.003% or more. The Ti content is more preferably 0.005% or more, and still more preferably 0.010% or more. On the other hand, any excessive Ti content leads to an increase in the amount of solid-solute Ti and precipitated TiC, thus degrading the toughnesses of a base metal and a HAZ zone. Thus, the Ti content is preferably 0.03% or less, and more preferably 0.02% -or less.

[Mg: more than 0% and 0.01% or less]

[0051] Magnesium (Mg) is an element that is effective in improving the toughness of steel through refinement of crystal grains, and also effective in improving the HIC resistance because of its desulfurization effect. To obtain these effects, the Mg content is preferably 0.0003% or more. The Mg content is more preferably 0.001% or more. On the other hand, an excessive Mg content saturates its effect. Thus, the upper limit of the Mg content is preferably 0.01%. The Mg content is more preferably 0.005% or less.

[0052] The steel plate of the present invention is a steel plate with high hydrogen-induced cracking resistance in which a decrease in an amount of Ca obtained by subtracting a Ca concentration in a slab from a Ca concentration in a molten steel in a tundish is a threshold value $Ca_{drop\theta}$ or less. Here, the threshold value $Ca_{drop\theta}$ means the maximum decrease in the amount of Ca previously determined and which does not cause hydrogen-induced cracking in a steel plate obtained by rolling the slab.

[Decrease in Amount of Ca]

[0053] The decrease in the amount of Ca obtained by subtracting the Ca concentration in the slab from the Ca concentration in the molten steel in the tundish is set to be the predetermined threshold value or less as mentioned above, thereby making it possible to produce the steel plate having the high hydrogen-induced cracking resistance and to dispatch products at an early stage as will be mentioned later. The reason for setting the above-mentioned decrease in the amount of Ca as an evaluation index will be described below.

[0054] The inventors have focused on MnS inclusions and progressed their studies regarding addition of Ca to a molten steel during a secondary refinement to suppress the formation of MnS.

[0055] When an added amount of Ca to the molten steel is appropriate, $CaO\text{-}Al_2O_3$ inclusions are formed in the molten steel. The $CaO\text{-}Al_2O_3$ has good wettability to the molten steel, and thus is not aggregated in the molten steel and remains fine without adversely affecting the HIC resistance.

[0056] However, when an added amount of Ca to the molten steel is not appropriate, for example, when adding Ca in an excessive amount that exceeds a predetermined amount required to suppress MnS formation and modify Al_2O_3, pure CaO inclusions are also formed in the steel, in addition to $CaO\text{-}Al_2O_3$ inclusions. The pure CaO inclusion has inferior wettability to the molten steel and thereby is more likely to be aggregated in the molten steel. CaO as the aggregate becomes a coarse inclusion, causing HIC.

[0057] The coarsen CaO inclusion has a smaller density than the molten steel, and most of CaO inclusions are allowed to float and then separated. However, as shown in Fig. 1, parts of CaO inclusions receive a buoyant force while falling down deeply into a cast strip along the flow of the molten steel within a mold, and then trapped in a solidification shell to form a CaO accumulation zone. The CaO accumulation zone serves as the starting point of HIC.

[0058] Thus, if an appropriate added amount of Ca to the molten steel can be determined in advance, the occurrence of HIC due to the CaO inclusions can be suppressed. To this end, it is necessary to precisely identify the content of inclusions in the molten steel before addition of Ca, the composition of the inclusions, and the sulfur concentration in the molten steel. However, in practice, it is almost impossible to identify these factors in advance, and thus the added amount of Ca is set at an amount enough to suppress the formation of MnS. Consequently, the added amount of Ca tends to become excessive, and thereby a CaO accumulation zone is more likely to be formed.

[0059] If the CaO accumulation zones constantly occur at the same site, an accumulation degree of CaO inclusions can be identified by analyzing the Ca concentration at that site. Furthermore, whether or not the CaO accumulation zone occurs in a cast strip can also be presumed.

[0060] However, as mentioned above, the positions where the CaO accumulation zones occur differ in the thickness direction of a cast strip, depending on casting conditions (casting speed, angle of a discharge port of an immersion nozzle, and the like). For example, as shown in Fig. 2, three slabs (A to C) with different casting conditions (casting speed and angle of the discharge port of the immersion nozzle) differ from one another in the position (e.g., positions a to c) at the high Ca concentration where the accumulation zone occurs. In this way, the position of the CaO accumulation zone cannot be predicted. Thus, it is difficult to evaluate whether the CaO accumulation zone occurs or not based on the accumulation degree (Ca concentration).

[0061] Then, the inventors have changed their viewpoints about examination positions for the Ca concentration and focused on the position with a low Ca concentration. When a CaO accumulation zone occurs, the Ca concentration at the CaO accumulation zone becomes high, while in a position where no CaO accumulation zone occurs, the CaO concentration becomes relatively low. Taking this into account, the inventors have examined the relationship between the "Ca concentration in any position in the thickness direction of a slab" and the "Ca concentration in a molten steel in a tundish" when CaO accumulation zones occur. As a result, in the position where no CaO accumulation zone occurs, the "Ca concentration in the slab" is relatively low, and thereby a "value obtained by subtracting the 'Ca concentration in the slab' from the 'Ca concentration in the molten steel in the tundish' ", that is, "a decrease in an amount of the Ca concentration from the tundish to the slab" is found to become large.

[0062] As such, when the "decrease in the amount of the Ca concentration from the tundish to the slab" is large, it can be considered that the accumulation zone does not occur in the position, but it occurs in another position. Therefore, HIC can be evaluated to occur. On the other hand, when the "decrease in the amount of the Ca concentration from the tundish to the slab" is small, it can be considered that there is almost no difference between the Ca concentration in the tundish and the Ca concentration in the slab, that is, there is no position with the high Ca concentration in the slab. In this case, since a CaO accumulation zone is considered not to occur in the slab, HIC can be evaluated not to occur.

[0063] As such, the present invention uses a value obtained by subtracting the "Ca concentration in the slab" from the "Ca concentration in the molten steel in the tundish (hereinafter referred to as the "decrease in the amount of Ca"), which relates to the presence or absence of the CaO accumulation zone, to thereby evaluate the HIC resistance.

[Determination of Threshold Value of Decrease in Amount of Ca]

[0064] Now, a description will be given on the way to determine a threshold value $Ca_{drop\theta}$ of the decrease in the amount of Ca, i.e., the maximum decrease in the amount of Ca that does not cause HIC in a steel plate obtained by rolling a slab in order to determine whether the obtained steel plate has excellent HIC resistance or not.

[0065] The threshold value $Ca_{drop\theta}$ is determined in advance, but a method for determination thereof is not particularly limited to the following method. An example of the method for determining the threshold value $Ca_{drop\theta}$ in advance will include the following processes (i) to (iii).

(i) The Ca concentration in the molten steel in the tundish and the Ca concentration in the slab are measured. A decrease in an amount of Ca is calculated by subtracting the Ca concentration in the slab from the Ca concentration in the molten steel in the tundish.
(ii) A hydrogen-induced cracking test is performed on a steel plate that is obtained by rolling a slab, which has been casted on the substantially same casting conditions as the above-mentioned slab.
(iii) The maximum decrease in the amount of Ca that avoids the occurrence of hydrogen-induced cracking is determined from the decrease in the amount of Ca measured by the step (i) and a result of the hydrogen-induced cracking test shown in the step (ii).

[0066] Specifically, a method for determining the above-mentioned threshold value $Ca_{drop\theta}$ will be described in detail below by taking first and second embodiments as examples.

[First Embodiment]

(Examination of Ca Concentration in Molten Steel in Tundish)

[0067] Molten steel is taken out of the tundish, and its Ca concentration (Ca_{TD1}) is analyzed. The molten steel in the tundish is constantly supplied from a ladle, so that the Ca concentration (Ca_{TD1}) remains constant even after taking out the molten steel.

(Examination of Ca concentration in Slab)

[0068] Next, a Ca concentration (Ca_{s1}) in a slab is examined. As shown in Fig. 3(a), a sample is taken out of a region R4 (hereinafter referred to as a "reference-side region R4") ranging from the reference-side surface of the slab to D/2 in the thickness direction thereof, and a Ca concentration Ca_{s1} in the region R4 is analyzed. The "reference-side region R4", as shown in Fig. 3(a), is in a range from D/2 to D in the thickness direction of the slab oriented from an opposite-reference-side surface thereof.

[0069] As mentioned above, the density of CaO inclusions is smaller than that of the molten steel, so that the CaO inclusions in the molten steel floats while receiving buoyant force due to a difference in the density between the CaO inclusions and molten steel. In a continuous casting machine provided with a curved portion and a horizontal portion, as illustrated in Fig. 1, after CaO inclusions float, they will be trapped in a solidification shell on the opposite-reference-side, whereby a CaO accumulation zone occurs on the opposite-reference side of the slab, but does not occur on the reference side thereof.

[0070] For this reason, in the present invention, as shown in Fig. 3 (a), the Ca concentration Ca_{s1} is examined within the "range from the reference-side surface to D/2 in the thickness direction (reference-side region R4) " where no CaO accumulation zone occurs, that is, a range of -0.50D from the center in the slab thickness D toward the reference-side surface in examples to be mentioned later. Based on the Ca concentration Ca_{s1} in the reference-side region R4, the "decrease in the amount of Ca" in the position where no CaO accumulation zone occurs can be calculated to precisely evaluate the presence or absence of the CaO accumulation zone.

[0071] Here, a "decrease Ca_{drop1} in Ca" is calculated by subtracting the "Ca concentration Ca_{s1} in the slab" from the "Ca concentration Ca_{TD1} in the tundish". Ca_{drop1} is represented by the following formula.

$$Ca_{drop1} = Ca_{TD1} - Ca_{S1}$$

(Rolling)

[0072] A slab obtained through casting on the same casting conditions as the slab in which the Ca concentration Ca_{s1} is measured as mentioned above is hot-rolled to produce a steel plate for measurement of a threshold value. For example, the rolling is performed on the following conditions. Specifically, after heating the slab to a temperature of 1050 to 1250°C, the hot-rolling is performed on the slab through two or more passes. In each pass, a surface temperature of the steel plate becomes 900°C or-higher, a cumulative rolling reduction is 40% or more at an average steel plate temperature of 1,000°C or higher, which is determined by calculation to be mentioned below, and a rolling reduction per pass is 10%

or more. Subsequently, another hot-rolling is performed such that a cumulative rolling reduction at 700°C or higher and lower than 900°C is 20% or more, and that a rolling-end temperature is 700°C or higher and lower than 900°C. Then, water-cooling on the steel plate is started from a temperature of 650°C or higher and stopped at a temperature of 350 to 600°C. Subsequently, the steel plate is air-cooled to the room temperature. The average steel plate temperature is determined in the following way. Specifically, based on data including a rolling pass schedule during rolling and a cooling method (water-cooling or air-cooling) between the passes, the temperature at any position of the steel plate in the thickness direction is determined by using an appropriate calculation method, such as a finite difference method. Then, the average steel plate temperature is defined as the average of the determined temperatures of the slab in a range from the front to back surface thereof.

