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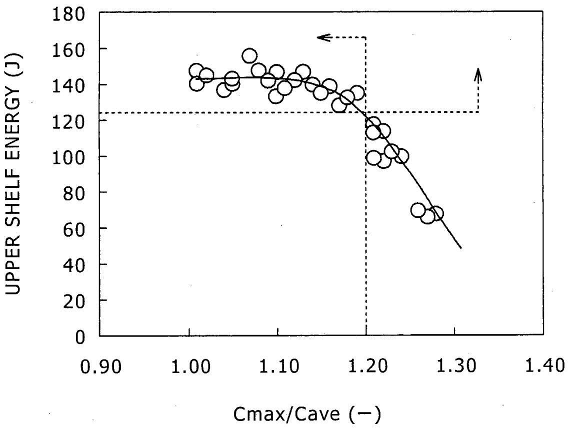
(54) STEEL PLATE WITH EXCELLENT HYDROGEN-INDUCED CRACKING RESISTANCE AND TOUGHNESS, AND LINE PIPE STEEL TUBE

(57) A steel plate with excellent hydrogen-induced cracking resistance and toughness is achieved in which fine HIC of approximately several μms is also sufficiently suppressed particularly in the steel plate surface layer part which will be under a harsh environment with a high hydrogen concentration. The steel plate with excellent hydrogen-induced cracking resistance and toughness of the present invention is characterized to contain specified elements with the remainder consisting of iron and inevitable impurities, in which the ratio of Ca amount and S amount (Ca/S) is 2.0 or more, and the ratio of the maximum Ca concentration (Cmax) of a region from the surface to 5 mm depth in the plate thickness direction and the average Ca concentration (Cave) in the region (Cmax/Cave) is 1.20 or less.

FIG. 2



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Description

[Technical Field]

[0001] The present invention relates to a steel plate with excellent hydrogen-induced cracking resistance and toughness and a steel pipe for a line pipe with excellent hydrogen-induced cracking resistance and toughness obtained using the steel plate suitable to a line pipe for transportation of natural gas and crude oil, a pressure vessel, a storage tank and the like.

[Background Art]

[0002] Accompanying development of bony resources such as crude oil and gas containing hydrogen sulfide, with respect to a line pipe, pressure vessel, and storage tank used for transportation, refining, and storage of them, so-called sour resistance such as hydrogen-induced cracking resistance and stress corrosion cracking resistance is required. The hydrogen-induced cracking (may be hereinafter referred to as "HIC") is known to be cracking caused by that hydrogen intrudes to the inside of steel accompanying a corrosion reaction by hydrogen sulfide and the like described above, and the hydrogen intruded gathers in non-metal inclusions and the like to begin with MnS and Nb (C, N) and is gasified.

[0003] Under a sour environment in particular, it is known that the hydrogen concentration of the region from the surface to 5 mm depth in the plate thickness direction (this region may be hereinafter referred to as "steel plate surface layer part") becomes higher compared to the steel plate center part, and it is known that cracking is liable to be caused from the origin of Ca-based oxide, Al-based oxide and the like of the steel plate surface layer part.

[0004] Conventionally, several proposals have been made with respect to the technology for improving the hydrogen-induced cracking resistance (may be hereinafter referred to as "HIC resistance"). For example, in Patent Literature 1, a steel is disclosed in which the hydrogen-induced cracking resistance is improved by suppressing the segregation degree of Mn, Nb, and Ti of the plate thickness center part. According to this method, although the HIC property of the center segregation part can be improved, the inclusion of the portion other than the center segregation part is not controlled sufficiently, and therefore it is considered to be hard to suppress cracking of the portion other than the center segregation part. In Patent Literature 2, a method is disclosed in which HIC originated from the MnS and Ca-based oxy-sulfide is suppressed by a parameter expression formed of the content of Ca, O, and S. Although the HIC resistance can be secured by such a method, in the steel plate surface layer part where the hydrogen concentration becomes especially high, as described below, fine HIC is liable to be generated, and it is supposed to be hard to secure high toughness of the surface layer part as well as to secure the HIC resistance.

[Citation List]

[Patent Literature]

[0005]

[Patent Literature 1] Japanese Unexamined Patent Application Publication No. 2010-209461
[Patent Literature 2] Japanese Unexamined Patent Application Publication No. Heisei 06-136440

[Summary of Invention]

[Technical Problem]

[0006] The present invention has been developed in view of such circumstances as described above, and its object is to achieve a steel plate and a steel pipe with excellent hydrogen-induced cracking resistance and toughness in which fine HIC of approximately several μms is also sufficiently suppressed particularly in the steel plate surface layer part in a harsh situation with a high hydrogen concentration in the sour environment.

[Solution to Problem]

[0007] The steel plate with excellent hydrogen-induced cracking resistance and toughness of the present invention which could solve the problems described above is characterized to satisfy:

C: 0.02-0.15% (% means mass%, hereinafter the same);
Si: 0.02-0.50%;

Mn: 0.6-2.0%;
P: over 0% and 0.030% or less;
S: over 0% and 0.003% or less;
Al: 0.010-0.08%;
Ca: 0.0003-0.0060%;
N: 0.001-0.01%; and
O (oxygen): over 0% and 0.0045% or less,
with the remainder consisting of iron and inevitable impurities, in which
the ratio of the Ca and the S (Ca/S) is 2.0 or more, and
the ratio of the maximum Ca concentration (Cmax) of a region from the surface to 5 mm depth in the plate thickness direction and the average Ca concentration (Cave) in the region (Cmax/Cave) is 1.20 or less.

[0008] The steel plate may further contain, as other elements, at least one element selected from at least either group of (a) and (b) below.

(a) A group consisting of:

B: over 0% and 0.005% or less;
V: over 0% and 0.1% or less;
Cu: over 0% and 1.5% or less;
Ni: over 0% and 1.5% or less;
Cr: over 0% and 1.5% or less;
Mo: over 0% and 1.5% or less; and
Nb: over 0% and 0.06% or less

(b) A group consisting of:

Ti: over 0% and 0.03% or less;
Mg: over 0% and 0.01% or less;
REM: over 0% and 0.02% or less; and
Zr: over 0% and 0.010% or less

[0009] The steel plate described above is suitable to the use of a line pipe and the use of a pressure vessel. Further, a steel pipe for a line pipe manufactured using the steel plate described above is also included in the present invention.

