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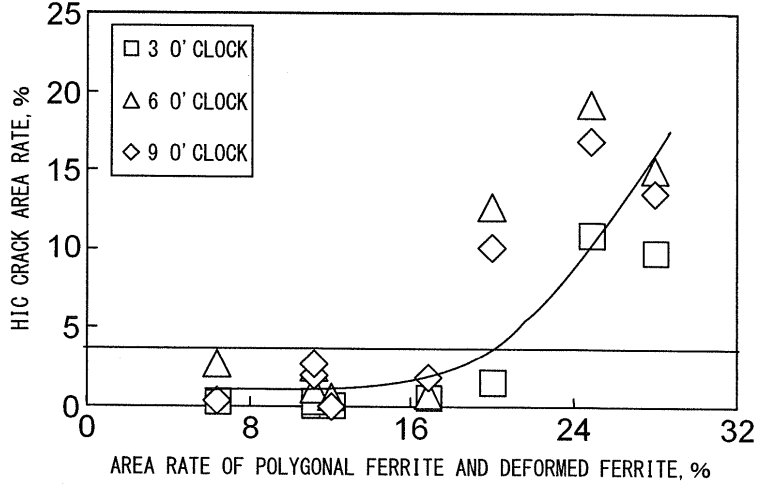
(54) HIGH-STRENGTH STEEL PIPE FOR LINE PIPE HAVING EXCELLENT HYDROGEN-INDUCED CRACKING RESISTANCE, HIGH-STRENGTH STEEL PIPE FOR LINE PIPE USING SAME, AND METHOD FOR MANUFACTURING SAME

(57) Steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance which can prevent cracking at the surface layer of steel pipe even if the ratio of thickness and outside diameter is 0.035 or more, characterized in that it has a predetermined chemical composition, has a maximum hardness of a surface layer region from the topmost surface of two front and back plate surfaces down to depth of 5 mm of 300Hv or less, and has a total fraction of polygonal ferrite and deformed ferrite with an aspect ratio of 3 or more at the surface layer region from the topmost surface of the two front and back plate surfaces down to depth of 5 mm of 0.1 to 20%.

FIG. 2



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Description

Technical Field

[0001] The present invention relates to steel pipe for line pipe use of the API standard X60 to X80 (TS=500 to 650 MPa) which is excellent in hydrogen induced crack resistance (below, referred to as "HIC resistance") and optimal for applications such as line pipe for transportation of oil, natural gas, etc. and to steel plate for line pipe use which is used for the same.

Background Art

[0002] An environment in which wet hydrogen sulfide (H_2S) gas is present (below, referred to as a "sour environment") is formed in the drilling, production, and transportation of oil and natural gas. The steel pipe which is used there is exposed to the sour environment. If the line pipe for transportation of oil, natural gas, etc. is exposed to a sour environment, hydrogen induced cracking (below, referred to as "HIC") may occur. This is because in a sour environment, hydrogen easily penetrates the steel from its surface.

[0003] HIC is due to the hydrogen which accumulates around the elongated MnS which is present at the centerline segregation of steel, accumulated carbonitrides of Ti or Nb or oxide-based inclusions in the oxide accumulation zone, and other defects in the steel.

[0004] In a sour environment, the hydrogen which penetrates the steel accumulates around defects to form a gas. If the stress intensity factor (K_I) due to that pressure exceeds the stress intensity factor (K_{IH}) of the steel which contains the hydrogen, HIC will occur. Furthermore, if the centerline segregation of the steel, the surroundings of inclusions, etc. harden, the HIC will easily propagate. Therefore, in the past, various proposals have been made regarding the line pipe which is used in a sour environment so as to improve the HIC resistance such as the suppression of the formation of elongated MnS, the accumulation of carbonitrides of Ti and Nb, and the accumulation of oxides and, further, suppression of the formation of hard phases due to center segregation.

[0005] PLTs 1 to 3 disclose methods of improving the HIC resistance by suppressing the segregation of Mn at the center of the steel plate. PLT 1 proposes steel plate which suppresses the ratio of Mn content of the segregated part to the average Mn content in the steel. PLTs 2 and 3 disclose limiting not only the size of Mn segregated spots but also the concentration of P of the segregated part and, furthermore, high strength line pipe using Ca.

[0006] PLT 4 discloses hot rolled steel plate excellent in HIC resistance which focuses on not only segregation of Mn, but also segregation of Nb. In PLTs 5 and 6, a method of suppressing inclusions of carbides, nitrides, etc. of Ti and Nb to improve the HIC resistance is disclosed.

[0007] PLTs 7 and 8 disclose steel pipes which suppress the segregation of Mn, Nb, and Ti and, furthermore, make the maximum hardness of the centerline segregation 300Hv or less to thereby prevent the occurrence of HIC.

Citations List

Patent Literature

[0008]

PLT 1: Japanese Patent Publication No. 6-220577A
PLT 2: Japanese Patent Publication No. 6-256894A
PLT 3: Japanese Patent Publication No. 6-271974A
PLT 4: Japanese Patent Publication No. 2002-363689A
PLT 5: Japanese Patent Publication No. 2006-63351A
PLT 6: Japanese Patent Publication No. 2008-7841A
PLT 7: Japanese Patent Publication No. 2010-209460A
PLT 8: Japanese Patent Publication No. 2010-209461A

Summary of Invention

Technical Field

[0009] As explained above, in the past, there has been much development work relating to suppression of segregation of Mn or control of the morphology of MnS utilizing Ca. However, if just controlling the (maximum Mn content of segregated part)/(average Mn content in steel) or size of Mn segregation spots, it is difficult to completely prevent HIC. Therefore, stricter control is necessary.