(HIC Test)

[0073] An HIC test is performed on the steel plate to check the presence or absence of HIC occurrence. An example of the HIC test is a method specified by the National Association of Corrosion and Engineer (NACE) standard TM0284-2003, as mentioned in examples below.

[0074] As shown in Fig. 3(b), a region to be subjected to the HIC test is a region R41 excluding the vicinity of the center in the thickness direction of the product region R40 and corresponding to the opposite-reference-side region. This is because, as shown in Fig. 1, the coarsened CaO accumulation zones are more likely to be formed on the opposite-reference-side of the slab, and thereby HIC due to the CaO tends to occur in the region corresponding to the opposite-reference-side region. Note that HIC due to the segregation tends to occur at the center in the thickness direction, so that the HIC due to the CaO cannot be evaluated at the center. For this reason, the occurrence of HIC is examined in the region 41 except for the vicinity of the center in the thickness direction.

(Determination of Threshold Value)

[0075] Subsequently, a threshold value $Ca_{drop\theta}$ for the decrease in the amount of Ca that does not cause HIC is determined based on the "decrease Ca_{drop1} in Ca" and "the result of the HIC test". By comparing a plurality of decreases Ca_{drop1} in Ca with the results of the HIC tests, the "threshold value $Ca_{drop\theta}$" is defined as the maximum decrease in the amount of Ca that never causes the HIC at all. In particular, the measurement and test results of a plurality of slabs are used to obtain the threshold value with higher accuracy, which can suppress the misjudgment of the presence or absence of HIC occurrence.

<Second Embodiment>

[0076] A second embodiment that differs from the first embodiment in the calculation method for a decrease in an amount of Ca will be described below with reference to Fig. 4. The same components as those in the above-mentioned first embodiment will be briefly described. Also in Fig. 4, the same components as those in the above-mentioned first embodiment are denoted by the same reference characters, and the description thereof will be omitted as appropriate.

(Examination of Ca Concentration in Molten Steel in Tundish)

[0077] A Ca concentration (Ca_{TD1}) in a molten steel in the tundish is examined.

(Examination of Ca concentration in Slab)

[0078] Next, as shown in Fig. 4, samples are taken out of two or more sites in the thickness: direction of each of slabs obtained through casting in the same charge, and a Ca concentration of each sample is analyzed. The minimum Ca concentration (Ca_{min1}) is selected from the two or more Ca concentrations obtained (Ca_{s1}, Ca_{s2}, ...).

[0079] Then, a value obtained by subtracting the "minimum Ca concentration Ca_{min1} in the slab" from the "Ca concentration Ca_{TD1} in the tundish" is used to calculate the "decrease Ca_{drop11} in Ca". Ca_{drop11} is represented by the following formula.

$$Ca_{drop11} = Ca_{TD1} - Ca_{min1}$$

[0080] Suppose that an examination position of the Ca concentration is set at one site within the entire range in the thickness direction of the slab. If the examination position corresponds to an accumulation zone, an extremely high Ca concentration is detected. The decrease in the amount of Ca calculated from such a high Ca concentration is small, which leads to the determination that no CaO accumulation zone occurs with no HIC occurring. However, in practice, some accumulation zones are generated, which can cause HIC.

[0081] Thus, in this embodiment, the Ca concentration in the slab is examined at different two or more sites of the slab in its thickness direction. The CaO accumulation zone is present in a specific position in the thickness direction that depends on the casting conditions. By changing the examination position in the thickness direction, a position where the CaO accumulation zone does not occur can also be covered by the examination.

[0082] The two or more Ca concentrations (Ca_{s1}, Ca_{s1}, ...) include not only the Ca concentration in the accumulation zone, but also the Ca concentration where no accumulation zone occurs. However, the minimum Ca concentration (Ca_{min1}) is selected from these concentrations, so that the Ca concentration in the position where no accumulation zone occurs can be selected. Based on this concentration, the decrease in the amount of Ca in the position where no CaO accumulation zone occurs can be calculated to precisely evaluate the presence or absence of the CaO accumulation zone.

[0083] Here, the formation mechanism of the CaO accumulation zone is the same as that of each of a CaO inclusion and an Al_2O_3 inclusion. The thickness of the accumulation zone of Al_2O_3 inclusions is reported to be 10 mm (see reference: ISIJ International, Vol. 43 (2003), No. 10, p. 1548-1555). From this report, the thickness of the accumulation zone of the CaO inclusion can also be estimated to be 10 mm. As such, as shown in Fig. 4, when respective examination positions for the Ca concentration are spaced apart from each other by more than 10 mm in the thickness direction, even if one of the examination position is in the accumulation zone, the other examination positions are located where no accumulation zone occurs. For this reason, two or more examination positions are preferably spaced apart from each other by more than 10 mm in the thickness direction. Note that Fig. 4 shows two examination positions, a distance I between the two examination positions being more than 10 mm in the thickness direction (distance I in the thickness direction between two examination positions > 10 mm).

[0084] As shown in Fig. 1, CaO inclusions are trapped in a wide range located in the vicinity of the curved portion of a casting route. Thus, in regions R1 and R2, each ranging from a corresponding one of both ends in the width direction to D/2 of the slab shown in Fig. 4, the CaO accumulation zone occurs widely in the thickness direction. Thus, within the regions R1 and R2, there is a possibility of failing to examine a position where no accumulation zone occurs even if the examination position for the Ca concentration is changed in the thickness direction. For this reason, the Ca concentration examination position is preferably set at a region R3 with a width W-D that is cooled only from the wide surface side, i.e., that excludes the regions ranging from both ends to D/2 in the width direction.

(Rolling)

[0085] A slab obtained through casting on the same casting conditions as the slab in which the Ca concentration Ca_{s1} or the like is measured as mentioned above is hot-rolled to produce a steel plate for measurement of a threshold value.

(HIC Test)

[0086] The HIC test is performed on the steel plate to check the presence or absence of HIC occurrence in the "region R41 corresponding to the vicinity of the opposite-reference-side surface". An example of the HIC test is a method specified by the NACE standard TM0284-2003, as mentioned in examples below.

(Determination of Threshold Value)

[0087] Subsequently, a threshold value $Ca_{drop\theta}$ for the decrease in the amount of Ca that does not cause HIC is determined based on the "decrease Ca_{drop11} in Ca" and the "result of the HIC test". In this embodiment, the "threshold value $Ca_{drop\theta}$" is defined as the maximum decrease in the amount of Ca that never causes the HIC at all.

[Measurement of Decrease in Amount of Ca of Charge as Determination Target]

[0088] A Ca concentration Ca_{TD11} in a molten steel of the charge as a determination target in the tundish is examined. For example, like the second embodiment, the Ca concentration is examined at different two or more sites in the thickness direction of the slab casted in the same charge. Then, the minimum Ca concentration (Ca_{min11}) is selected from two or more Ca concentrations (Ca_{s11}, Ca_{s12}, ...). The two or more examination positions are preferably spaced apart from each other by more than 10 mm in the thickness direction.

[0089] Then, the "decrease Ca_{drop} in Ca" as the determination target is calculated by subtracting the "minimum Ca concentration Ca_{min11} in the slab" from the "Ca concentration Ca_{TD11} in the tundish". Ca_{drop} is represented by the following formula.

$$Ca_{drop} = Ca_{TD11} - Ca_{min11}$$

[Evaluation of Decrease in Amount of Ca of Charge as Determination Target]

[0090] The Ca_{drop} as the determination target is compared with the threshold value $Ca_{drop\theta}$. When the Ca_{drop} is the threshold value $Ca_{drop\theta}$ or less, the obtained steel plate is determined to have excellent HIC resistance. When the Ca_{drop} exceeds the threshold value $Ca_{drop\theta}$, the obtained steel plate is determined to be inferior in the HIC resistance.

[0091] The examination position (examined surface) of the slab is preferably a stationary part, but may be a non-stationary part. The term "non-stationary part" as used herein means a part casted when the casting condition is varied, for example, a part casted at an initial stage of casting, such as when the casting speed increases, or a part casted at the end of casting, such as when the casting speed decreases. When intended to examine the non-stationary part, as shown in Fig. 5, a part adjacent to the region subjected to the HIC test is preferably examined. Such a part exhibits substantially the same HIC resistance and can be evaluated more precisely.

[0092] The steel plate in the present invention is a steel plate in which the "decrease Ca_{drop} in Ca" is calculated by subtracting the Ca concentration in the slab from the Ca concentration in the tundish at a stage of the slab before rolling, and the "decrease Ca_{drop} in Ca" satisfies the following formula: $Ca_{drop} \leq$ threshold value $Ca_{drop\theta}$. It is considered that the steel plate in the present invention satisfies the relationship of the above-mentioned $Ca_{drop} \leq$ threshold value $Ca_{drop\theta}$, and that no CaO accumulation zone is generated in the slab, resulting in no occurrence of HIC.

[0093] Accordingly, in this embodiment, the "decrease in the amount of Ca concentration from the tundish to the slab" is used for evaluation of the HIC resistance. This can precisely evaluate the quality of the internal structure (accumulation degree of CaO inclusions) of the cast strip. Thus, based on the evaluation result, the HIC resistance can be evaluated at the stage of the cast strip. Consequently, the HIC test that would require several weeks can be omitted, thereby significantly shortening a time period from the manufacture to dispatching.

[0094] The present application claims priority to Japanese Patent Application No. 2014-266491 filed on December 26, 2014 and Japanese Patent Application No. 2015-202378 filed on October 13, 2015, the disclosure of both of which is incorporated herein by reference in its entirety.

Examples

[0095] The present invention will be more specifically described below by way of examples, but is not limited to the following Examples. Various modifications can be made to these Examples as long as they are adaptable to the above-mentioned and below-mentioned concepts and are included within the scope of the present invention.

(1) Casting

[0096] Tables 1-1 to 4 and Figs. 6 and 7 show the experimental conditions and results for determining the threshold value. Slabs, each having a thickness D of 280 mm and a width W of 2100 mm, were obtained by continuous casting. The casting conditions in the first embodiment are shown in Tables 1-1 and 1-2, and the casting conditions in the second embodiment are shown in Tables 2-1 and 2-2. In Examples, 25 charges for each were cast to obtain each of a steel plate of API (The American Petroleum Institute) X65 grade and a steel plate of API X70 grade.