[Advantageous Effects of Invention]

[0010] According to the present invention, because the distribution of the Ca concentration in the plate thickness direction of the steel plate is made uniform, in the steel plate surface layer part where the hydrogen concentration becomes especially high, even fine HIC of approximately several μms can be sufficiently suppressed. As a result, the steel plate and the steel pipe with excellent hydrogen-induced cracking resistance and toughness can be provided.

[Brief Description of Drawings]

[0011]

[Fig. 1] Fig. 1 is a drawing showing the HIC generation rate according to each Ca concentration of the inclusion that becomes the origin of HIC.
[Fig. 2] Fig. 2 is a drawing showing the relationship between Cmax/Cave and the upper shelf energy.

[Description of Embodiments]

[0012] The present inventors made a lot of intensive studies in order to solve the problems described above. First, in order to find out anew the cause of generation of HIC in the steel plate surface layer part under the harshest condition in the sour environment, the present inventors executed the HIC test (NACE test) specified in NACE (National Association of Corrosion Engineers) TM0284 using various steel plates. This NACE test is a test for evaluating occurrence of HIC after a specimen that is a steel plate is immersed for 96 hours in a mixed aqueous solution of pH 2.7 of 5% NaCl solution and 0.5% acetic acid saturated with hydrogen sulfide gas of 1 atm.

[0013] Next, with respect to the steel plate surface portion after the HIC test, the present inventors executed the Charpy test according to ASTM A370. As a result, even when the cracking was not observed in "the microscopic observation under 100 magnifications" specified in the NACE test, there was a case the result of the Charpy test after the HIC test was poor, or poor in the toughness.

[0014] In order to investigate the reason of it, the microscopic observation was performed with increased magnifications, and it was found out that many fine cracks were generated originated from the inclusions. More specifically, it was found out first that fine HIC of the observation limit or less which could not be observed in the microscopic observation under 100 magnifications specified in the NACE test was generated much originated from the inclusions, and it was the cause of deterioration of the toughness after the HIC test.

[0015] Further, the inclusion composition that became the origin of generation of HIC including the fine HIC described above was investigated. More specifically, the microstructure was observed with respect to the steel plate for which the HIC test (NACE test) described in the example shown below was executed. Also, the Ca concentration of the inclusion observed was obtained. This Ca concentration in the inclusion is the rate (mass%, hereinafter shown merely as %) of Ca relative to the componential composition constituting the inclusion and excluding O and N. The rate (%) of the inclusions that became the origin of generation of HIC out of the inclusions with 50% or more of the Ca concentration in the inclusion and the rate (%) of the inclusions that became the origin of generation of HIC out of the inclusions with 20% or less of the Ca concentration in the inclusion were obtained respectively. The result is shown in Fig. 1. In this Fig. 1, the rate of the inclusions that became the origin of generation of HIC described above is shown by "HIC generation rate (%)" of the vertical axis. As shown in this Fig. 1, it was found out that the inclusion whose Ca concentration was as high as 50% or more in particular (the inclusion with 50% or more of the Ca concentration is hereinafter referred to as "Ca-based inclusion") was liable to become an origin of generation of HIC including the fine HIC described above.

[0016] The Ca-based inclusions described above tend to coagulate, are merged, and gather locally during casting. It is supposed that, because much amount of these Ca-based inclusions are present in the steel plate surface layer region, much amount of fine HIC originated from these Ca-based inclusions and hardly confirmed by a method of prior art is generated locally, and causes deterioration of the toughness.

[0017] Also, in the present invention, in controlling the Ca-based inclusions of the region from the surface to 5 mm depth in the plate thickness direction or the steel plate surface layer part, it was supposed that, when much amount of the Ca-based inclusions were present in the steel plate surface layer part, a position with high Ca concentration existed in the steel plate surface layer part. Therefore, as shown in the example described below, the ratio of the maximum Ca concentration (Cmax) and the average Ca concentration of plural positions (the average Ca concentration of a region from the surface to 5 mm depth in the plate thickness direction; Cave) (Cmax/Cave) in measuring the Ca concentration in plural positions at equal intervals from the surface to 5 mm depth in the plate thickness direction was used as the controlling factor of the amount of the Ca-based inclusions of the steel plate surface layer part.

[0018] Next, the relationship between this Cmax/Cave and the toughness of the steel plate surface layer part after the HIC test which was more specifically the Charpy absorption energy or particularly the upper shelf energy was investigated. As a result, as shown in the example described below, a clear correlation was recognized between the both. In other words, the present inventors found out first that the toughness of the steel plate surface layer part after the HIC test could be improved by controlling the above (Cmax/Cave). In addition, it was found out that, in order to achieve the upper shelf energy: 125 J or more as excellent toughness, Cmax/Cave only had to be 1.20 or less as evaluated in the example described below. The Cmax/Cave is preferably 1.19 or less, more preferably 1.18 or less, and still more preferably 1.15 or less. Although the Cmax/Cave is preferable to be as small as possible from the viewpoint of improving the toughness, the lower limit is approximately 1.00 at which the Ca amount of the steel plate surface layer part and inside the steel becomes equal.

[0019] In order to secure excellent HIC resistance, it is necessary to control the componential composition of steel such as a steel plate and a steel pipe obtained using the steel plate in addition to control the steel plate surface layer part described above. Further, in order to also secure the properties other than the HIC resistance described above such as excellent HAZ toughness and weldability required as a steel plate for a line pipe and a steel plate for a pressure vessel for example, the componential composition of the steel plate should be made as described below. Below, the reasons for determining each component will be described.

[Componential composition]

[C: 0.02-0.15%]

[0020] C is an indispensable element for securing the strength of the base plate and the weld part, and should be contained by 0.02% or more. C amount is preferably 0.03% or more, and more preferably 0.05% or more. On the other hand, when C amount is too much, the HAZ toughness and the weldability deteriorate. Also, when C amount is excessive, NbC and island martensite which become an origin of HIC and a fracture development route are liable to be formed.

Therefore, C amount should be 0.15% or less. C amount is preferably 0.12% or less, and more preferably 0.10% or less.

[Si: 0.02-0.50%]

[0021] Si is an element having a deoxidizing action and effective in improving the strength of the base plate and the weld part. In order to secure such effects, Si amount is made 0.02% or more. Si amount is preferably 0.05% or more, and more preferably 0.15% or more. However, when Si amount is too much, the weldability and the toughness deteriorate. When Si amount is excessive, island martensite is formed, HIC is generated and develops. Therefore, Si amount should be suppressed to 0.50% or less. Si amount is preferably 0.45% or less, and more preferably 0.35% or less.