[0010] Further, even if segregation of Mn is eliminated, segregation of Nb becomes a problem. For segregation of Nb as well, control of the (maximum Nb content of segregated part)/(average Nb content in steel) alone is not enough. Stricter control is necessary. Further, even if controlling the length of Nb-Ti-C-N-based inclusions or suppressing the planar density and length of (Ti, Nb)(C, N)-based inclusions, with this alone, it was difficult to reliably prevent the occurrence of HIC.

[0011] Furthermore, in recent years, in line pipe, there have been many projects cutting across the deep ocean floor. To prevent the steel pipe from being crushed, steel pipe with extremely high ratios (t/D) of thickness (t) and outside diameter (D) (t/D≥0.035) has been demanded. In production of high t/D steel pipe, when shaping steel plate to steel pipe, shaping strain is applied to the inside and outside surfaces of steel pipe and inclusions are formed near the inside and outside surfaces of the steel pipe. In a sour environment etc., HIC frequently occurs if there are inclusions present near the inside and outside surfaces of the steel pipe. Therefore, production of high t/D steel pipe which can be used in a sour environment was difficult.

[0012] The present invention was made in consideration of the above actual situation and has as its object the provision of steel pipe for line pipe use which is extremely high in t/D, has excellent HIC resistance as steel pipe as a whole, and prevents HIC at the surface layer of the steel plate and therefore is optimal for steel pipe which is used for line pipe laid across deep ocean floors etc. and line pipe steel plate which is used for the same.

Solution to Problem

[0013] The inventors engaged in intensive studies on the conditions for obtaining steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance which has excellent HIC resistance near the inside and outside surfaces of the steel pipe and can prevent HIC at the surface layer even if the t/D is high and the steel plate used for the same.

[0014] To give an excellent HIC resistance near the inside and outside surfaces of steel pipe and prevent HIC at the surface layer even if the t/D is high, it is necessary to not only lower the hardness of the centerline segregation such with conventional steel pipe for line pipe use, but also to lower the hardness of the surface layer region. In general, the surface layer region is fast in cooling rate and easily hardens. The inventors discovered that by optimizing the cooling conditions after rolling steel plate, it becomes possible to make the hardness of the surface layer region of steel plate, which in the past was about 350Hv, 300Hv or less and, as a result, suppress the occurrence of HIC from inclusions near the inside and outside surfaces even with high t/D steel pipe and obtain steel pipe which has excellent HIC resistance near the inside and outside surfaces of steel pipe. The present invention was made based on this discovery and has as its gist the following:

(1) A steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance, a steel plate composing a base material of the steel pipe; the steel plate containing, by mass%, C: 0.02 to 0.08%, Si: 0.01 to 0.5%, Mn: 1.2 to 1.8%, Nb: 0.001 to 0.10%, Ca: 0.0005 to 0.0050%, N: 0.0010 to 0.0060%, O: 0.0001 to 0.0035%, and a balance consisting of Fe and unavoidable impurities, wherein contents are restricted to P: 0.01% or less, S: 0.0020% or less, Al: 0.030% or less, and Ti: 0.030% or less, and contents of S and Ca satisfy S/Ca<0.5; the steel plate satisfying: maximum Mn segregation ratio: 2.0 or less, Nb segregation ratio: 4.0 or less, Ti segregation ratio: 4.0 or less, length of center-porosities at centerline segregation: 0.1 mm or less, maximum hardness of centerline segregation: 300 Hv or less, maximum hardness of surface layer region from topmost surface of two front and back plate surfaces down to depth of 5 mm: 300Hv or less, and a total fraction of polygonal ferrite and deformed ferrite with an aspect ratio of 3 or more at surface layer region from topmost surface of two front and back plate surfaces down to depth of 5 mm: 0.1 to 20%; and thickness "t" [mm] of the steel plate and outside diameter D [mm] of the steel pipe after pipemaking satisfying t≥25 and t/D≥0.035.

(2) The steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance of (1), the steel plate further containing, by mass%, one or more of Ni: 0.01 to 2.0%, Cu: 0.01 to 1.0%, Cr: 0.01 to 1.0%, Mo: 0.01 to 0.60%, W: 0.01 to 1.0%, V: 0.01 to 0.10%, Zr: 0.0001 to 0.050%, Ta: 0.0001 to 0.050%, B: 0.0001 to 0.0020%, REM: 0.0001 to 0.01%, Mg: 0.0001 to 0.01%, Y: 0.0001 to 0.005%, Hf: 0.0001 to 0.005%, and Re: 0.0001 to 0.005%.

(3) The steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance of (1) or (2), wherein there is no deformed ferrite with an aspect ratio of 3 or more at surface layer region from topmost surface of two front and back plate surfaces down to depth of 5 mm.

(4) A steel plate for high strength line pipe use excellent in hydrogen induced crack resistance, the steel plate used for the steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance of (1) or (2).

(5) A steel plate for high strength line pipe use excellent in hydrogen induced crack resistance , the steel plate used for the steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance of (3).

(6) A method of production of a steel plate for high strength line pipe use excellent in hydrogen induced crack

resistance comprising the steps of: a step of producing molten steel containing, by mass%, C: 0.02 to 0.08%, Si: 0.01 to 0.5%, Mn: 1.2 to 1.8%, Nb: 0.001 to 0.10%, Ca: 0.0005 to 0.0050%, N: 0.0010 to 0.0060%, O: 0.0001 to 0.0035%, and a balance consisting of Fe and unavoidable impurities, wherein contents are restricted to P: 0.01% or less, S: 0.0020% or less, Al: 0.030% or less, and Ti: 0.030% or less, contents of S and Ca satisfy S/Ca<0.5, and a content of hydrogen after secondary refining is 2.5 ppm or less; a step of making the molten steel a steel slab by continuous cast; a step of heating the steel slab to 1000°C or more; a step of hot rolling the heated steel slab by a reduction ratio in a recrystallization temperature region of 2 or more and a reduction ratio in the non-recrystallization temperature region of 3 or more to obtain a steel plate; and a cooling step of cooling the steel plate from a 750°C or more to 400 to 600°C, the cooling step including at least two self-reheating treatments making the steel plate rise in temperature, and in the self-reheating treatment, a start temperature of a first self-reheating treatment being 300°C or more, and an end temperature of all self-reheating treatments being less than 750°C.