[0097] Here, the conditions shown in Tables 1-1, 1-2, 2-1, and 2-2 will be described.

<Compositions of Molten Steel in Tundish>

[0098] The concentrations of C, Mn, Nb, P, and Ca were measured by an emission spectroscopy. The S concentration was very low and thus was difficult to measure by the emission spectroscopy. Then, the S concentration was measured by using a combustion-infrared absorption method.

<Casting Conditions>

- Specific Water Content

[0099] Specific Water Content = (whole secondary cooling water amount per unit time from directly under the mold to a final roll of a continuous casting machine [1/min.]/(weight of cast strip production per unit time [kg/min.])

- Casting Speed

[0100] The casting speed is a drawing speed of the cast strip [m/min.], and calculated from the diameter (circumferential length) and the rotational speed (the number of revolutions per unit time) of a roll (major roll) in contact with the cast strip.

(2) Examination of Decrease in Amount of Ca

[0101] When the entire length of the slab was 10 m, the molten steel in the tundish was taken out, and the Ca concentration Ca_{TD1} in the molten steel in the tundish was examined. After casting, a Ca concentration Ca_{s1} in the slab or Ca_{min1} was examined. Tables 1-1 and 1-2 show examination positions and the Ca concentrations Ca_{s1} when examining the Ca concentrations in the reference-side regions R4 of the slabs. Tables 3-1, 3-2, and 4 show examination positions and the Ca concentrations at the respective positions when examining the Ca concentrations at two to ten different sites (the total number of N shown in Tables 3-1, 3-2, and 4 = 2 to 10) in the thickness direction of the slab. In Tables 3-1, 3-2, and 4, the Ca concentration in each of samples Nos. 51 to 57 and 69 to 100 was measured at two sites. In each of samples Nos. 58 to 64, the Ca concentration was checked at three to eight sites. In each of samples Nos. 65 to 68, the Ca concentration was checked at ten sites. Among the measured plurality of Ca concentrations, the minimum Ca concentration Ca_{min1} is shown for each sample in these tables. The two to ten sites are spaced apart from one another by more than 10 mm in the thickness direction.

[Table 1-1]

Sample No.	Component of molten steel in tundish						Casting conditions		Product grade	Examination position of Ca concentration in slab		Ca concentration in slab Ca_{s1} [ppm]
	C (% by mass)	Mn (% by mass)	Nb (% by mass)	S (ppm by mass)	P (ppm by mass)	Ca Ca_{TD1} (ppm by mass)	Specific water content [L/kg-steel]	Casting speed Vc [m/min]		Distance from the center in the thickness direction*		
										In terms of D (thickness D)	[mm]	
1	0.06	1.32	0.036	6	58	33	0.4	1.0	X70	-0.49D	-69	32
2	0.05	1.28	0.037	6	60	27	0.4	1.1		-0.47D	-66	22
3	0.05	1.30	0.037	6	41	30	0.4	1.3		-0.21D	-29	28
4	0.06	1.27	0.037	5	68	28	0.6	1.0		-0.03D	-4	23
5	0.06	1.32	0.038	4	47	30	0.6	1.1		-0.48D	-67	28
6	0.06	1.33	0.036	5	57	31	0.6	1.2		-0.16D	-22	23
7	0.05	1.31	0.036	4	54	31	0.8	1.0		-0.32D	-45	25
8	0.06	1.33	0.037	7	65	33	0.8	1.1		-0.37D	-52	30
9	0.05	1.28	0.040	3	70	34	0.8	1.3		-0.20D	-28	28
10	0.05	1.33	0.038	4	65	34	1.0	1.0		-0.36D	-50	32
11	0.06	1.31	0.035	3	52	33	1.0	1.1		-0.26D	-36	25
12	0.06	1.31	0.036	7	42	32	1.0	1.3		-0.13D	-18	31
13	0.06	1.29	0.037	6	63	28	1.2	1.2		-0.00D	0	26
14	0.06	1.30	0.039	7	61	30	1.2	1.1		-0.21D	-29	28
15	0.06	1.27	0.037	3	57	30	1.2	1.3		-0.32D	-45	24
16	0.05	1.29	0.036	6	48	31	1.4	1.0		-0.31D	-43	28
17	0.05	1.30	0.038	5	46	26	1.4	1.1		-0.22D	-31	18
18	0.05	1.32	0.037	7	49	26	1.4	1.2		-0.03D	-4	20

(continued)

Sample No.	Component of molten steel in tundish						Casting conditions		Product grade	Examination position of Ca concentration in slab		Ca concentration in slab Ca_{s1} [ppm]
										Distance from the center in the thickness direction*		
	C (% by mass)	Mn (% by mass)	Nb (% by mass)	S (ppm by mass)	P (ppm by mass)	Ca Ca_{TD1} (ppm by mass)	Specific water content [L/kg-steel]	Casting speed Vc [m/min]		In terms of D (thickness D)	[mm]	
19	0.05	1.31	0.037	7	42	34	1.4	1.3		-0.21D	-29	27
20	0.06	1.34	0.038	3	59	28	1.4	1.0		-0.29D	-41	25
21	0.05	1.27	0.036	6	66	32	1.4	1.1		-0.19D	-27	26
22	0.06	1.29	0.036	5	44	34	1.4	1.2		-0.47D	-66	29
23	0.05	1.27	0.035	3	67	31	1.4	1.3		-0.30D	-42	30
24	0.05	1.29	0.037	3	63	31	1.4	1.0		-0.46D	-64	28
25	0.05	1.28	0.035	5	46	29	1.4	1.1		-0.37D	-52	28

*: Positive (+) is defined as the direction from the center in the thickness direction toward an opposite-reterence-side surface, while positive (-) is defined as the direction from the center toward a reference-side surface.

[Table 1-2]

Sample No.	Component of molten steel in tundish						Casting conditions		Product grade	Examination position of Ca concentration in slab		Ca concentration in slab Ca_{s1} [ppm]
	C (% by mass)	Mn (%bay mass)	Nb (% by mass)	S (ppm by mass)	P (ppm by mass)	Ca Ca_{TD1} (ppm by mass)	Specific water content [L/kg-steel]	Casting speed Vc [m/min]		Distance from the center in the thickness direction*		
										In terms of D (thickness D)	[mm]	
26	0.06	1.28	0.033	5	52	29	0.4	1.0	X65	-0.37D	52	23
27	0.06	1.25	0.033	4	61	26	0.4	1.1		-0.35D	49	23
28	0.06	1.27	0.034	7	45	31	0.4	1.3		-0.23D	32	27
29	0.06	1.23	0.035	7	51	31	0.6	1.0		-0.01D	1	25
30	0.06	1.27	0.031	7	66	29	0.6	1.1		-0.40D	56	25
31	0.05	1.26	0.031	4	56	27	0.6	1.2		-0.49D	69	24
32	0.05	1.24	0.035	5	43	30	0.8	1.0		-0.17D	24	24
33	0.06	1.25	0.030	4	70	29	0.8	1.1		-0.15D	21	26
34	0.06	1.26	0.034	6	64	33	0.8	1.3		-0.36D	50	31
35	0.05	1.27	0.035	6	48	33	1.0	1.0		-0.37D	52	29
36	0.06	1.20	0.034	5	50	31	1.0	1.1		-0.40D	56	28
37	0.06	1.27	0.032	3	63	32	1.0	1.3		-0.10D	14	28
38	0.05	1.22	0.035	7	44	33	1.2	1.2		-0.24D	34	28
39	0.06	1.25	0.034	3	50	27	1.2	1.1		-0.37D	52	23
40	0.05	1.26	0.031	4	42	25	1.2	1.3		-0.26D	36	22
41	0.05	1.25	0.034	7	50	33	1.4	1.0		-0.39D	55	30
42	0.06	1.23	0.034	4	68	29	1.4	1.1		-0.41D	57	21
43	0.06	1.23	0.033	4	50	33	1.4	1.2		-0.25D	35	29

(continued)

Sample No.	Component of molten steel in tundish						Casting conditions		Product grade	Examination position of Ca concentration in slab		Ca concentration in slab Ca_{s1} [ppm]
	C (% by mass)	Mn (%bay mass)	Nb (% by mass)	S (ppm by mass)	P (ppm by mass)	Ca Ca_{TD1} (ppm by mass)	Specific water content [L/kg-steel]	Casting speed Vc [m/min]		Distance from the center in the thickness direction*		
										In terms of D (thickness D)	[mm]	
44	0.05	1.20	0.034	6	58	34	1.4	1.3		-0.25D	35	32
45	0.06	1.23	0.033	5	43	29	1.4	1.0		-0.13D	18	27
46	0.06	1.28	0.034	3	64	33	1.4	1.1		-0.49D	69	26
47	0.05	1.26	0.034	7	46	26	1.4	1.2		-0.49D	69	20
48	0.06	1.28	0.032	5	54	29	1.4	1.3		-0.17D	24	26
49	0.06	1.23	0.034	5	52	30	1.4	1.0		-0.10D	14	28
50	0.05	1.28	0.035	5	44	26	1.4	1.1		-0.27D	38	19

*: Positive (+) is defined as the direction from the center in the thickness direction toward an opposite-reference-side surface, while positive (-) is defined as the direction from the center toward a reference-side surface.