[Mn: 0.6-2.0%]

[0022] Mn is an element effective in improving the strength of the base plate and the weld part, and is contained by 0.6% or more in the present invention. Mn amount is preferably 0.8% or more, and more preferably 1.0% or more. However, when Mn amount is too much, MnS is formed, not only the hydrogen-induced cracking resistance deteriorates, but also the HAZ toughness and the weldability deteriorate. Therefore, the upper limit of Mn amount is made 2.0% or less. Mn amount is preferably 1.8% or less, more preferably 1.5% or less, and still more preferably 1.2% or less.

[P: over 0% and 0.030% or less]

[0023] P is an element inevitably included in steel. When P amount exceeds 0.030%, deterioration of the toughness of the base plate and the HAZ part is extreme, and the hydrogen-induced cracking resistance also deteriorates. Therefore, in the present invention, P amount is suppressed to 0.030% or less. P amount is preferably 0.020% or less, and more preferably 0.010% or less.

[S: over 0% and 0.003% or less]

[0024] S is an element that forms much amount of MnS and extremely deteriorates the hydrogen-induced cracking resistance when it is contained excessively, and therefore the upper limit of S amount is made 0.003% in the present invention. S amount is preferably 0.002% or less, more preferably 0.0015% or less, and still more preferably 0.0010% or less. Thus, from the viewpoint of improving the hydrogen-induced cracking resistance, S amount is preferable to be as little as possible.

[Al: 0.010-0.08%]

[0025] Al is a strong deoxidizing element. When Al amount is less, the Ca concentration in oxide is liable to increase or the Ca-based inclusions are liable to be formed in the steel plate surface layer part, and fine HIC is generated. Therefore, in the present invention, Al should be made 0.010% or more. Al amount is preferably 0.020% or more, and more preferably 0.030% or more. On the other hand, when Al amount is too much, the oxide of Al is formed in a cluster shape and becomes the origin of the hydrogen-induced cracking. Therefore, Al amount should be 0.08% or less. Al amount is preferably 0.06% or less, and more preferably 0.05% or less.

[Ca: 0.0003-0.0060%]

[0026] Ca has an action of controlling the form of sulfide, and has an effect of suppressing formation of MnS by forming CaS. In order to secure this effect, Ca amount should be made 0.0003% or more. Ca amount is preferably 0.0005% or more, and more preferably 0.0010% or more. On the other hand, when Ca amount exceeds 0.0060%, much amount of HIC is generated from the origins of the Ca-based inclusions. Therefore, in the present invention, the upper limit of Ca amount is made 0.0060%. Ca amount is preferably 0.0045% or less, more preferably 0.0035% or less, and still more preferably 0.0025% or less.

[N: 0.001-0.01%]

[0027] N is an element precipitating as TiN in the steel microstructure, suppressing coarsening of the austenitic grain of the HAZ part, promoting the ferritic transformation, and improving the toughness of the HAZ part. In order to secure these effects, N should be contained by 0.001% or more. N amount is preferably 0.003% or more, and more preferably 0.0040% or more. However, when N amount is too much, the HAZ toughness deteriorates adversely because of presence of solid-solutionized N, and therefore N amount should be 0.01% or less. N amount is preferably 0.008% or less, and more preferably 0.0060% or less.

[O: over 0% and 0.0045% or less]

[0028] O (oxygen) is preferable to be less from the viewpoint of improving the cleanliness. When much amount of O is contained, in addition to that the toughness deteriorates, HIC is generated from the origin of the oxide, and the hydrogen-induced cracking resistance deteriorates. From this viewpoint, O amount should be 0.0045% or less, is preferably 0.0030% or less, and more preferably 0.0020% or less.

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

[0029] When S becomes excessive relative to Ca, MnS is formed mainly in the plate thickness center part, and HIC is generated originated from MnS. In order to suppress that, Ca/S should be 2.0 or more, preferably 2.5 or more, and more preferably 3.0 or more. Also, the upper limit of Ca/S becomes approximately 15 from Ca amount and S amount specified in the present invention.

[0030] The composition of steel (steel plate, steel pipe) of the present invention is as described above, and the remainder is iron and inevitable impurities. Also, in addition to the elements described above, (a) by further containing at least one element selected from a group consisting of B, V, Cu, Ni, Cr, Mo, and Nb of the amount described below, the strength and toughness can be improved further, and (b) by further containing at least one element selected from a group consisting of Ti, Mg, REM, and Zr of the amount described below, the HAZ toughness can be enhanced further, desulfurization is promoted, and the HIC resistance can be improved further. Below, these elements will be described in detail.

[B: over 0% and 0.005% or less]

[0031] B enhances the quenchability, increases the strength of the base plate and the weld part, is bonded with N in the process the HAZ part having been heated in welding is cooled to precipitate BN, promotes ferritic transformation from inside the austenitic grain, and therefore improves the HAZ toughness. In order to secure these effects, it is preferable to contain B amount by 0.0002% or more. B amount is more preferably 0.0005% or more, and still more preferably 0.0010% or more. However, when B amount becomes excessive, the toughness of the base plate and the HAZ part deteriorate, deterioration of the weldability is caused, and therefore B amount is preferably 0.005% or less. B amount is more preferably 0.004% or less, and still more preferably 0.0030% or less.

[V: over 0% and 0.1% or less]

[0032] V is an element effective in improving the strength, and, in order to secure this effect, it is preferable to contain V by 0.003% or more, and more preferably 0.010% or more. On the other hand, when V content exceeds 0.1%, the weldability and the base plate toughness deteriorate. Therefore, V amount is preferably 0.1% or less, and more preferably 0.08% or less.

[Cu: over 0% and 1.5% or less]

[0033] Cu is an element effective in improving the quenchability and increasing the strength. In order to secure these effects, it is preferable to contain Cu by 0.01% or more. Cu amount is more preferably 0.05% or more, and still more preferably 0.10% or more. However, because the toughness deteriorates when Cu content exceeds 1.5%, 1.5% or less is preferable. Cu amount is more preferably 1.0% or less, and still more preferably 0.50% or less.