(7) The method of production of a steel plate for high strength line pipe use excellent in hydrogen induced crack resistance of (6), the molten steel further containing, by mass%, one or more of Ni: 0.01 to 2.0%, Cu: 0.01 to 1.0%, Cr: 0.01 to 1.0%, Mo: 0.01 to 0.60%, W: 0.01 to 1.0%, V: 0.01 to 0.10%, Zr: 0.0001 to 0.050%, Ta: 0.0001 to 0.050%, B: 0.0001 to 0.0020%, REM: 0.0001 to 0.01%, Mg: 0.0001 to 0.01%, Y: 0.0001 to 0.005%, Hf: 0.0001 to 0.005%, and Re: 0.0001 to 0.005%.

(8) A method of production of a steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance, the steel pipe made from the steel plate obtained by the method of production of a steel plate for high strength line pipe use excellent in hydrogen induced crack resistance of (6) or (7), comprising the steps of: a step of shaping the steel plate into a tube shape; and a step of welding both plate edge beveled; wherein a thickness "t" [mm] of the steel plate and an outside diameter D [mm] of the steel pipe after pipemaking pipe satisfy t≥25 and t/D≥0.035. Advantageous Effect of Invention

[0015] The steel pipe for high strength line pipe use and steel plate for high strength line pipe use of the present invention have little segregation of Mn, Nb, and Ti, are suppressed in length of non-pressed bonded parts of the centerline segregation and maximum hardness, and further are suppressed in hardness of surface layer region. As a result, the HIC resistance is reliable and sufficiently excellent and is extremely excellent as a material of line pipe which is used in a sour environment.

Brief Description of Drawings

[0016]

FIG. 1 is a view which shows a relationship between a ratio S/Ca of contents of S and Ca and a length rate of HIC (CLR) in an HIC test.

FIG. 2 is a view which shows a relationship between a total area rate of polygonal ferrite and deformed ferrite and an area rate of HIC in an HIC test.

FIG. 3A is a view which shows an example of a cooling pattern of steel plate in a method of production of the present invention.

FIG. 3B is a view which shows another example of a cooling pattern of steel plate in a method of production of the present invention.

FIG. 3C is a view which shows an example of a cooling pattern of steel plate in a conventional method of production.

FIG. 4A is a SEM image of the surface layer structure of steel pipe for line pipe use of the present invention.

FIG. 4B is a view which shows the hardness distribution of the surface layer structure of steel pipe for line pipe use of the present invention.

FIG. 5A is a SEM image of the surface layer structure of conventional steel pipe for line pipe use.

FIG. 5B is a view which shows the hardness distribution of the surface layer structure of conventional steel pipe for line pipe use.

Description of Embodiments

[0017] Below, the present invention will be explained in detail.

[0018] The steel pipe for line pipe use of the present invention has a thickness "t" of steel plate [mm] and outside diameter D of steel pipe after pipemaking [mm] satisfying t≥25 and t/D≥0.035. The segregation ratios of Mn, Nb, and Ti, the length and maximum hardness of the non-press-bonded part at the centerline segregation and the maximum hardness and structure of the surface layer region from the two front and back surfaces down to a depth of 5 mm are suitably prescribed.

[0019] First, the reasons for limitation of the composition of components of the steel base material which is used for the steel pipe and steel plate of the present invention will be explained. Below, "%" all indicate mass%.

C: 0.02 to 0.08%

[0020] C is an element which improves the strength of steel. 0.02% or more has to be added. If the amount of C exceeds 0.08%, the formation of carbides is promoted and the HIC resistance deteriorates. To secure a more superior HIC resistance and suppress the drop in weldability and toughness, the amount of C is preferably made 0.06% or less.

Si: 0.01 to 0.5%

[0021] Si is a deoxidizing element. 0.01% or more has to be added. If the amount of Si exceeds 0.5%, the toughness of the heat affected zone (HAZ) deteriorates.

Mn: 0.8 to 1.8%

[0022] Mn is an element which improves the strength and toughness. 0.8% or more has to be added. If the amount of Mn exceeds 1.8%, the HIC resistance deteriorates. To further suppress HIC, the amount of Mn is preferably made 1.6% or less.

Nb: 0.001 to 0.10%

[0023] Nb is an element which forms carbides and nitrides, promotes finer grains of the steel plate as rolled, and contributes to the improvement of strength. To obtain this effect, 0.0001% or more of Nb has to be added. If excessively adding Nb, the maximum Nb segregation ratio increases, the accumulation of carbonitrides of Nb is invited, and the HIC resistance deteriorates, so the upper limit of the amount of Nb is made 0.10%. If improving the HIC resistance more, the amount of Nb is preferably made 0.05% or less.

Ca: 0.0005 to 0.0050%

[0024] Ca is an element which forms the sulfide CaS, suppresses the formation of MnS which flattens in the rolling direction, and remarkably contributes to improvement of the HIC resistance. If the amount of addition of Ca is less than 0.0005%, the effect is not obtained. If the amount of addition of Ca exceeds 0.0050%, the oxides accumulate and the HIC resistance deteriorates.