[Table 2-1]

Sample No.	Component of molten steel in tundish						Casting conditions		Product grade
	C (% by mass)	Mn (% by mass)	Nb (% by mass)	S (ppm by mass)	P (ppm by mass)	Ca Ca_{TD1} (ppm by mass)	Specific water content [L/kg-steel]	Casting speed Vc [m/min]	
51	0.06	1.32	0.036	6	58	33	0.4	1.0	X70
52	0.05	1.28	0.037	6	60	27	0.4	1.1	
53	0.05	1.30	0.037	6	41	30	0.4	1.3	
54	0.06	1.27	0.037	5	68	28	0.6	1.0	
55	0.06	1.32	0.038	4	47	30	0.6	1.1	
56	0.06	1.33	0.036	5	57	31	0.6	1.2	
57	0.05	1.31	0.036	4	54	31	0.8	1.0	
58	0.06	1.33	0.037	7	65	33	0.8	1.1	
59	0.05	1.28	0.040	3	70	34	0.8	1.3	
60	0.05	1:33	0.038	4	65	34	1.0	1.0	
61	0.06	1.31	0.035	3	52	33	1.0	1.1	
62	0.06	1.31	0.036	7	42	32	1.0	1.3	
63	0.06	1.29	0.037	6	63	28	1.2	1.2	
64	0.06	1.30	0.039	7	61	30	1.2	1.1	
65	0.06	1.27	0.037	3	57	30	1.2	1.3	
66	0.05	1.29	0.036	6	48	31	1.4	1.0	
67	0.05	1.30	0.038	5	46	26	1.4	1.1	
68	0.05	1.32	0.037	7	49	26	1.4	1.2	
69	0.05	1.31	0.037	7	42	34	1.4	1.3	
70	0.06	1.34	0.038	3	59	28	1.4	1.0	
71	0.05	1.27	0.036	6	66	32	1.4	1.1	
72	0.06	1.29	0.036	5	44	34	1.4	1.2	
73	0.05	1.27	0.035	3	67	31	1.4	1.3	
74	0.05	1.29	0.037	3	63	31	1.4	1.0	
75	0.05	1.28	0.035	5	46	29	1.4	1.1	

[Table 2-2]

Sample No.	Component of molten steel in tundish						Casting conditions		Product grade
	C (% by mass)	Mn (% by mass)	Nb (% by mass)	S (ppm by mass)	P (ppm by mass)	Ca Ca_{TD1} (ppm by mass)	Specific water content[L/kg-steel]	Casting speed Vc[m/min]	
76	0.06	1.28	0.033	5	52	29	0.4	1.0	
77	0.06	1.25	0.033	4	61	26	0.4	1.1	
78	0.06	1.27	0.034	7	45	31	0.4	1.3	

(continued)

Sample No.	Component of molten steel in tundish						Casting conditions		Product grade
	C (% by mass)	Mn (% by mass)	Nb (% by mass)	S (ppm by mass)	P (ppm by mass)	Ca Ca_{TD1} (ppm by mass)	Specific water content[L/kg-steel]	Casting speed Vc[m/min]	
79	0.06	1.23	0.035	7	51	31	0.6	1.0	X65
80	0.06	1.27	0.031	7	66	29	0.6	1.1	
81	0.05	1.26	0.031	4	56	27	0.6	1.2	
82	0.05	1.24	0.035	5	43	30	0.8	1.0	
83	0.06	1.25	0.030	4	70	29	0.8	1.1	
84	0.06	1.26	0.034	6	64	33	0.8	1.3	
85	0.05	1.27	0.035	6	48	33	1.0	1.0	
86	0.06	1.20	0.034	5	50	31	1.0	1.1	
87	0.06	1.27	0.032	3	63	32	1.0	1.3	
88	0.05	1.22	0.035	7	44	33	1.2	1.2	
89	0.06	1.25	0.034	3	50	27	1.2	1.1	
90	0.05	1.26	0.031	4	42	25	1.2	1.3	
91	0.05	1.25	0.034	7	50	33	1.4	1.0	
92	0.06	1.23	0.034	4	68	29	1.4	1.1	
93	0.06	1.23	0.033	4	50	33	1.4	1.2	
94	0.05	1.20	0.034	6	58	34	1.4	1.3	
95	0.06	1.23	0.033	5	43	29	1.4	1.0	
96	0.06	1.28	0.034	3	64	33	1.4	1.1	
97	0.05	1.26	0.034	7	46	26	1.4	1.2	
98	0.06	1.28	0.032	5	54	29	1.4	1.3	
99	0.06	1.23	0.034	5	52	30	1.4	1.0	
100	0.05	1.28	0.035	5	44	26	1.4	1.1	

[Table 3-1]

Sample No.	The number N in total		Examined contents of slab									
		Minimum Ca concentration Ca_{min1} [ppm]	Examination position of Ca concentration and Ca concentration									
			N=1		N=2		N=3		N=4		N=5	
			Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]
51	2	30	10	30	20	37	-	-	-	-	-	-
52	2	25	10	25	40	30	-	-	-	-	-	-
53	2	27	-10	27	60	31	-	-	-	-	-	-
54	2	26	-10	26	80	33	-	-	-	-	-	-
55	2	25	130	25	100	26	-	-	-	-	-	-
56	2	30	-130	30	-120	30	-	-	-	-	-	-
57	2	26	-130	26	-110	27	-	-	-	-	-	-
58	3	31	10	31	30	31	50	30	-	-	-	-
59	4	32	-10	32	-30	31	-50	32	-70	33	-	-
60	5	30	-50	30	-10	30	10	30	50	30	90	31
61	6	30	-100	30	-80	30	-40	31	-20	31	20	29
62	7	28	10	28	30	28	50	28	70	28	90	27
63	7	25	10	25	20	25	30	26	40	25	50	25
64	8	28	10	28	20	28	30	27	40	28	50	33
65	10	29	10	29	20	29	30	29	40	35	50	29
66	10	30	10	30	-130	29	-110	30	-70	30	-50	30
67	10	25	10	25	20	25	30	25	40	24	50	26
68	10	23	10	23	20	23	-130	23	-120	23	-80	23
69	2	31	20	31	50	31	-	-	-	-	-	-

(continued)

Sample No.	The number N in total		Examined contents of slab									
		Minimum Ca concentration Ca_{min1} [ppm]	Examination position of Ca concentration and Ca concentration									
			N=1		N=2		N=3		N=4		N=5	
			Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]
70	2	20	40	20	80	21	-	-	-	-	-	-
71	2	29	60	29	100	29	-	-	-	-	-	-
72	2	32	80	32	120	33	-	-	-	-	-	-
73	2	30	-20	30	-50	30	-	-	-	-	-	-
74	2	27	-40	27	-80	28	-	-	-	-	-	-
75	2	27	-60	27	-130	28	-	-	-	-	-	-

*: Positive (+) is defined as the direction from the center in the thickness direction toward an opposite-reference-side surface, while positive (-) is defined as the direction from the center toward a reference-side surface.

[Table 3-2]

Sample No.	The number N in total		Examined contents of slab									
		Minimum Ca concentration Ca_{min1} [ppm]	Examination position of Ca concentration and Ca concentration									
			N=6		N=7		N=8		N=9		N=10	
			Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]
51	2	30	-	-	-	-	-	-	-	-	-	-
52	2	25	-	-	-	-	-	-	-	-	-	-
53	2	27	-	-	-	-	-	-	-	-	-	-
54	2	26	-	-	-	-	-	-	-	-	-	-
55	2	25	-	-	-	-	-	-	-	-	-	-
56	2	30	-	-	-	-	-	-	-	-	-	-
57	2	26	-	-	-	-	-	-	-	-	-	-
58	3	31	-	-	-	-	-	-	-	-	-	-
59	4	32	-	-	-	-	-	-	-	-	-	-
60	5	30	-	-	-	-	-	-	-	-	-	-
61	6	30	50	30	-	-	-	-	-	-	-	-
62	7	28	110	28	130	28	-	-	-	-	-	-
63	7	25	60	31	70	25	-	-	-	-	-	-
64	8	28	60	28	70	27	80	28	-	-	-	-
65	10	29	60	30	70	30	80	29	90	29	110	28
66	10	30	0	30	40	38	60	31	90	31	110	30
67	10	25	60	25	70	32	80	25	90	26	110	26
68	10	23	-50	22	-20	29	0	24	10	23	30	23
69	2	31	-	-	-	-	-	-	-	-	-	-

(continued)

Sample No.	The number N in total		Examined contents of slab									
		Minimum Ca concentration Ca_{min1} [ppm]	Examination position of Ca concentration and Ca concentration									
			N=6		N=7		N=8		N=9		N=10	
			Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]
70	2	20	-	-	-	-	-	-	-	-	-	-
71	2	29	-	-	-	-	-	-	-	-	-	-
72	2	32	-	-	-	-	-	-	-	-	-	-
73	2	30	-	-	-	-	-	-	-	-	-	-
74	2	27	-	-	-	-	-	-	-	-	-	-
75	2	27	-	-	-	-	-	-	-	-	-	-

*: Positive (+) is defined as the direction from the center in the thickness direction toward an opposite-reference-side surface, while positive (-) is defined as the direction from the center toward a reference-side surface.

[Table 4]

Sample No.	The number N in total		Examined contents of slab			
		Minimum Ca concentration Ca_{min1} [ppm]	Examination position of Ca concentration and Ca concentration			
			N=1		N=2	
			Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]	Distance from the center in the thickness direction* [mm]	Ca concentration [ppm]
76	2	26	10	26	20	37
77	2	22	10	22	40	30
78	2	25	10	25	60	29
79	2	30	10	30	80	38
80	2	27	10	27	100	28
81	2	25	10	25	120	25
82	2	26	10	26	140	27
83	2	28	20	28	50	29
84	2	30	40	38	80	30
85	2	29	60	34	100	29
86	2	29	80	29	120	29
87	2	30	20	30	50	37
88	2	30	40	30	50	38
89	2	24	50	24	60	30
90	2	20	-70	20	-80	20
91	2	32	-90	32	-100	33
92	2	27	-110	27	-120	27
93	2	28	-130	28	-140	28
94	2	32	-20	32	-30	32
95	2	26	-10	26	-20	26
96	2	30	-10	30	-40	31
97	2	22	-10	22	-60	23
98	2	25	-10	25	-80	26
99	2	29	-10	29	-100	29
100	2	24	-10	24	-120	24
*: Positive (+) is defined as the direction from the center in the thickness direction toward an opposite-reference-side surface, while positive (-) is defined as the direction from the center toward a reference-side surface.						

(3) Rolling

[0102] Then, after heating the slab to a temperature of 1050 to 1250°C, the hot-rolling was performed on the slab through two or more passes, in each of which a surface temperature of the steel plate was set at 900°C or higher, a cumulative rolling reduction was 40% or more at an average steel plate temperature of 1000°C or higher, which was determined by the calculation, and a rolling reduction per pass was 10% or more. Further, another hot-rolling was performed such that the cumulative rolling reduction at a temperature of 700°C or higher and less than 900°C was 20%

or more, and that the surface temperature at the end of the rolling was 850°C. Thereafter, cooling of the rolled steel plate was started at a cooling start surface temperature of 950°C and an average cooling rate of 10°C/s. The cooling was stopped at a temperature of 350 to 600°C. Subsequently, the air-cooling was carried out until the room temperature, thereby eventually producing steel plates with various component compositions, each steel plate having the size of 9 to 50 mm in thickness × 2000 to 3500 mm in width × 12000 to 35000 mm in length.

(4) HIC Test

[0103] To determine a threshold value tθ, in Examples, the HIC test was performed after the rolling.

(a) Samples were cut out of the respective steel plates obtained after the rolling, and the HIC test was performed on the samples. The HIC test was performed according to the method specified by the NACE standard TM0284-2003.

(b) After the HIC test, each sample was cut at three sites, and then respective cross sections (three cross sections) were observed with a microscope to confirm the presence or absence of HIC. An observation region was set at the region R41 in the "product region R40 corresponding to the opposite-reference-side region" shown in Fig. 3(b) except for a region ranging from the center in the thickness direction of a product, within the ±5.3% of the thickness.