[Ni: over 0% and 1.5% or less]

[0034] Ni is an element effective in improving the strength and toughness of the base plate and the weld part. In order to secure the effect, it is preferable to make Ni amount 0.01% or more. Ni amount is more preferably 0.05% or more, and still more preferably 0.10% or more. However, when much amount of Ni is contained, the cost increases extremely as a structural steel, and therefore it is preferable to make Ni amount 1.5% or less from the economical viewpoint. Ni amount is more preferably 1.0% or less, and still more preferably 0.50% or less.

[Cr: over 0% and 1.5% or less]

[0035] Cr is an element effective in improving the strength, and, in order to secure this effect, it is preferable to contain

Cr by 0.01% or more. Cr amount is more preferably 0.05% or more, and still more preferably 0.10% or more. On the other hand, when Cr amount exceeds 1.5%, the HAZ toughness deteriorates. Therefore it is preferable to make Cr amount 1.5% or less. Cr amount is more preferably 1.0% or less, and still more preferably 0.50% or less.

[Mo: over 0% and 1.5% or less]

[0036] Mo is an element effective in improving the strength and toughness of the base plate. In order to secure the effects, it is preferable to make Mo amount 0.01% or more. Mo amount is more preferably 0.05% or more, and still more preferably 0.10% or more. However, when Mo amount exceeds 1.5%, the HAZ toughness and weldability deteriorate. Therefore Mo amount is preferably 1.5% or less, more preferably 1.0% or less, and still more preferably 0.50% or less.

[Nb: over 0% and 0.06% or less]

[0037] Nb is an element effective in enhancing the strength and base plate toughness without deteriorating the weldability. In order to secure the effects, it is preferable to make Nb amount 0.002% or more. Nb amount is more preferably 0.010% or more, and still more preferably 0.020% or more. However, when Nb amount exceeds 0.06%, the toughness of the base plate and HAZ deteriorates. Therefore, in the present invention, it is preferable that the upper limit of Nb amount is made 0.06%. Nb amount is more preferably 0.050% or less, further more preferably 0.040% or less, and still more preferably 0.030% or less.

[Ti: over 0% and 0.03% or less]

[0038] Ti is an element required for improving the toughness of the HAZ part because Ti prevents coarsening of the austenitic grain and promotes the ferritic transformation in the HAZ part in welding by precipitating as TiN in steel. Also, because Ti exhibits the desulfurizing action, Ti is an element effective also in improving the HIC resistance. In order to secure these effects, it is preferable to contain Ti by 0.003% or more. Ti amount is more preferably 0.005% or more, and more preferably 0.010% or more. On the other hand, when Ti amount becomes excessive, the toughness of the base plate and the HAZ part deteriorates because of solid solution of Ti and precipitation of TiC, and therefore it is preferable to make Ti amount 0.03% or less. Ti amount is more preferably 0.02% or less.

[Mg: over 0% and 0.01% or less]

[0039] Mg is an element effective in improving the toughness through miniaturization of the grain, and is an element exhibiting the desulfurizing action and effective also in improving the HIC resistance. In order to secure these effects, it is preferable to contain Mg by 0.0003% or more. Mg amount is more preferably 0.001% or more. On the other hand, even when Mg is contained excessively, the effects saturate, and therefore it is preferable that the upper limit of Mg amount is made 0.01%. Mg amount is more preferably 0.005% or less.

[REM: over 0% and 0.02% or less]

[0040] REM (rare earth element) is an element effective in suppressing formation of MnS by the desulfurizing action and enhancing the hydrogen-induced cracking resistance. In order to exert such effects, it is preferable to contain REM by 0.0002% or more. REM amount is more preferably 0.0005% or more, and still more preferably 0.0010% or more. On the other hand, even when much amount of REM is contained, the effects saturate. Therefore, it is preferable that the upper limit of REM amount is made 0.02%. From the viewpoint of suppressing blockage of the immersion nozzle in casting and improving the productivity, REM amount is more preferably 0.015% or less, further more preferably 0.010% or less, and still more preferably 0.0050% or less. Also, in the present invention, the REM means the lanthanoid elements (15 elements from La to Lu), Sc (Scandium), and Y.

[Zr: over 0% and 0.010% or less]

[0041] Zr is an element contributing to improvement of the HIC resistance by the desulfurizing action, and contributing also to improvement of the HAZ toughness by forming and finely dispersing oxide. In order to exert these effects, it is preferable to make Zr amount 0.0003% or more. Zr amount is more preferably 0.0005% or more, further more preferably 0.0010% or more, and still more preferably 0.0015% or more. On the other hand, when Zr is added excessively, coarse inclusions are formed, and the hydrogen-induced cracking resistance and the base plate toughness are deteriorated. Therefore, it is preferable to make Zr amount 0.010% or less. Zr amount is more preferably 0.0070% or less, further more preferably 0.0050% or less, and still more preferably 0.0030% or less.

[0042] The steel plate specified in the present invention has been described above. The method for manufacturing the steel plate of the present invention is not particularly limited as far as it is a method of obtaining the steel plate surface layer part specified above. As the method for easily obtaining the steel plate having the steel plate surface layer part specified above, a method described below can be cited.

[Manufacturing method]

[0043] After the steel is molten so as to have the componential composition described above, the molten steel is poured to the mold through the ladle and tundish, however, in order to obtain a steel plate having the steel plate surface layer part specified in the present invention, in the step of pouring the molten steel to the tundish and performing continuous casting, it is recommendable to satisfy all of (1)-(3) below.

> (1) In the tundish, the flow channel cross-sectional area at the molten steel pouring position to the mold is made larger than the flow channel cross-sectional area at the molten steel pouring position from the ladle. In other words, a tundish in which each flow channel cross-sectional area is thus designed is used.
> (2) Casting is performed while Ar is blown in from the position of 50 mm or more from the upper part of the discharge port of the pouring nozzle at the flow rate of 0.04-9.7 L (liter)/t (ton).
> (3) The solidifying rate at the position of 1-3 m from the meniscus position of the molten steel in the mold toward the drawing out direction is made 0.26 mm/s or less.

[0044] Each condition of above (1)-(3) will be explained below in order.