N: 0.0010 to 0.0060%

[0025] N is an element which forms TiN, NbN, and other nitrides. To utilize nitrides to refine the austenite grain size at the time of heating, the amount of addition of N has to be made 0.0010% or more. If the content of N exceeds 0.0060%, carbonitrides of Ti and Nb easily accumulate and the HIC resistance deteriorates. When toughness is demanded, to suppress coarsening of TiN, the amount of N is preferably made 0.0035% or less.

O: 0.0001 to 0.0035%

[0026] O is an impurity. To suppress the accumulation of oxides and improve the HIC resistance, it is restricted to 0.0035% or less. To suppress the formation of oxides and improve the base material and HAZ toughness, the amount of O is preferably made 0.0035% or less, more preferably 0.0020% or less. The smaller the amount of O the better, but to make it less than 0.0001%, the refining time becomes long and the cost rises, so the lower limit is made 0.0001%.

P: 0.01% or less

[0027] P is an impurity. If the content exceeds 0.01%, the HIC resistance deteriorates. Further, the HAZ toughness deteriorates. Therefore, the content of P is restricted to 0.01% or less.

S: 0.020% or less

[0028] S is an element which forms MnS which is elongated in the rolling direction at the time of hot rolling and thereby lowers the HIC resistance. In the present invention, the amount of S has to be reduced to 0.0020% or less. To improve the HIC resistance characteristic, the amount of S is preferably made 0.0010% or less. The smaller the amount of S, the better, but making it less than 0.0001% is difficult. From the viewpoint of the manufacturing cost, the lower limit is preferably made 0.0001% or more.

Al: 0.030% or less

[0029] Al is a deoxidizing element, but if the amount of addition exceeds 0.030%, accumulated clusters of Al oxides are formed. When particularly good toughness is demanded, the amount of Al is preferably made 0.017% or less. The lower limit value of the amount of Al is not particularly set, but to reduce the amount of oxygen in the molten steel, Al is preferably added in an amount of 0.0005% or more.

Ti: 0.030% or less

[0030] Ti is an element which is usually utilized as a deoxidizing agent or for refinement of the crystal grains as a nitride-forming element, but is an element which lowers the HIC resistance and toughness due to formation of carbonitrides. Therefore, the content of Ti is restricted to 0.030% or less.

S/Ca<0.5

[0031] In the present invention, by adding Ca and forming CaS, S is fixed and the formation of MnS is suppressed. To obtain excellent HIC resistance, furthermore, the ratio of S/Ca has to be suitably restricted. FIG. 1 shows the relationship between the CLR (length ratio of HIC) and S/Ca in an HIC test of 0.04%C-1.25%Mn steel. As shown in FIG. 1, if the ratio of S/Ca becomes 0.5 or more, HIC is formed. If the ratio of S/Ca becomes 0.5 or more, MnS is formed and MnS which is elongated at the time of rolling is formed. As a result, the HIC resistance deteriorates. Therefore, the ratio of S/Ca has to be made less than 0.5.

[0032] In addition, the steel pipe for line pipe use and the steel plate for line pipe use of the present invention may, in accordance with need, have one type or two types or more of elements selected from Ni, Cu, Cr, Mo, W, V, Zr, Ta, and B added to them as elements which improve the strength and toughness. The reasons for limitation of the amounts of addition of these optional added elements are as follows:

Ni: 0.01 to 2.0%

[0033] Ni is an element which is effective for improvement of toughness and strength. To obtain this effect, 0.01% or more has to be added. If the amount of addition of Ni exceeds 2.0%, the HIC resistance and weldability deteriorate.

Cu: 0.01 to 1.0%

[0034] Cu is an element which is effective for improvement of the strength without causing a drop in toughness. To obtain this effect, 0.01% or more has to be added. If the amount of addition of Cu exceeds 1.0%, cracking easily occurs at the time of heating a steel slab or at the time of welding.

Cr: 0.01 to 1.0%

[0035] Cr is an element which improves the strength of steel by precipitation strengthening. To obtain this effect, 0.01% or more has to be added. If the amount of addition of Cr exceeds 1.0%, the hardenability rises, a bainite structure is formed, and as a result the HIC resistance and toughness fall.

Mo: 0.01 to 0.60%

[0036] Mo is an element which improves the hardenability and simultaneously forms carbonitrides and improves the strength. To obtain this effect, 0.01% or more has to be added. If the amount of addition of Mo exceeds 0.60%, the cost rises. If the steel excessively rises in strength, the HIC resistance and toughness sometimes deteriorate, so the amount of addition of Mo is 0.20% or less.

W: 0.01 to 1.0%

[0037] W is an element which is effective for improvement of strength. To obtain this effect, 0.01% or more has to be added. If the amount of addition of W exceeds 1.0%, the toughness sometimes deteriorates.

Zr: 0.0001 to 0.050%

[0038] Zr, like V, is an element which forms carbides and nitrides and contributes to improvement of the strength. To obtain this effect, 0.0001% or more has to be added. If the amount of addition of Zr exceeds 0.050%, the toughness sometimes deteriorates.

Ta: 0.0001 to 0.050%

[0039] Ta also, like V, is an element which forms carbides and nitrides and contributes to improvement of the strength. To obtain this effect, 0.0001% or more has to be added. If the amount of addition of Ta exceeds 0.050%, the toughness sometimes deteriorates.

B: 0.0001 to 0.0020%

[0040] B is an element which segregates at the grain boundaries of the steel and remarkably contributes to improvement of the hardenability. To obtain this effect, 0.0001% or more of B has to be added. B is an element which forms BN, causes solid solution N to fall, and contributes to improvement of the toughness of the heat affected zone, so 0.0005% or more is preferably added. If the amount of addition of B exceeds 0.0020%, segregation at the grain boundaries is suppressed and the toughness sometimes deteriorates.