(5) Determination of Threshold Value of Decrease in Amount of Ca

[0104] Fig. 6 shows the result of determination of a threshold value in the first embodiment, specifically, showing the relationship among the "Ca concentration Ca_{TD1} in the molten steel in the tundish" examined in the process (2), the "Ca concentration Ca_{S1} in the slab" shown in each of Tables 1-1 and 1-2, and the HIC test results thereof. Fig. 7 shows the result of determination of the threshold value in the second embodiment, specifically, showing the relationship among the "Ca concentration Ca_{TD1} in the molten steel in the tundish" examined in the process (2), the minimum Ca concentration Ca_{min1} in the slab shown in each of Tables 3-1, 3-2, and 4, and the HIC test results thereof.

[0105] As can be seen from Fig. 6, in the determination method of the first embodiment, when the decrease in the amount of Ca was 4 ppm or less, no HIC occurred. On the other hand, when the decrease in the amount of Ca exceeded 4 ppm, HIC occurred in some cases, but did not occur in others. This result shows that to surely avoid the occurrence of HIC, the decrease in the amount of Ca satisfies the formula below: decrease in the amount of Ca ≤ 4 ppm. Therefore, in Examples of the first embodiment, the threshold value of the decrease in the amount of Ca was set at 4 ppm, namely, $Ca_{drop\theta}$ = 4 ppm.

[0106] Also, as can be seen from Fig. 7, in the determination method of the second embodiment, when the decrease in the amount of Ca was 4 ppm or less, no HIC occurred. On the other hand, when the decrease in the amount of Ca exceeded 4 ppm, HIC occurred in some cases, but did not occur in others. This result shows that to surely avoid the occurrence of HIC, the decrease in the amount of Ca satisfies the formula below: decrease in the amount of Ca ≤ 4 ppm. Therefore, also in Examples of the second embodiment, the threshold value of the decrease in the amount of Ca was set at 4 ppm, namely, $Ca_{drop\theta}$ = 4 ppm.

[0107] Note that the "threshold value of the decrease in the amount of Ca" is determined based on all products, regardless of the strength grade. This is because the easiness of occurrence of HIC due to coarse CaO is not related to the strength grade of products.

(6) Evaluation of Slab as Determination Target

[0108] The HIC resistance of each slab as the determination target having a component composition shown in Table 5 was evaluated using the threshold value.

[0109] The steel with the component composition shown in Table 5 was melted and subjected to continuous casting, thereby producing a slab having a thickness D of 280mm and a width W of 2100 mm.

[0110] Then, the Ca concentration Ca_{TD11} in the molten steel in the tundish of the charge as the determination target was examined, and the-minimum Ca concentration (Ca_{min11}) in the slab as the determination target was determined, whereby the decrease Ca_{drop} in Ca of the slab as the determination target was calculated as mentioned above. Then, the threshold value $Ca_{drop\theta}$ = 4 ppm, which was determined in the first and second embodiments as mentioned in the section (5), was used to determine the evaluation of the HIC resistance. Specifically, when the decrease Ca_{drop} in Ca of the slab as the determination target was 4 ppm or less, the HIC due to CaO did not occur, that is, the HIC resistance was rated as OK. On the other hand, when the decrease Ca_{drop} in Ca was more than 4 ppm, the HIC occurred due to the CaO, that is, the HIC resistance was rated as NG. These results are shown in Table 6.

[0111] Then, after heating the slab to a temperature of 1050 to 1250°C, each slab was processed by either of two types of hot-rolling and cooling methods, denoted as "TMCP" or "QT" in a "hot-rolling and cooling method" column shown in Table 6. Consequently, steel plates (each having 9 to 90 mm in thickness x 2000 to 3500 mm in width x 12000 to 35000 mm in length) with various component compositions were produced. The "TMCP" was a method that involved: hot-rolling through two or more passes, in each of which a surface temperature of the steel plate was set at 900°C or higher, a cumulative rolling reduction was 40% or more at an average steel plate temperature of 1000°C or higher, determined by the calculation, and a rolling reduction per pass was 10% or more; and then another hot-rolling such that a cumulative rolling reduction was 20% or more at a temperature of 700°C or higher and lower than 900°C and that the surface temperature at the end of the rolling was 850°C. The "TMCP" method further involved: starting to cool the rolled steel plate from a cooling start surface temperature of 950°C at an average cooling rate of 10°C/s and then stopping the cooling at a temperature of 350 to 600°C, followed by air-cooling to the room temperature. The "QT" was a method that involved: hot-rolling, followed by air-cooling to the room temperature; quenching by reheating the rolled steel plate to a temperature of 850°C or higher and 950°C or lower; and tempering the steel plate at 600 to 700°C.

[0112] The HIC test was performed on the steel plate according to the method specified by the NACE standard TM0284-2003 to check the presence or absence of cracking in the HIC resistance test. The results are shown in Fig. 6.

[Table 5]

Steel type	Component composition (% by mass) Balance being iron and inevitable impurities																			Ca/S	(Ca-1.25S)/O
	C	Si	Mn	P	S	Al	Ca	N	O	REM	Zr	B	V	Cu	Ni	Cr	Mo	Nb	Ti	Mg		
1	0.03	0.15	1.42	0.005	0.0002	0.033	0.0015	0.0042	0.0013	0.0015	0.0012	0	0	0.33	0	0	0	0	0.011	0	7.5	0.96
2	0.11	0.45	0.81	0.011	0.0005	0.015	0.0022	0.0046	0.0018	0.0018	0.0009	0	0	0	0.29	0	0	0.027	0.015	0	4.4	0.88
3	0.06	0.35	1.05	0.005	0.0002	0.033	0.0015	0.0042	0.0013	0.0015	0.0012	0	0	0.15	0.15	0.20	0	0.032	0.011	0	7.5	0.96
4	0.06	0.35	1.15	0.004	0.0005	0.025	0.0022	0.0046	0.0018	0.0018	0.0009	0	0	0.12	0.21	0.24	0.09	0.027	0.015	0	4.4	0.88
5	0.11	0.25	1.19	0.003	0.0003	0.025	0.0017	0.0038	0.0013	0.0011	0.0012	0	0	0	0.22	0	0	0.021	0.014	0	5.7	1.02
6	0.08	0.42	0.97	0.008	0.0009	0.057	0.0024	0.0037	0.0016	0	0.0065	0	0	0	0	0	0	0.048	0.007	0	2.7	0.80
7	0.10	0.26	1.01	0.004	0.0007	0.027	0.0027	0.0048	0.0025	0.0071	0	0	0	0	0.11	0.42	0	0.007	0	0	3.9	0.73
8	0.05	0.19	1.22	0.009	0.0009	0.036	0.0017	0.0051	0.0022	0	0	0	0	0	0	0	0	0.041	0	0	1.9	0.26
9	0.09	0.33	0.92	0.011	0.0005	0.029	0.0027	0.0037	0.0011	0	0	0	0	0	0.17	0	0	0.017	0.018	0	5.4	1.89
10	0.06	0.31	1.28	0.005	0.0005	0.031	0.0029	0.0039	0.0014	0.0014	0.0012	0	0	0.16	0.23	0.21	0	0.033	0.014	0	5.8	1.63
11	0.06	0.28	1.25	0.006	0.0004	0.036	0.0026	0.0031	0.0019	0.0018	0.0009	0	0	0.16	0.24	0.20	0	0.033	0.015	0	6.5	1.11
12	0.06	0.32	1.32	0.006	0.0006	0.032	0.0033	0.0043	0.0017	0.0016	0.0007	0	0	0.17	0.24	0.22	0.12	0.036	0.011	0	5.5	1.50
13	0.06	0.32	1.27	0.004	0.0007	0.031	0.0031	0.0040	0.0026	0.0015	0.0011	0	0	0.15	0.23	0.20	0	0.034	0.013	0	4.4	0.86
14	0.06	0.33	1.16	0.005	0.0003	0.031	0.0014	0.0045	0.0016	0.0016	0.0008	0	0	0.15	0.25	0.20	0.09	0	0.013	0	4.7	0.64
15	0.06	0.31	1.45	0.005	0.0003	0.039	0.0018	0.0051	0.0017	0.0018	0.0006	0	0	0.15	0.23	0.23	0.08	0.010	0.013	0	6.0	0.84
16	0.06	0.31	1.13	0.006	0.0003	0.035	0.0014	0.0048	0.0016	0.0019	0.0008	0	0	0.15	0.25	0.26	0.09	0.010	0.012	0	4.7	0.64
17	0.06	0.31	1.14	0.005	0.0009	0.031	0.0015	0.0040	0.0015	0.0016	0.0009	0	0	0.15	0.23	0.20	0.09	0	0.013	0	1.7	0.25
18	0.06	0.31	1.43	0.005	0.0004	0.0036	0.0037	0.0036	0.0015	0.0019	0.0009	0	0	0.14	0.24	0.24	0.09	0.011	0.011	0	9.3	2.13

[Table 6]

Steel type	Hot-rolling and cooling method	Ca concentration Ca_{TD11} in molten steel in tundish (% by mass)	Ca concentration Ca_{min11} (% by mass) in slab	Decrease in the amount of Ca (ppm)	Evaluation of HIC resistance of slab	Presence or absence of cracking in HIC resistance test
1	TMCP	0.0015	0.0012	3	OK	Absence
2	TMCP	0.0022	0.0020	2	OK	Absence
3	TMCP	0.0015	0.0012	3	OK	Absence
4	TMCP	0.0022	0.0020	2	OK	Absence
5	TMCP	0.0017	0.0016	1	OK	Absence
6	TMCP	0.0024	0.0022	2	OK	Absence
7	TMCP	0.0027	0.0025	2	OK	Absence
8	TMCP	0.0017	0.0015	2	OK	Presence
9	TMCP	0.0027	0.0022	5	NG	Presence
10	TMCP	0.0029	0.0025	4	OK	Absence
11	TMCP	0.0026	0.0024	2	OK	Absence
12	TMCP	0.0033	0.0030	3	OK	Absence
13	TMCP	0.0031	0.0027	4	OK	Absence
14	QT	0.0014	0.0011	3	OK	Absence
15	QT	0.0018	0.0015	3	OK	Absence
16	QT	0.0014	0.0011	3	OK	Absence
17	QT	0.0015	0.0013	2	OK	Presence
18	QT	0.0037	0.0030	7	NG	Presence

[0113] Tables 5 and 6 show the following steel types Nos. 1 to 7 and 10 to 16 satisfied the specified component composition and suppressed the decrease in the amount of Ca of each slab to the threshold value or less, thereby producing the steel plates of the present invention with excellent HIC resistance.