(1) Flow channel cross-sectional area

[0045] Because the Ca-based inclusion has high melting point and has large contact angle against molten steel, it is liable to form coagulation and is liable to become a coarse inclusion. Therefore, this Ca-based inclusion should be made to sufficiently float and be separated inside the tundish. When this floating and separating are insufficient, the coarse Ca-based inclusion is made to float for example at a curved section in continuous casting, and is liable to gather at the surface layer. In order to make the inclusion sufficiently float and be separated inside the tundish, it is better to make the average flow rate of the molten steel inside the tundish slow. By reducing the average flow rate of the molten steel, the floating time can be made longer, and floating and separating can be promoted by turbulence in pouring the molten steel from the ladle. In order to reduce the average flow rate of the molten steel inside the tundish, such tundish is used that the flow channel cross-sectional area at the molten steel pouring position to the mold in the tundish is larger than the flow channel cross-sectional area at the molten steel pouring position from the ladle. Although the ratio expressed by (flow channel cross-sectional area at molten steel pouring position to mold)/(flow channel cross-sectional area at molten steel pouring position from ladle) only has to be over 1.00, the ratio is preferably 1.50 or more. Also, the upper limit of the ratio is approximately 5.0.

(2) Ar blow-in

[0046] By performing casting while blowing in Ar at the position of 50 mm or more from the upper part of the discharge port at which the molten steel inside the nozzle becomes an unfilled state, the Ca-based inclusions and the Ar bubbles can be merged and floating and separating can be promoted inside the nozzle and the mold. In order to obtain this effect, it is preferable to make the Ar flow rate 0.04 L/t or more. The Ar flow rate is more preferably 0.10 L/t or more, and still more preferably 0.20 L/t or more. On the other hand, when the Ar flow rate exceeds 9.7 L/t, the Ar bubbles remain in the surface layer of the slab, and are liable to remain in the steel plate as the defects. Therefore, the Ar flow rate is preferably 9.7 L/t or less, more preferably 9.0 L/t or less, and still more preferably 8.0 L/t or less.

(3) Solidifying rate

[0047] In general, the inclusions which are present in the vicinity of the solidification interface are liable to be taken in to the interface when the solidifying rate is high, and a part of the inclusions is pushed out from the solidification interface to the center part not yet solidified when the solidifying rate is low. In the present invention, by reducing the solidifying rate, the inclusions are prevented from gathering in the steel plate surface layer part. More specifically, the solidifying rate at the position of 1-3 m from the meniscus position of the molten steel inside the mold toward the drawing out direction where "the region from the surface to 5 mm depth" of the object of the present invention is solidified is made 0.26 mm/s or less. The solidifying rate is preferably 0.22 mm/s or less, and more preferably 0.18 mm/s or less. Also, the lower limit value of the solidifying rate becomes approximately 0.05 mm/s from the viewpoint of productivity and the like.

The solidifying rate can be adjusted by controlling the water amount density of the cooling water and the casting rate.

[0048] In the present invention, the step after casting as described above is not particularly the object, and the steel plate can be manufactured by performing hot rolling according to an ordinary method, or by reheating and performing heat treatment after the hot rolling. Also, using the steel plate, a steel pipe for a line pipe can be manufactured by a method generally employed. The steel pipe for a line pipe obtained using the steel plate of the present invention is also excellent in the HIC resistance and the toughness.

[0049] The present application is to claim the benefit of the right of priority based on Japanese Patent Application No. 2013-073310 applied on March 29, 2013. Entire contents of the description of Japanese Patent Application No. 2013-073310 applied on March 29, 2013 are incorporated by reference into the present application.

[Examples]

[0050] Although the present invention will be described below more specifically referring to examples, the present invention is not to be limited by the examples below, it is a matter of course that the present invention can be also implemented with modifications being appropriately added within the range adaptable to the purposes described above and below, and any of them is to be included within the technical range of the present invention.

[0051] Steel with the componential composition shown in Table 1 was molten, and a slab with 280 mm thickness was obtained by continuous casting. The conditions of the continuous casting in the manufacturing step are as shown in Table 2. In the column of "(1) flow channel cross-sectional area" of Table 2, the case of using the tundish whose flow channel cross-sectional area at the molten steel pouring position to the mold was larger than the flow channel cross-sectional area at the molten steel pouring position from the ladle was marked with "○", and the case other than that was marked with "x". Also, in the present example, in the case of "○" described above, such tundish was used that the ratio of (flow channel cross-sectional area at molten steel pouring position from ladle)/(flow channel cross-sectional area at molten steel pouring position to mold) was 1.05 or more. Further, in the column of "(2) Ar blow in" of Table 2, the case casting was performed while Ar was blown in from the position of 50 mm or more from the upper part of the discharge port of the pouring nozzle at the flow rate of 0.04-9.7 L/t was marked with "○", and the case other than that was marked with "×". Also, in the column of "(3) solidifying rate" of Table 2, the case the solidifying rate at the position of 1-3 m from the meniscus position of the molten steel in the mold toward the drawing out direction was made 0.26 mm/s or less was marked with "○", and the case other than that was marked with "×".

[0052] Thereafter, after heating the slab manufactured by continuous casting so as to become 1,050-1,250°C, the steel plate (plate thickness: 12-90 mm) with various componential compositions was obtained by the hot rolling/cooling method of 2 patterns as shown "TMCP" (Thermo Mechanical Control Process) or "QT" (Quenching and Tempering) in the column "hot rolling/cooling method" of Table 2. In "TMCP" described above, hot rolling was performed so that the cumulative draft of 900°C or above in terms of the surface temperature of the steel plate became 30% or more, and hot rolling was further performed so that the cumulative draft of 700°C or above and below 900°C became 20% or more with the rolling finish temperature of 700°C or above and below 900°C. Thereafter, water cooling was started from a temperature of 650°C or above, the water cooling was stopped at a temperature of 350-600°C, and air cooling was thereafter performed to the room temperature. Also, in "QT" described above, air cooling was performed to the room temperature after the hot rolling, the steel plate was reheated to a temperature of 850°C or above and 950°C or below and was quenched, and was thereafter subjected to tempering treatment at 600-700°C.

[0053] Also, using each steel plate, Cmax/Cave was measured as shown below. Further, the HIC resistance was evaluated by executing the HIC test, and the toughness was evaluated by executing the Charpy impact test.

[Measurement of Cmax/Cave]

[0054] The distribution of the Ca concentration of the region from the surface to 5 mm depth in the plate thickness direction of the steel plate was measured by fluorescence spectroscopic analysis. More specifically, first, in order to exfoliate the scale layer of the steel plate, the portion from the steel plate surface to 0.5 mm was ground, and the Ca concentration of the ground surface that corresponded to the surface of the steel plate was measured. Next, after the steel plate was ground by 0.5 mm in the plate thickness direction, the Ca concentration of the ground surface was measured. This procedure was repeated with 0.5 mm pitch in the plate thickness direction, and the Ca concentration of 10 cross sections in total from the surface to 5 mm depth in the plate thickness direction was measured. The maximum value of the Ca concentration in 10 cross sections was made Cmax, the average value of the Ca concentration of 10 cross sections was made Cave, and Cmax/Cave was obtained.