[0041] Furthermore, the steel pipe for line pipe use and steel plate for line pipe use of the present invention may in accordance with need have one type or two types or more of a REM (rare earth metal), Mg, Y, Hf, and Re added to them so as to control the oxides, sulfides, and other inclusions. The reasons for limitation of the amounts of addition of these optional added elements are as follows:

REM (Rare Earth Metal): 0.0001 to 0.01%

[0042] An REM is an element which is added as a deoxidizing agent and a desulfurizing agent. To obtain this effect, 0.0001% or more has to be added. If the amount of addition of REM exceeds 0.010%, coarse oxides are formed and the HIC resistance and the toughness of the base material and HAZ sometimes fall.

Mg: 0.0001 to 0.01%

[0043] Mg is an element which is added as a deoxidizing agent and a desulfurizing agent. In particular, it forms fine oxides which contributes to improvement of the HAZ toughness. To obtain this effect, adding 0.0001% or more of Mg is necessary. If the amount of addition of Mg exceeds 0.010%, oxides easily accumulate and coarsen and the HIC resistance and base material and HAZ toughness sometimes fall.

Y: 0.0001 to 0.005%

[0044] Y, like Ca, is an element which forms sulfides, suppresses the formation of MnS elongated in the rolling direction, and contributes to improvement of the HIC resistance. To obtain such an effect, it is necessary to add Y in an amount of 0.0001% or more. If the amount of addition of Y exceeds 0.005%, oxides increase, accumulate, and coarsen and the HIC resistance deteriorates.

Hf: 0.0001 to 0.005%

[0045] Hf, like Ca, is an element which forms sulfides, suppresses the formation of MnS elongated in the rolling direction, and contributes to improvement of the HIC resistance. To obtain such an effect, it is necessary to add Hf in an amount of 0.0001% or more. On the other hand, if the amount of addition of Hf exceeds 0.005%, oxides increase, accumulate, and coarsen and the HIC resistance deteriorates.

Re: 0.0001 to 0.005%

[0046] Re, like Ca, is an element which forms sulfides, suppresses the formation of MnS elongated in the rolling direction, and contributes to improvement of the HIC resistance. To obtain such an effect, it is necessary to add Re in an amount of 0.0001% or more. If the amount of addition of Re exceeds 0.005%, oxides increase, accumulate, and coarsen and the HIC resistance deteriorates.

[0047] The balance other than the above elements is Fe and unavoidable impurities. Note that, the above-mentioned

Ni, Cu, Cr, Mo, W, V, Zr, Ta, and B may all be contained in fine amounts of less than the above lower limit values as impurities. Further, REM, Mg, Y, Hf, and Re may also be contained in extremely fine amounts of less than the lower limit values as impurities.

[0048] Next, the structures of the steel pipe and steel plate for line pipe use of the present invention will be explained.

[0049] Maximum Mn Segregation Ratio: 2.0 or less, Nb Segregation Ratio: 4.0 or less, Ti Segregation Ratio: 4.0 or less HIC is due to the hydrogen which accumulates around the elongated MnS present at the centerline segregation of the steel, the accumulated carbonitrides of Ti and NB, etc.

[0050] To suppress elongated coarse MnS, the maximum Mn segregation ratio of the steel plate and steel pipe has to be made 2.0 or less. Furthermore, by suppressing segregated carbonitrides of Ti and Nb, it is possible to remarkably prevent the occurrence of HIC of the steel pipe for line pipe use and steel plate for line pipe use.

[0051] To suppress segregated carbonitrides of Ti and Nb, it is sufficient to make the amount of N 0.0050% or less, the amount of C 0.06% or less, and the maximum segregation ratio of Nb and Ti 4.0 or less.

[0052] The "maximum Mn segregation ratio" is the maximum amount of Mn at the centerline segregation compared with the average amount of Mn in the distribution of concentration of Mn in the plate thickness direction of steel plate and in the distribution of concentration of Mn in the thickness direction of the pipe wall of steel pipe. Similarly, the Nb segregation ratio and the Ti segregation ratio are the averaged maximum amount of Nb (amount of Ti) at the centerline segregation compared with the average amount of Nb (amount of Ti) in the distributions of concentration of Nb and Ti in the plate thickness direction of steel plate and in the distributions of concentration of Nb and Ti in the thickness direction of the pipe wall of steel pipe.

[0053] The maximum Mn segregation ratio is found by measuring the distribution of concentration of Mn of steel plate and steel pipe by an EPMA (electron probe micro analyzer) or CMA (computer aided micro analyzer) able to perform image processing on the measurement results of the EPMA. The measured object is an HIC test piece (20 mm widthx20mm thickness machined from both surface of full thickness×100 mm length), while a region of the HIC test piece of 20 mm width (test piece width)x20mm thickness machined from both surface of full thickness (HIC) test piece thickness was made the measurement region. For the Nb segregation ratio and the Ti segregation ratio as well, the same region may be measured by EPMA or CMA to measure the distribution of concentration of Nb and the distribution of concentration of Ti. The probe diameter of the EPMA (or CMA) is made 2 μm.