[0114] In contrast, in steel types Nos. 9 and 18, the decrease in the amount of Ca of each slab exceeded the threshold value, so that the evaluation result of the HIC resistance of the slab was rated as NG. In the HIC test after the rolling, some cracks were caused in the steel plates. Thus, these steel types Nos. 9 and 18 were confirmed to be inferior in the HIC resistance. In steel types Nos. 9 and 18, the chemical component compositions of the steel plates deviated from the requirements made by the present invention. That is, in the steel plate made of the steel type No. 9, the contents of REM and Zr were 0%, and the value (Ca - 1. 25S)/O deviated from the requirement, resulting in inferior HIC resistance. In the steel plate made of the steel type No. 18, the value (Ca - 1. 25S) /O deviated from the requirement, resulting in inferior HIC resistance. In steel types Nos. 8 and 17, the decrease in the amount of Ca of each slab was restrained to be lower than the threshold value, but the chemical component composition of each of the steel plates deviated from the requirement made by the present invention. That is, in the steel plate made of the steel type No. 8, the contents of REM and Zr were 0%, and the value (Ca/S) deviated from the requirement, resulting in inferior HIC resistance. In steel type No. 17, the value (Ca/S) deviated from the requirement, resulting in inferior HIC resistance.

[0115] In the examples in which the evaluation of the HIC resistance of the slab was rated as OK, a time period required from starting of casting to completion of a production of the steel plate, that is, a time period until dispatching the steel plate with the sour resistance (casting → rolling → dispatching) was 19 days. In contrast, in cases where the steel plate obtained after the rolling was subjected to the HIC test and then evaluated for the HIC resistance, a time period required from starting of casting to dispatching (casting → rolling → HIC test → dispatching) was 28 days, which was a long duration. In Examples, the HIC test after the rolling was able to be omitted, which could significantly shorten the time period from starting of the casting to dispatching, e.g., from 28 days to 19 days.

[0116] In the examples in which the evaluation of the HIC resistance of the slab was rated as NG, re-melting was started at the stage of the slab. Thus, a time period required from starting of casting to completion of a production of the steel plate, that is, a time period until dispatching the steel plate with the sour resistance (casting → re-melting → rolling → dispatching) was 54 days. In contrast, in cases where the steel plate obtained after the rolling was subjected to the HIC test and then evaluated for the HIC resistance as the product, when the evaluation result was NG, re-melting was started after the HIC test. Eventually, a time period required from starting of casting to dispatching of the steel plate as the product (casting → rolling → HIC test → re-melting → rolling → HIC test → dispatching) was 72 days, which was a longer duration. In Examples, since the HIC test after the rolling was able to be omitted, even though the re-melting was necessary, the time period from starting of the casting to dispatching could be shortened, e.g., from 72 days to 54 days.

[0117] As mentioned above, according to the present invention, the HIC resistance can be evaluated at the stage of the slab as the cast strip without conducting the HIC test after the rolling, thereby making it possible to significantly shorten the manufacturing lead time. In Examples, the HIC test is used for both the determination of the threshold value for evaluating the HIC resistance of a slab and the confirmation of HIC. Thus, the determination method of the present invention has high accuracy.

Claims

1. A steel plate having excellent hydrogen-induced cracking resistance, comprising, in percent by mass:

    0.02 to 0.15% of C;
    0.02 to 0.50% of Si;
    0.6 to 2.0% of Mn;
    more than 0% and 0.030% or less of P;
    more than 0% and 0.003% or less of S;
    0.010 to 0.08% of Al;
    0.0003 to 0.0060% of Ca;
    0.001 to 0.01% of N;
    more than 0% and 0.0045% or less of O; and
    one or more elements selected from more than 0% and 0.02% or less of REM and more than 0% and 0.010% or less of Zr,
    with the balance being iron and inevitable impurities, wherein
    a ratio (Ca/S) of the Ca to the S is 2.0 or more,
    the Ca, the S, and the O satisfy the formula below: $(Ca - 1.25S)/O \leq 1.80$, and
    a decrease in an amount of Ca obtained by subtracting a Ca concentration in a slab from a Ca concentration in a molten steel in a tundish is a threshold value $Ca_{drop\theta}$ or less, the threshold value $Ca_{drop\theta\theta}$ being a maximum decrease in an amount of Ca that avoids occurrence of hydrogen-induced cracking in the steel plate obtained by rolling the slab.

2. The steel plate according to claim 1, wherein the threshold value $Ca_{drop\theta}$ is a value previously determined by method including following (i) to (iii):

    (i) the Ca concentration in the molten steel in the tundish and the Ca concentration in the slab are measured, and the decrease in the amount of Ca is calculated by subtracting the Ca concentration in the slab from the Ca concentration in the molten steel in the tundish;
    (ii) a hydrogen-induced cracking test is performed on a steel plate that is obtained by rolling a slab, which has been casted on the same casting conditions as the above-mentioned slab; and
    (iii) the maximum decrease in the amount of Ca that avoids the occurrence of hydrogen-induced cracking is determined from the decrease in the amount of Ca measured by the step (i) and a result of the hydrogen-induced cracking test shown in the step (ii).

3. The steel plate according to claim 2, wherein the slab casted on the same casting conditions as the above-mentioned slab is the slab in which the decrease in the amount of Ca is measured.

4. The steel plate according to any one of claims 1 to 3, wherein the Ca concentration in the slab is a minimum one of two or more Ca concentrations obtained by examining the Ca concentration at two or more different sites in the thickness direction of the slab.

5. The steel plate according to any one of claims 1 to 3, wherein the threshold value $Ca_{drop\theta}$ is 4 ppm.

6. The steel plate according to any one of claims 1 to 3, further comprising, as another element, in percent by mass, one or more elements selected from the group consisting of:

more than 0% to 0.005% or less of B,
more than 0% and 0.1% or less of V,
more than 0% and 1.5% or less of Cu,
more than 0% and 1.5% or less of Ni,
more than 0% to 1.5% or less of Cr,
more than 0% and 1.5% or less of Mo, and
more than 0% and 0.06% or less of Nb.

7. The steel plate according to any one of claims 1 to 3, further comprising, as another element, in percent by mass, one or more elements selected from the group consisting of:

more than 0% and 0.03% or less of Ti, and
more than 0% and 0.01% or less of Mg.

8. The steel plate according to any one of claims 1 to 3 for use in line pipe.

9. The steel plate according to any one of claims 1 to 3 for use in pressure container.

10. A steel pipe for line pipe, formed of the steel plate according to any one of claims 1 to 3.

Fig.1

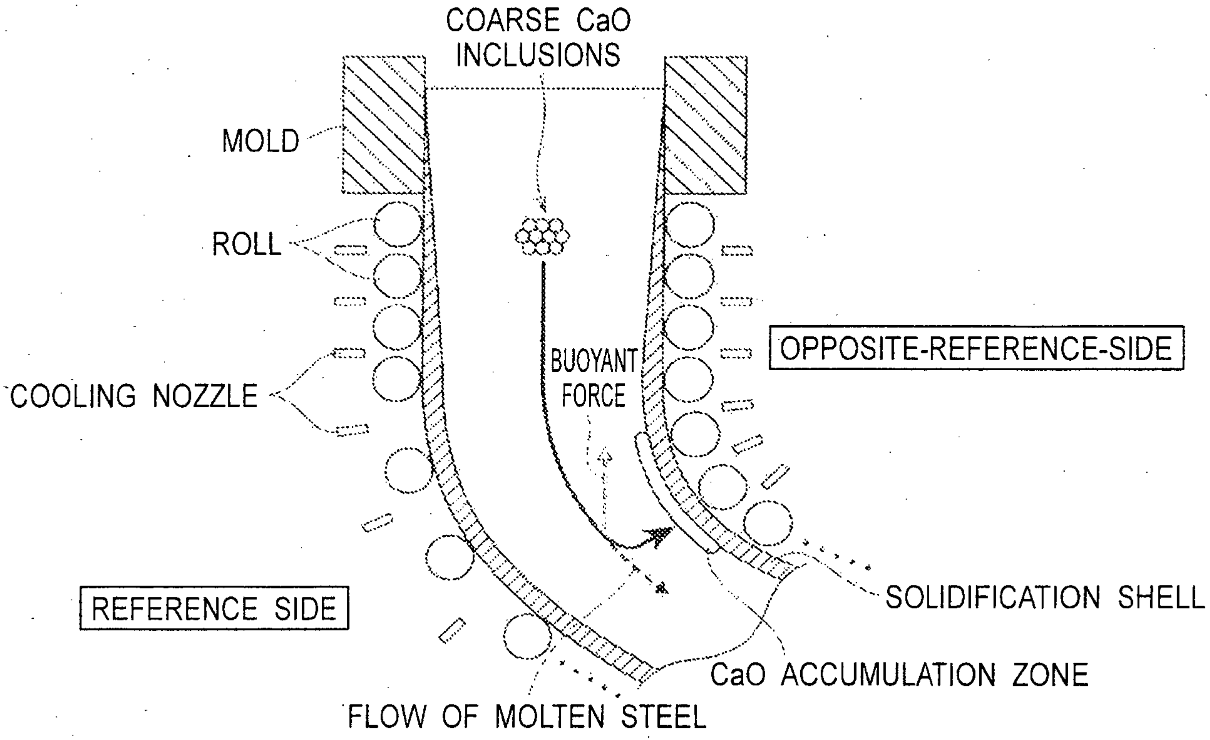

COARSE CaO INCLUSIONS
MOLD
ROLL
COOLING NOZZLE
BUOYANT FORCE
OPPOSITE-REFERENCE-SIDE
REFERENCE SIDE
SOLIDIFICATION SHELL
CaO ACCUMULATION ZONE
FLOW OF MOLTEN STEEL