[HIC test (NACE test)]

[0055] The HIC test was performed for evaluation according to NACE standard TM0284-2003. More specifically, from

1/4W position and 1/2W position in the width direction of each steel plate, 3 pieces each or 6 pieces in total of the specimens (size: plate thickness×100 mm (width)×20 mm (rolling direction)) were taken. Also, the specimen was immersed for 96 hours in a mixed aqueous solution containing 0.5% NaCl and 0.5% acetic acid of 25°C saturated with hydrogen sulfide of 1 atm, evaluation of the cross section was executed according to NACE standard TM0284-2003 FIGURE 3, and CLR (Crack Length Ratio: the ratio (%) of the total of the crack length relative to the specimen width) was measured. Further, the case the CLR was 3% or less was evaluated to be excellent in the HIC resistance (○), and the case the CLR exceeded 3% was evaluated to be poor in the HIC resistance (×).

[Charpy impact test]

[0056] After the NACE test, from right below the surface of the specimen, according to ASTM A370, the Charpy test specimens with 5 mm in the plate thickness direction×10 mm in the rolling direction were taken by 3 pieces in the direction perpendicular to the rolling direction, and a notch was worked in the plate thickness direction of the steel plate. The Charpy impact test was executed according to ASTM A370, the test temperature was changed variously in 0°C-80°C, and the Charpy absorption energy at 0% of the percent brittle fracture or the upper shelf energy was obtained. Also, the case this upper shelf energy was 125 J or more was evaluated to be excellent in the toughness.

[0057] These results are shown in Table 2.

[Table 1]

No.	Componential composition (mass%), remainder is iron and inevitable impurities																			Ca/S
	C	Si	Mn	P	S	Al	Ca	N	O	Ti	B	V	Cu	Ni	Cr	Mo	Nb	Mg	REM	Zr	
1	0.06	0.30	0.99	0.006	0.0010	0.040	0.0026	0.0048	0.0018	0	0	0	0	0	0	0	0	0	0	0	2.60
2	0.08	0.25	1.02	0.006	0.0002	0.028	0.0009	0.0047	0.0014	0.012	0	0	0.16	0.22	0.2	0	0.031	0	0	0	4.50
3	0.09	0.35	1.06	0.005	0.0007	0.024	0.0031	0.0047	0.0015	0.009	0	0	0.14	0	0	0	0.055	0	0.0027	0	4.43
4	0.07	0.05	1.04	0.025	0.0003	0.036	0.0037	0.0039	0.0023	0.017	0	0	0	0.28	0	0	0	0	0.0008	0.0072	12.33
5	0.04	0.40	1.07	0.005	0.0006	0.033	0.0036	0.0037	0.0027	0.022	0	0	0	0	0.43	0	0.021	0	0.0089	0.0022	6.00
6	0.09	0.15	1.25	0.012	0.0014	0.022	0.0042	0.0043	0.0016	0	0	0	0	0	0	0	0	0	0	0	3.00
7	0.06	0.30	1.03	0.007	0.0020	0.035	0.0040	0.0045	0.0020	0.012	0	0	0.15	0.22	0.11	0	0.027	0	0.011	0.0008	2.00
8	0.03	0.12	1.85	0.005	0.0001	0.012	0.0037	0.0035	0.0041	0	0	0	0.75	0.35	0	0	0.008	0.0025	0	0	37.00
9	0.15	0.25	1.15	0.007	0.0003	0.055	0.0020	0.0028	0.0017	0.005	0	0.025	0.3	0.2	0	0.05	0.017	0	0	0	6.67
10	0.07	0.32	1.57	0.011	0.0011	0.024	0.0022	0.0061	0.0020	0.016	0	0.072	0	0	0.27	0	0.037	0	0.0015	0.0015	2.00
11	0.11	0.22	1.33	0.005	0.0006	0.041	0.0015	0.0051	0.0027	0	0	0	0	0	0	0.33	0	0	0	0	2.50
12	0.06	0.33	1.15	0.005	0.0003	0.032	0.0012	0.0041	0.0015	0.012	0	0	0.17	0.24	0.09	0.12	0.033	0	0.0012	0.0005	4.00
13	0.03	0.45	0.65	0.011	0.0013	0.065	0.0027	0.0061	0.0019	0	0.0027	0	0	0.92	0.91	0.55	0	0	0	0	2.08
14	0.13	0.35	1.01	0.005	0.0012	0.025	0.0022	0.0038	0.0015	0	0	0.085	0	0	0	0	0.029	0	0	0.0032	1.83
15	0.06	0.29	1.07	0.006	0.0005	0.029	0.0032	0.0038	0.0014	0.011	0	0	0.02	0.28	0.14	0	0.029	0	0.0016	0.0009	6.40
16	0.07	0.25	1.19	0.008	0.0012	0.032	0.0041	0.0061	0.0020	0	0	0	0	0	0	0	0	0	0	0	3.42
17	0.13	0.15	0.87	0.009	0.0007	0.066	0.0022	0.0032	0.0017	0.017	0	0	0	0	0	0	0.017	0	0	0	3.14
18	0.03	0.42	1.07	0.015	0.0003	0.017	0.0017	0.0045	0.0013	0	0	0	0	0	0	0	0	0	0.0023	0	5.67
19	0.07	0.33	1.01	0.007	0.0008	0.025	0.0035	0.0051	0.0041	0.009	0	0	0	0	0	0	0.044	0	0	0.0019	4.38
20	0.05	0.05	0.95	0.005	0.0005	0.043	0.0032	0.0037	0.0011	0.013	0	0	0	0	0	0	0	0	0	0	6.40
21	0.09	0.22	1.22	0.006	0.0010	0.027	0.0027	0.0042	0.0021	0.005	0	0	0	0	0	0	0	0	0	0	2.70
22	0.05	0.30	1.17	0.005	0.0005	0.031	0.0016	0.0039	0.0017	0.014	0	0	0.16	0.23	0.21	0.09	0	0	0.0017	0.0009	3.20
23	0.13	0.28	1.13	0.006	0.0005	0.045	0.0028	0.0045	0.0028	0.006	0	0.026	0.30	0.19	0	0.04	0.017	0	0	0	5.60
24	0.07	0.32	1.44	0.006	0.0009	0.025	0.0036	0.0047	0.0021	0.011	0	0	0.15	0.23	0.28	0.09	0.010	0	0.0021	0.0011	4.00
25	0.12	0.23	1.17	0.004	0.0005	0.035	0.0019	0.0032	0.0015	0	0	0.025	0.20	0.15	0	0.07	0.013	0	0	0	3.80
26	0.08	0.25	1.41	0.009	0.0008	0.042	0.0032	0.0042	0.0019	0.012	0	0	0	0	0	0	0	0	0	0	4.00
27	0.06	0.31	1.14	0.005	0.0009	0.034	0.0015	0.0040	0.0015	0.013	0	0	0.15	0.23	0.20	0.09	0	0	0.0013	0.0009	1.67
28	0.08	0.25	1.41	0.009	0.0008	0.042	0.0032	0.0042	0.0019	0.012	0	0	0	0	0	0	0	0	0	0	4.00
29	0.12	0.19	1.36	0.006	0.0007	0.039	0.0019	0.0055	0.0032	0	0	0	0	0	0	0.25	0	0	0	0	2.71
30	0.06	0.30	1.55	0.012	0.0012	0.026	0.0028	0.0058	0.0023	0.014	0	0.068	0	0	0.25	0	0.039	0	0.0013	0.0011	2.17
31	0.04	0.42	0.96	0.006	0.0005	0.028	0.0035	0.0035	0.0025	0.015	0	0	0	0	0.37	0	0.018	0	0	0	7.00