[0054] The maximum Mn segregation ratio is found by measuring the concentration of Mn using an EPMA by a 50 μm beam diameter in a measurement region of a 20 mm width (HIC test piece width)x20mm thickness machined from both surface of full thickness (HIC test piece thickness) at equal intervals in the plate thickness direction and plate width direction to measure the distribution of concentration of Mn and make the average value at the measured distribution of concentration of Mn the average Mn concentration. Next, a region of 1 mm (width)×1 mm (thickness) including the location of the greatest concentration of the amount of Mn was measured for 50 points × 50 points of Mn concentration at equal intervals in the plate thickness direction and plate width direction while changing the beam diameter to 2 μm. The maximum Mn concentration was found from the distribution. Further, the ratio of the maximum Mn concentration which is obtained by a 2 μm beam diameter and the average Mn concentration which is obtained by a 50 μm beam diameter is defined as the "maximum Mn segregation ratio".

[0055] The Nb segregation ratio and the Ti segregation ratio are similarly found by measuring the distributions of concentration of Nb and Ti using an EPMA by a 50 μm beam diameter in a measurement region of a 20 mm width (HIC test piece width)x20mm thickness machined from both surface of full thickness (HIC test piece thickness), then measuring the concentrations of Nb and Ti by a 2 μm beam diameter in the region of 1 mm (width)×1 mm (thickness) of the locations where the amounts of Nb and Ti are most concentrated.

[0056] If there are carbonitrides of Nb and Ti and other inclusions present, the segregation ratio sometimes becomes larger in appearance, but if there are inclusions, it is possible to judge these as regions where the peaks sharply rise in the distributions of concentration of Nb and Ti, so the segregation ratios are found after subtracting the measurement values of these regions.

[0057] Next, the specific method for suppressing the maximum Mn segregation ratio, Nb segregation ratio, and Ti segregation ratio will be explained.

[0058] To suppress Mn, Nb, and Ti, soft reduction at the time of the final solidification at continuous casting is optimum. The soft reduction at the time of final solidification is performed for eliminating the mixture of solidified parts and nonsolidified parts due to uneven cooling during casting. Due to this, it is possible to eliminate the spaces accompanying shrinkage upon solidification to keep down the flow of molten steel at the unsolidified parts to cause uniform solidification of the steel slab.

[0059] Further, if applying soft reduction after nonuniform solidification occurs in the width direction, it becomes no longer possible to suppress flow of molten steel at the non-solidified parts due to the large deformation resistance of the solidified parts. Therefore, to prevent such W-type solidification from occurring, it is preferable to perform soft reduction while controlling the amount of reduction in accordance with the distribution of the center solidified phase rate in the width direction at the final solidified position of the cast slab. Due to this, center segregation is suppressed even in the width direction, and the maximum Mn segregation ratio, Nb segregation ratio, and Ti segregation ratio can be made further smaller.

Length of Center-porosities of Centerline segregation: 0.1 mm or less

[0060] If the centerline segregation of the steel plate has a center-porosity of a length of 0.1 mm or more, it becomes a starting point of HIC and the HIC resistance deteriorates. A "center-porosity" is a space which is formed in a steel slab at the time of solidification which is not press-bonded due to hot rolling, but remains in the steel plate. The length of a center-porosity can be measured by an ultrasonic or other nondestructive test.

[0061] The cause of center-porosities remaining at the centerline segregation is mainly the hydrogen which is contained in the steel slab before hot rolling. When producing steel by a converter and secondary refining, then continuously casting it, the steel solidifies and shrinks upon cooling, so spaces are easily formed in particular at the center part of the steel slab. If the spaces are negative in pressure, if the amount of hydrogen which is contained in the steel slab is large, the hydrogen gas will penetrate into the spaces. The hydrogen which is contained in the steel when produced by secondary refining remains almost as is in the spaces in the steel slab after continuous casting.

[0062] At the time of heating for hot rolling after continuous casting, the structure of the steel slab is austenite with a large amount of hydrogen which can form a solid solution in a face-centered cubic structure, so the hydrogen is not dispersed to the outside of the steel slab. If heating the steel slab and reducing it by hot rolling, the spaces inside the steel slab become smaller, but the pressure of the hydrogen gas which is contained in the spaces becomes higher in reverse proportion to the size of the spaces. Therefore, it is not possible to press bond the spaces due to the hot rolling. Center-porosities remain inside the steel plate, in particular, the centerline segregation.

[0063] The inventors investigated in detail the relationship between the amount of hydrogen in the steel and the length of the center-porosities and as a result learned that if suppressing the amount of hydrogen in the steel to 2.5 ppm or less, the length of the center-porosities which remain at the centerline segregation of the steel plate becomes 0.1 mm or less. The amount of hydrogen in the steel which is referred to here was found by measuring the molten steel which was sampled after secondary refining by the combustion method.

[0064] To reduce the amount of hydrogen in the secondary refining, it is sufficient to reduce the hydrogen partial pressure in the atmosphere when performing the secondary refining. For example, by blowing an inert gas, nitrogen, etc. into the atmosphere, it is possible to lower the hydrogen partial pressure.

[0065] Note that, the amount of hydrogen which remains in the steel plate after hot rolling decreases compared with the amount of hydrogen after the secondary refining since the hydrogen is dispersed to the outside if the steel plate is cooled and the metal structure transforms from austenite to ferrite, bainite, martensite, pearlite, etc.

Maximum Hardness of Centerline segregation: 300Hv or less

[0066] For improvement of the HIC resistance, it is effective to make the maximum hardness of the centerline segregation 300Hv or less. By making the upper limit of the maximum hardness of the centerline segregation 300Hv or less, it is possible to reliably prevent occurrence of HIC. The maximum hardness of the centerline segregation is measured by a Vicker's hardness test at a 25 g load based on JIS Z 2244 after corrosion by a Nital solution which consists of 3% nitric acid and 97% ethanol. The "centerline segregation" is a portion where the concentration of Mn which is measured by EPMA or CMA becomes maximum.