Fig.2

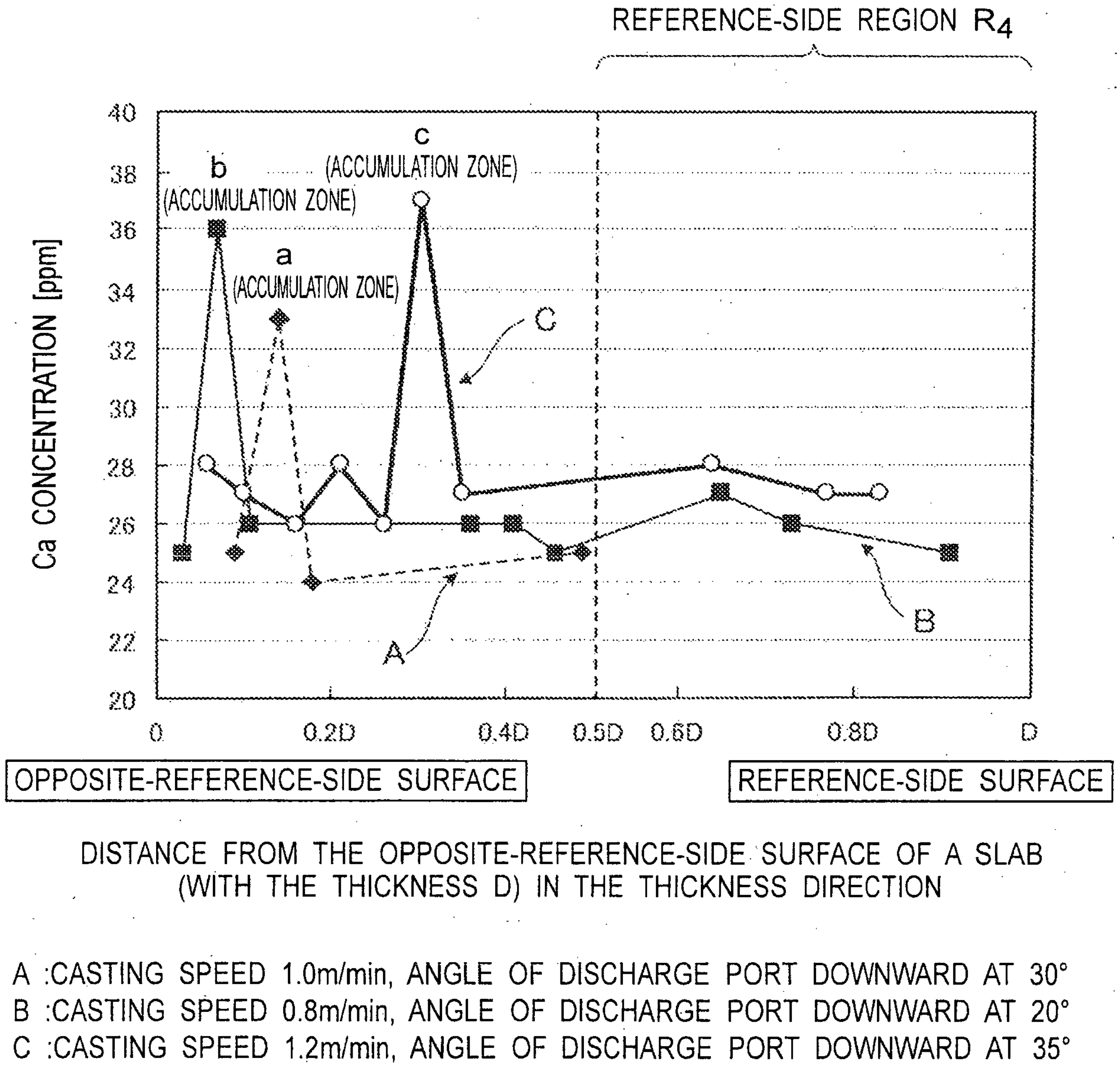

REFERENCE-SIDE REGION R_4
Ca CONCENTRATION [ppm]
40
38
36
34
32
30
28
26
24
22
20
b
(ACCUMULATION ZONE)
c
(ACCUMULATION ZONE)
a
(ACCUMULATION ZONE)
C
A
B
0
0.2D
0.4D
0.5D
0.6D
0.8D
D
OPPOSITE-REFERENCE-SIDE SURFACE
REFERENCE-SIDE SURFACE
DISTANCE FROM THE OPPOSITE-REFERENCE-SIDE SURFACE OF A SLAB (WITH THE THICKNESS D) IN THE THICKNESS DIRECTION
A :CASTING SPEED 1.0m/min, ANGLE OF DISCHARGE PORT DOWNWARD AT 30°
B :CASTING SPEED 0.8m/min, ANGLE OF DISCHARGE PORT DOWNWARD AT 20°
C :CASTING SPEED 1.2m/min, ANGLE OF DISCHARGE PORT DOWNWARD AT 35°

Fig.3 (a)

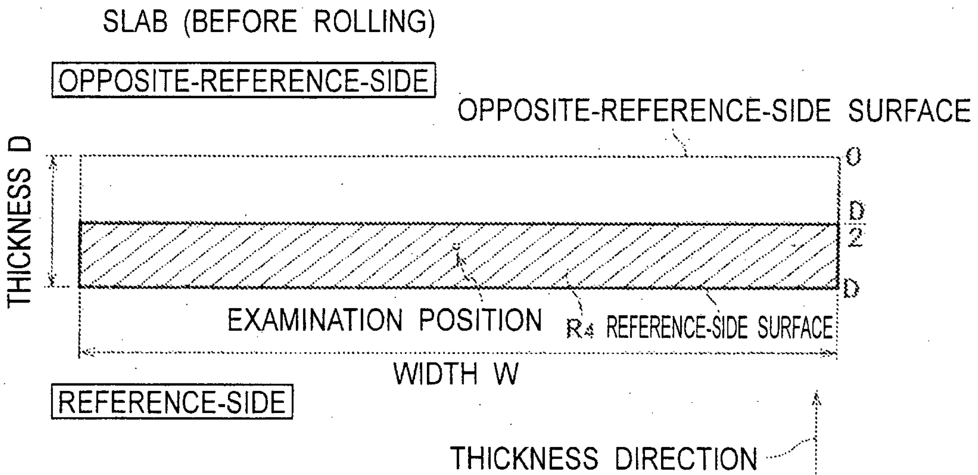


Fig.3 (b)

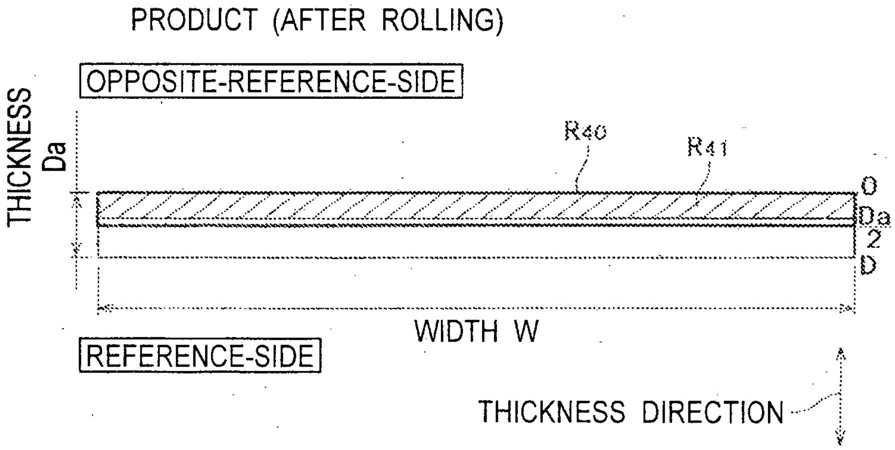


Fig.4

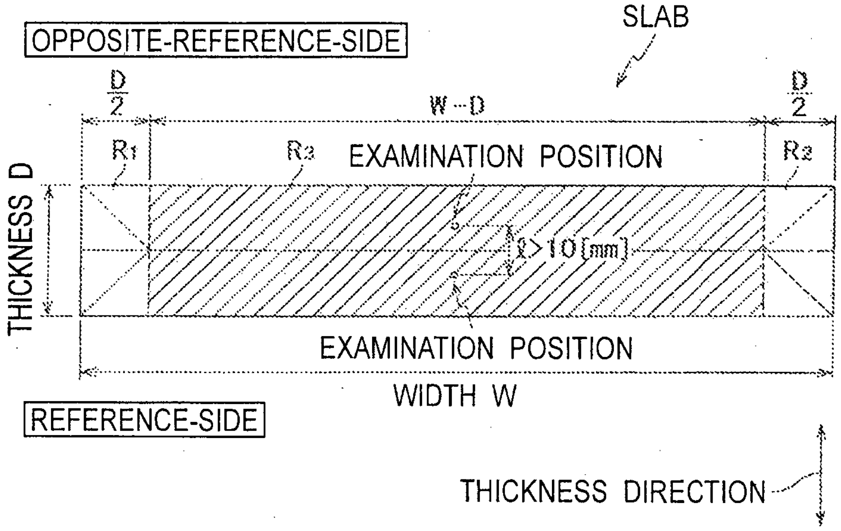


Fig.5

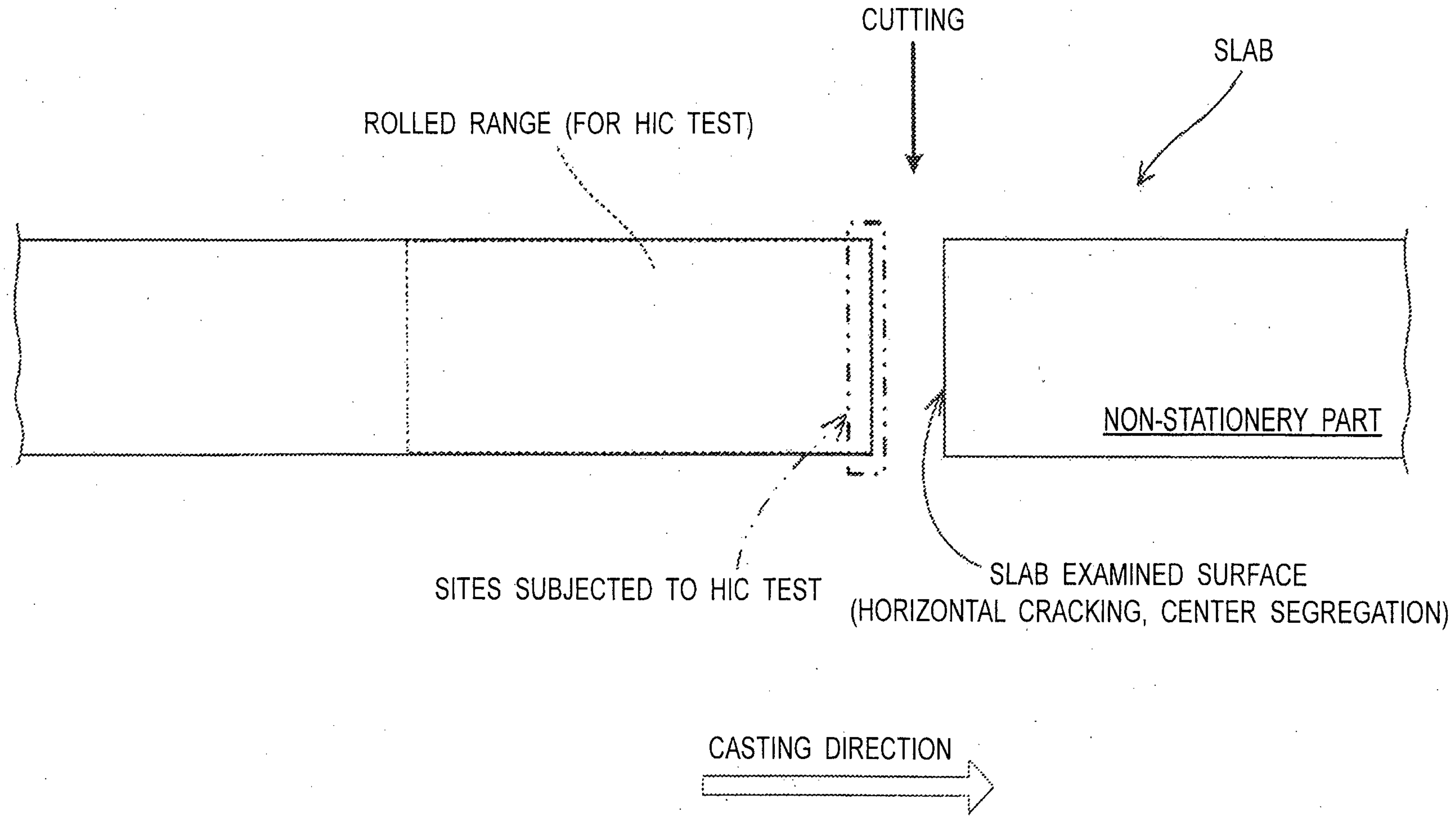

CUTTING
SLAB
ROLLED RANGE (FOR HIC TEST)
NON-STATIONERY PART
SITES SUBJECTED TO HIC TEST
SLAB EXAMINED SURFACE
(HORIZONTAL CRACKING, CENTER SEGREGATION)
CASTING DIRECTION