[Table 2]

No.	Continuous casting			Hot rolling/cooling method	Cmax/Cave	HIC resistance CLR	Toughness Upper shelf energy (J)
	(1) Flow channel cross-sectional area	(2) Ar blow in	(3) Solidifying rate				
1	○	○	○	TMCP	1.01	○	147
2	○	○	○	TMCP	1.10	○	146
3	○	○	○	TMCP	1.14	○	139
4	○	○	○	TMCP	1.17	○	127
5	○	○	○	TMCP	1.09	○	142
6	○	○	○	TMCP	1.16	○	138
7	○	○	○	TMCP	1.19	○	135
8	○	○	○	TMCP	1.13	○	146
9	○	○	○	TMCP	1.04	○	136
10	○	○	○	TMCP	1.07	○	155
11	○	○	○	TMCP	1.10	○	133
12	○	○	○	TMCP	1.01	○	140
13	○	○	○	TMCP	1.05	○	140
14	○	○	○	TMCP	1.02	×	144
15	×	○	○	TMCP	1.28	○	67
16	○	×	○	TMCP	1.22	○	96
17	○	×	○	TMCP	1.24	○	99
18	○	×	○	TMCP	1.21	○	117
19	○	×	○	TMCP	1.21	○	98
20	○	×	×	TMCP	1.27	×	65
21	○	○	×	TMCP	1.21	○	117
22	○	○	○	QT	1.12	○	142
23	○	○	○	QT	1.08	○	147
24	○	○	○	QT	1.05	○	143
25	○	○	○	QT	1.15	○	135
26	○	○	○	QT	1.11	○	137
27	○	○	○	QT	1.18	×	132
28	×	○	○	QT	1.22	○	113
29	○	×	○	QT	1.23	○	102
30	○	×	×	QT	1.26	×	69
31	○	○	×	QT	1.21	○	112

[0058] From Table 1 and Table 2, followings are found out. It is found out that Nos. 1-13 and Nos. 22-26 are excellent in the HIC resistance and is excellent also in the toughness because the componential composition specified in the present invention is satisfied, and Cmax/Cave of the steel plate surface layer part satisfies the range specified in the present invention.

[0059] On the other hand, Nos. 14 and 27 resulted to be poor in the HIC resistance because the componential composition (Ca/S) deviated from the stipulation of the present invention although Cmax/Cave of the steel plate surface layer part satisfied the range specified in the present invention. Also, in Nos. 15-21 and Nos. 28-31, because Cmax/Cave of the steel plate surface layer part did not satisfy the range specified in the present invention, the toughness became poor. In Nos. 15-19, 21, 28, 29, and 31 in particular, although the HIC resistance could be secured, the toughness became poor.

[0060] Fig. 2 is a drawing showing the relationship between Cmax/Cave and the upper shelf energy obtained using the result of the Table 2. From this Fig. 2, it is known that Cmax/Cave only has to be made 1.20 or less in order to secure excellent toughness of 125 J or more of the upper shelf energy.

[Industrial Applicability]

[0061] Because the steel plates related to the present invention are excellent in the hydrogen-induced cracking resistance and the toughness, they are used suitably to a line pipe for transportation, a pressure vessel, a storage tank and the like of natural gas and crude oil.

Claims

1. A steel plate with excellent hydrogen-induced cracking resistance and toughness, comprising:

C: 0.02-0.15% (% means mass%, hereinafter the same);
Si: 0.02-0.50%;
Mn: 0.6-2.0%;
P: over 0% and 0.030% or less;
S: over 0% and 0.003% or less;
Al: 0.010-0.08%;
Ca: 0.0003-0.0060%;
N: 0.001-0.01%; and
O (oxygen): over 0% and 0.0045% or less,
with the remainder consisting of iron and inevitable impurities;
wherein
the ratio of the Ca and the S (Ca/S) is 2.0 or more, and
the ratio of the maximum Ca concentration (Cmax) of a region from the surface to 5 mm depth in the plate thickness direction and the average Ca concentration (Cave) in the region (Cmax/Cave) is 1.20 or less.

2. The steel plate according to claim 1, further comprising, as other elements, at least one element selected from at least either group of (a) and (b) below.