Maximum Hardness of Surface Layer Region From Topmost Surface of Two Front and Back Plate Surfaces Down to 5 mm: 300Hv or less

[0067] If making the maximum hardness of the region from the topmost surfaces of the front and back plate surfaces at the steel plate (rolling surfaces) down to 5 mm in the thickness direction of the plate (surface layer region) and the region from the topmost surfaces of the inside and outside of the steel pipe down to 5 mm in the thickness direction of the pipe walls (depth direction) both 300Hv or less, the HIC resistance can be reliably raised. That is, by making the upper limit of the maximum hardness of the surface layer region from the topmost surface down to 5 mm 300Hv or less, even in steel pipe for line pipe use with a high t/D of 0.035 or more, it is possible to reliably prevent the occurrence of HIC due inclusions, blisters, etc. at the surface layer. The maximum hardness of the surface layer region is found by conducting a Vicker's hardness test at predetermined intervals in the depth direction (for example, 0.1 mm intervals) from the topmost surface to a position of a depth of 5 mm and using the highest value among the values as the maximum hardness. Specifically, this is investigated by corroding the surface by a Nital solution which consists of 0.13% nitric acid and 97% ethanol, then conducting a Vicker's hardness test based on JIS Z 2244 by a 25 g load at 50 points x 50 points at 0.1 mm intervals from the topmost surface to a position at a depth of 5 mm.

[0068] Total Fraction of Polygonal Ferrite and Deformed Ferrite With Aspect Ratio of 3 or More at Surface Layer

Region From Topmost Surfaces of Two Front and Back Plate Surfaces Down to Depth of 5 mm: 0.1 to 20% To improve the HIC resistance, basically, the steel structure of the base material is preferably a uniform and fine acicular ferrite or bainite structure. Therefore, the structure of the steel base material for high strength line pipe of the present invention considering the HIC resistance is basically preferably bainite or acicular ferrite. However, heavy wall pipe for line pipe use often is required to have properties able to withstand a drop weight test such as DWTT.

[0069] In the case of heavy wall pipe, in the structure of conventional steel pipe for line pipe use, properties able to withstand a drop weight test such as DWTT cannot be obtained, but if forming 0.1% or more polygonal ferrite or deformed ferrite, the DWTT characteristics are improved. However, if the structure becomes one of a total fraction of polygonal ferrite and deformed ferrite of the surface layer region of over 20%, the HIC resistance rapidly deteriorates.

[0070] FIG. 2 shows a relationship between a total area rate of polygonal ferrite and deformed ferrite at the surface layer of steel pipe and an area rate of HIC. In the figure, 3 o'clock, 6 o'clock, and 9 o'clock are positions in the circumferential direction of the steel pipe from which the test piece is taken. The weld zone was made 0 o'clock. Test pieces were taken from positions of 3 o'clock (90°), 6 o'clock (180°), and 9 o'clock (270°) as seen from the bottom part of the steel pipe and observed for structure.

[0071] If the total area ratio of polygonal ferrite and deformed ferrite at the surface layer exceeds 20%, the HIC area ratio greatly exceeds 3%. Therefore, even when the surface layer region contains polygonal ferrite and deformed ferrite, to reliably improve the HIC resistance, it is preferable to suppress the total fraction of the polygonal ferrite and the deformed ferrite to an area ratio of 20% or less. From the viewpoint of the HIC resistance, the smaller the deformed ferrite the better. The fraction of the deformed ferrite is preferably an area ratio of 10% or less. Absence is more preferable.

[0072] The method of measurement of the fractions of the polygonal ferrite and deformed ferrite is to take five 200X optical micrographs, extract the polygonal ferrite and deformed ferrite, and find the values by image analysis. When observed by a 200X optical microscope, the white regions are polygonal ferrite or deformed ferrite. Regions with an aspect ratio (ratio of horizontal length and vertical length) of less than 3 are defined as polygonal ferrite, while regions with an aspect ratio of 3 or more are defined as deformed ferrite.

[0073] Here, to suppress the total fraction of the polygonal ferrite and deformed ferrite at the surface layer region to 0.1% to 20%, the later explained method of production may be used. That is, if making the rolling end temperature and/or water cooling start temperature 750°C or more, it is possible to make the fraction of the polygonal ferrite and deformed ferrite at the surface layer region 20% or less. However, if the rolling end temperature and/or the water cooling start temperature decreases below 750°C, the polygonal ferrite and deformed ferrite of the surface layer region increase exceeding 20% as a general trend, so the rolling end temperature and/or the water cooling start temperature preferably is made 750°C or more. Further, to make the fraction of the polygonal ferrite and deformed ferrite 10% or less, it is more preferable to make the rolling end temperature or the water cooling start temperature 770°C or more.

[0074] The above "fraction" means the area rate when observing the L cross-section (surfaces in plate thickness direction and rolling direction). Further, the structure other than the above polygonal ferrite and deformed ferrite, that is, the structure accounting for 80% or more of the area of the surface layer region, should be bainite and/or acicular ferrite pearlite.

[0075] The structure at the inside from the above surface layer region is not particularly limited, but to secure properties for steel plate and steel pipe for high strength line pipe use with a tensile strength of 500 MPa or more such as base material high strength, base material toughness, HAZ toughness, weldability, etc., it is sufficient to make the structure mainly acicular ferrite or bainite.

[0076] Next, the preferable method for producing the steel plate for line pipe use and the steel pipe for line pipe use of the present invention will be explained.

[0077] In the steelmaking process, steel which has the above-mentioned chemical composition is produced by an ordinary method so that the amount of hydrogen in the molten steel after secondary refining becomes 2.5 ppm or less, then is continuously cast to obtain a steel slab, then the steel slab is reheated and rolled by heavy plate rolling to obtain steel plate. At the time of continuous casting, as explained above, it is preferable to apply soft reduction while controlling the amount of reduction in accordance with the distribution of the center solidification rate in the width direction at the final solidification position of the cast slab.