Fig.6

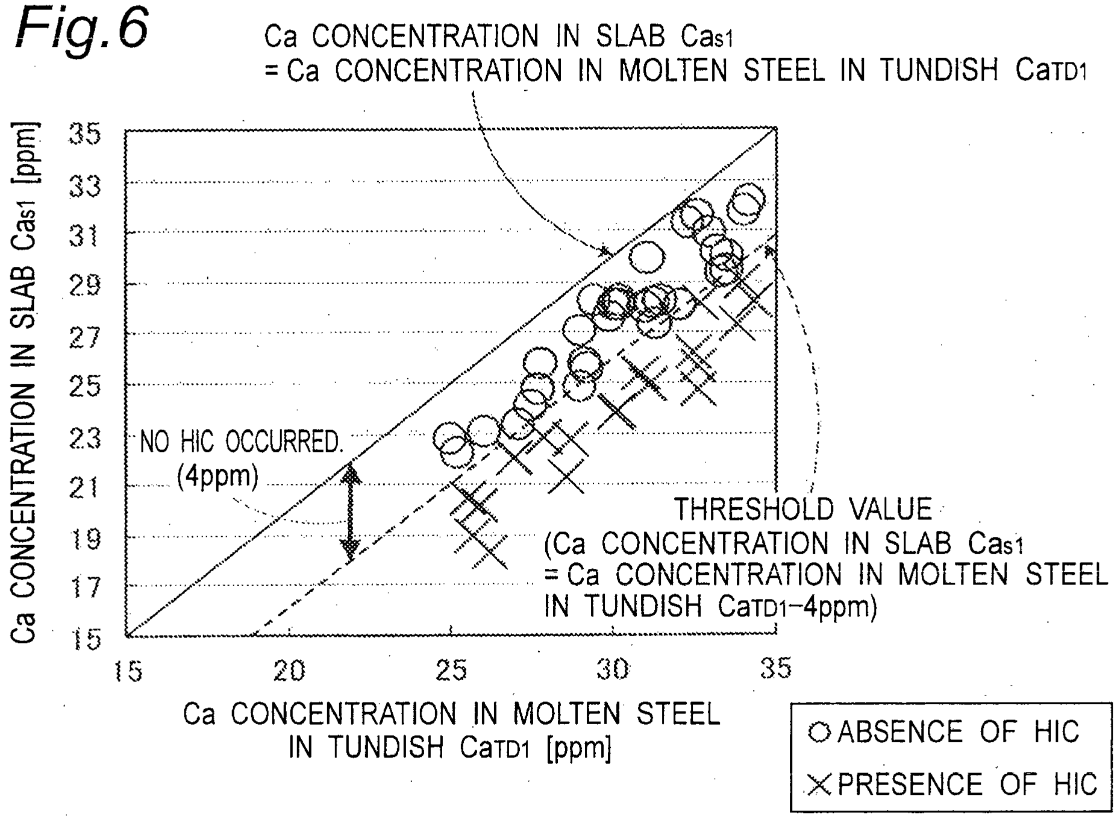
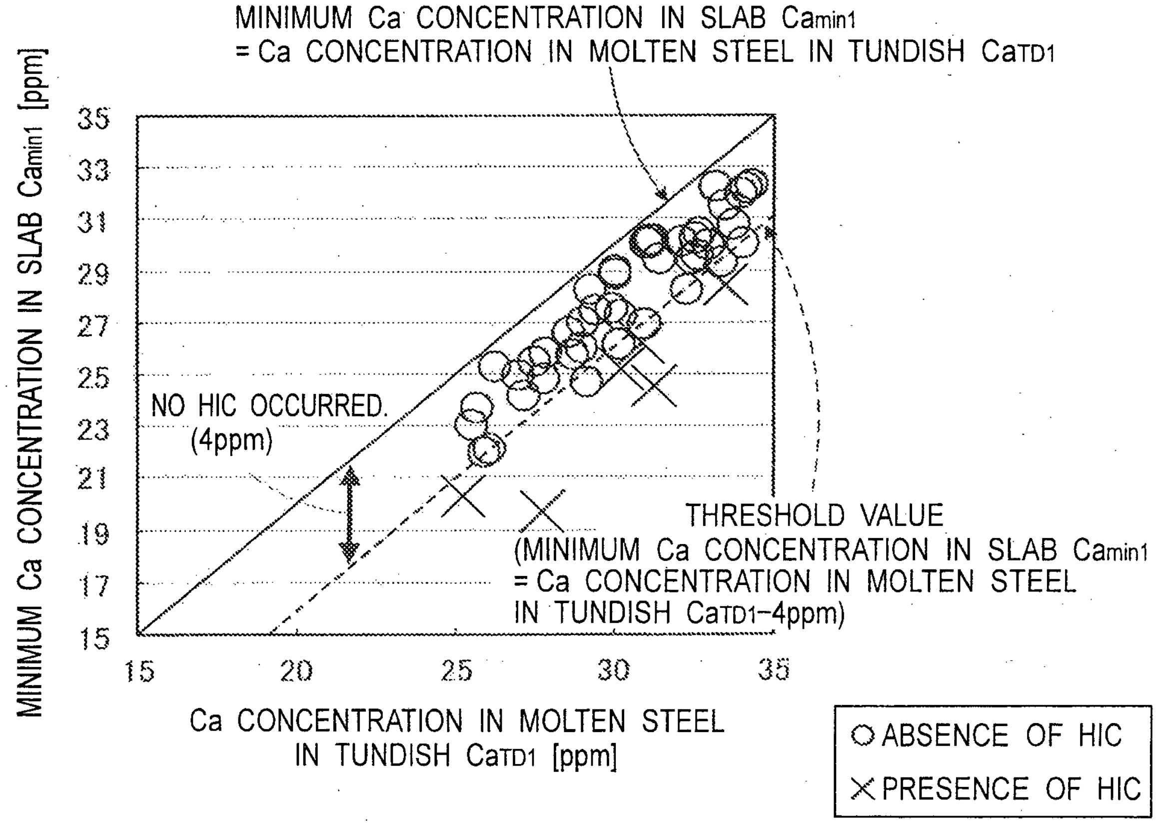

Ca CONCENTRATION IN SLAB Cas1
= Ca CONCENTRATION IN MOLTEN STEEL IN TUNDISH CaTD1
Ca CONCENTRATION IN SLAB Cas1 [ppm]
35
33
31
29
27
25
23
21
19
17
15
NO HIC OCCURRED.
(4ppm)
THRESHOLD VALUE
(Ca CONCENTRATION IN SLAB Cas1
= Ca CONCENTRATION IN MOLTEN STEEL
IN TUNDISH CaTD1−4ppm)
15
20
25
30
35
Ca CONCENTRATION IN MOLTEN STEEL
IN TUNDISH CaTD1 [ppm]
○ ABSENCE OF HIC
× PRESENCE OF HIC

Fig.7


MINIMUM Ca CONCENTRATION IN SLAB Camin1
= Ca CONCENTRATION IN MOLTEN STEEL IN TUNDISH CaTD1
MINIMUM Ca CONCENTRATION IN SLAB Camin1 [ppm]
35
33
31
29
27
25
23
21
19
17
15
NO HIC OCCURRED.
(4ppm)
THRESHOLD VALUE
(MINIMUM Ca CONCENTRATION IN SLAB Camin1
= Ca CONCENTRATION IN MOLTEN STEEL
IN TUNDISH CaTD1−4ppm)
15
20
25
30
35
Ca CONCENTRATION IN MOLTEN STEEL
IN TUNDISH CaTD1 [ppm]
○ ABSENCE OF HIC
× PRESENCE OF HIC

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/085869

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/14*(2006.01)i, *C22C38/58*(2006.01)i, *C21C7/04*(2006.01)n, *C21D8/02*(2006.01)n

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)
C22C38/00-38/60, C21C7/04, C21D8/02

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2012-36462 A (Nippon Steel Corp.), 23 February 2012 (23.02.2012), invention examples 1 to 3 (Family: none)	1-10
X	WO 2013/147197 A1 (Nippon Steel & Sumitomo Metal Corp.), 03 October 2013 (03.10.2013), No.19 & EP 2832879 A1 No.19 & CN 104024461 A & KR 10-2014-0116913 A	7-10

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

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 28 March 2016 (28.03.16)	Date of mailing of the international search report 05 April 2016 (05.04.16)
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)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/085869

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2013-213242 A (Kobe Steel, Ltd.), 17 October 2013 (17.10.2013), No.3 & US 2013/0260164 A1 No.3 & EP 2644729 A2 & KR 10-2013-0111392 A & CN 103361549 A	6-10
X	JP 2013-237101 A (Kobe Steel, Ltd.), 28 November 2013 (28.11.2013), steels M, Q, T, U (Family: none)	6-10
X	JP 2014-214371 A (Kobe Steel, Ltd.), 17 November 2014 (17.11.2014), invention example 9 (Family: none)	7-10

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- JP 2006198649 A **[0011]**
- JP 62277539 A **[0011]**
- JP 2002214222 A **[0011]**
- JP H10122854 A **[0011]**
- JP H10249505 A **[0011]**
- JP 2000292418 A **[0011]**
- JP 2014266491 A **[0094]**
- JP 2015202378 A **[0094]**

Non-patent literature cited in the description

- *ISIJ International,* 2003, vol. 43 (10), 1548-1555 **[0083]**