(a) A group consisting of:

B: over 0% and 0.005% or less;
V: over 0% and 0.1% or less;
Cu: over 0% and 1.5% or less;
Ni: over 0% and 1.5% or less;
Cr: over 0% and 1.5% or less;
Mo: over 0% and 1.5% or less; and
Nb: over 0% and 0.06% or less

(b) A group consisting of:

Ti: over 0% and 0.03% or less;
Mg: over 0% and 0.01% or less;
REM: over 0% and 0.02% or less; and
Zr: over 0% and 0.010% or less

3. The steel plate according to claim 1 or 2 used for a line pipe.

4. The steel plate according to claim 1 or 2 used for a pressure vessel.

5. A steel pipe for a line pipe manufactured using the steel plate according to claim 1 or 2.

FIG. 1

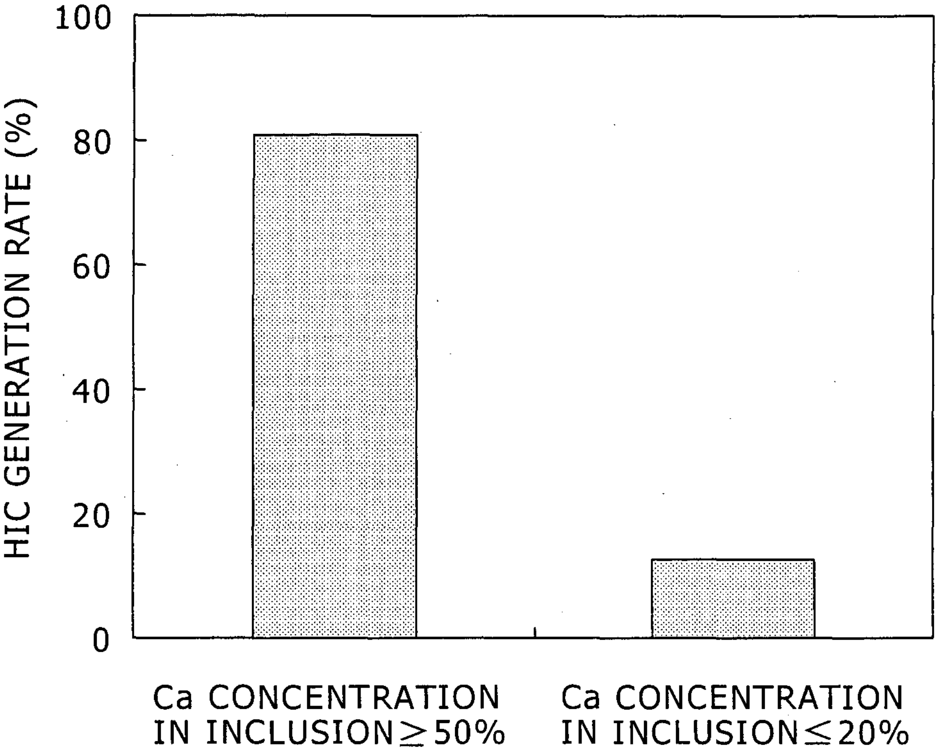
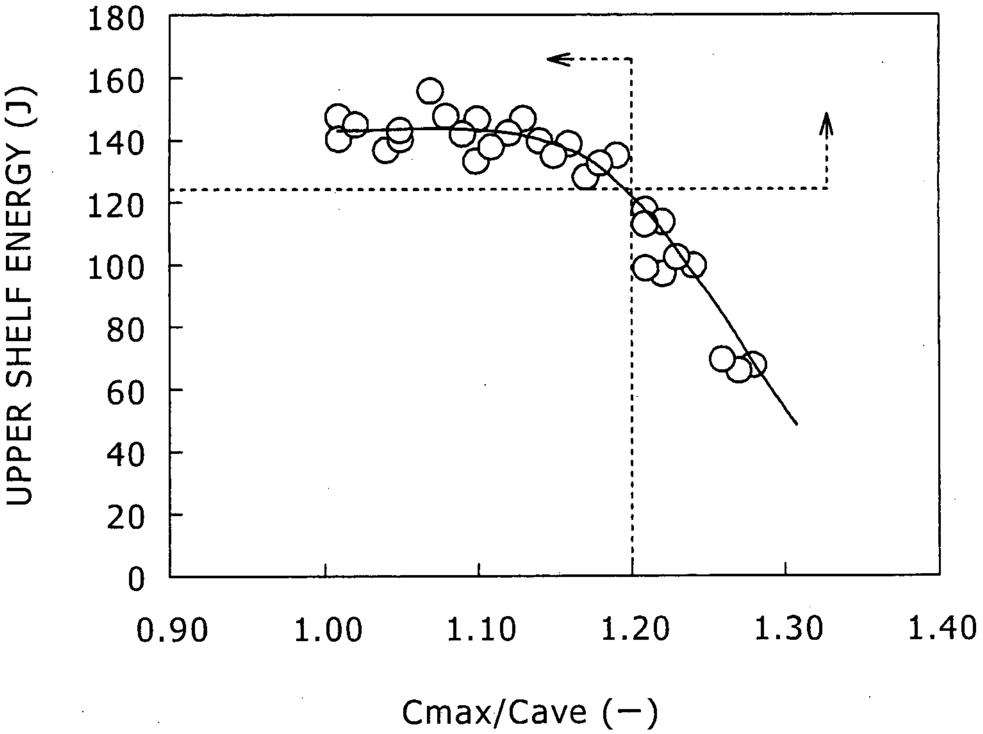

HIC GENERATION RATE (%)
100
80
60
40
20
0
Ca CONCENTRATION IN INCLUSION≥50%
Ca CONCENTRATION IN INCLUSION≤20%

FIG.2


180
160
140
120
100
80
60
40
20
0
UPPER SHELF ENERGY (J)
0.90
1.00
1.10
1.20
1.30
1.40
Cmax/Cave (−)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/058222

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/06*(2006.01)i, *C22C38/58*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00, C22C38/06, C22C38/58

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	1996-2014
Kokai Jitsuyo Shinan Koho	1971-2014	Toroku Jitsuyo Shinan Koho	1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2002-348609 A (NKK Corp.), 04 December 2002 (04.12.2002), entire text (Family: none)	1-5
A	JP 55-128536 A (Sumitomo Metal Industries, Ltd.), 04 October 1980 (04.10.1980), entire text & US 4325748 A & GB 2049729 A & DE 3012188 A & FR 2452526 A & IT 1128245 B & IT 8067470 D0	1-5
A	JP 2009-136909 A (JFE Steel Corp.), 25 June 2009 (25.06.2009), 0001, 0010 (Family: none)	1-5

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

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
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"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 03 June, 2014 (03.06.14)	Date of mailing of the international search report 10 June, 2014 (10.06.14)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/058222

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-109947 A (Nippon Steel Corp.), 18 April 2000 (18.04.2000), 0001, 0002, 0009 (Family: none)	1-5

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

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- JP 2010209461 A **[0005]**
- JP HEISEI06136440 A **[0005]**
- JP 2013073310 A **[0049]**