[0078] If making the reheating temperature of the steel slab after continuous casting 1000°C or more, making the reduction ratio at the recrystallization temperature region 2 or more, and making the reduction ratio at the non-recrystallization region 3 or more to perform heavy plate rolling, it is possible to make the average old austenite particle size 20 μm or less. After finishing rolling, the steel plate is water cooled by a start temperature of 750°C or more and a stop temperature of 400 to 600°C. The "stop temperature" of water cooling referred to here means the highest temperature of the temperature of the steel plate which rises due to reheating after the cooling water is stopped.

[0079] The recrystallization temperature region is the temperature region where recrystallization occurs after rolling. With the components of the steel of the present invention, it is generally over 900°C. The non-recrystallization temperature region is a temperature region where no recrystallization or ferrite transformation occurs after rolling and is generally 750 to 900°C with the components of the steel of the present invention. The rolling in the recrystallization temperature region is called "recrystallization rolling" or "rough rolling", while the rolling in the non-recrystallization temperature region is called the "non-recrystallization rolling" or "final rolling".

[0080] By starting water cooling from a 750°C or higher temperature after non-recrystallization rolling and making the water cooling stop temperature 400°C or more, the maximum hardness of the centerline segregation can be suppressed to 300Hv or less. If making the water cooling start temperature less than 750°C, a large amount of ferrite is formed before the start of cooling, C (carbon) is discharged from the ferrite to the austenite, and C is concentrated at the austenite phase. As a result, the austenite phase where C concentrates transforms to hard martensite which contains a large amount of C in the cooling process.

[0081] As opposed to this, if making the water cooling start temperature 750°C or more, it is possible to suppress the formation of hard martensite, so it is possible to suppress the maximum hardness of the centerline segregation to 300Hv or less. Further, if making the water cooling stop temperature 400°C or more, after the transformation, the hard martensite partially breaks down, so the maximum hardness of the centerline segregation can be suppressed to 300Hv or less. If the water cooling stop temperature is too high, the steel pipe deteriorates in strength, so the water cooling stop temperature is made 600°C or less.

[0082] Furthermore, to suppress the maximum hardness of the surface layer region from the topmost surface down 5 mm to 300Hv or less, in addition to making the water cooling stop temperature 400°C to 600°C or less, it is necessary to optimize the cooling pattern of the surface layer. Specifically, when cooling the surface layer, by performing reheating treatment at least two times, it is possible to make the maximum hardness from the topmost layer down to 5 mm 300Hv or less. This is because by performing reheating, a tempering effect is exhibited and the surface layer region can be lowered in hardness. The lower limit of the reheating temperature is preferably made 300°C, while the upper limit temperature is preferably 750°C. If the reheating temperature becomes less than 300°C, 50% or more of martensite is formed and hardens and the surface layer no longer deteriorates in hardness. If the reheating temperature exceeds 750°C, the surface layer region deteriorates too much in hardness.

[0083] FIG. 3A and FIG. 3B show examples of cooling patterns of the cooling step in the present invention. In the graph, 1 is the change in temperature due to self-reheating treatment, the temperature of 2 is the reheating start temperature, and the temperature of 3 is the reheating end temperature. In the graph, the temperature of 4 is the water cooling stop temperature. Such a cooling pattern can be controlled by switching the nozzle for spraying cooling water on and off and adjusting the amount of water.

[0084] FIG. 3C shows the cooling pattern by the conventional method of production. After stopping the cooling water, the steel plate rises in temperature, so a single reheating is included.

[0085] Furthermore, by making the above-mentioned water cooling start temperature 750°C or more, the structure of the surface layer region from the topmost surface down to 5 mm can be suppressed to a total fraction of polygonal ferrite and deformed ferrite of 20% or less. If the water cooling start temperature becomes lower than 750°C, it becomes lower than the γ/α-transformation temperature of 500 MPa or more steel, so polygonal ferrite or deformed ferrite is easily formed and the total fraction of polygonal ferrite and deformed ferrite exceeds 20%.

[0086] When using the steel plate which was obtained in the above way to produce steel pipe for line pipe use, the base material steel plate need only be shaped into a tube, then arc welded at both plate edge beveled to obtain a welded steel pipe. Here, as the shaping step, a UOE step of shaping steel plate by a C-press, U-press, and O-press is preferable. Further, as arc welding, from the viewpoint of the toughness of the weld metal and productivity, it is preferable to employ submerged arc welding. The input heat at the time of arc welding is not particularly limited, but is usually preferably 2.0 to 15.0kJ/mm.

[0087] Below, the present invention will be explained in more detail by examples. Note that, the following examples are for showing the specific effects due to the present invention. The conditions which are described in the examples do not limit the technical scope of the present invention of course.

Examples

[0088] The Steels 1 to 35 which have the chemical compositions which are shown in Table 1A to Table 1C were produced and continuously cast to thickness 240 mm or 300 mm steel slabs. Further, Table 1A to Table 1C show analysis values of the amounts of hydrogen of the molten steel.

[0089] In continuous casting, at the time of final solidification, soft reduction is performed by a reduction rate of about 2%. Each obtained steel slab was heated to 1100 to 1250°C, hot rolled at an over 900°C recrystallization temperature region, then hot rolled in the 750 to 950°C non-recrystallization temperature region.

[0090] After hot rolling, water cooling was started from 750°C or more and the water cooling was stopped at 400 to 600°C in temperature. During that time, self-reheating treatment was performed once or twice to raise the temperature of the steel plate. The temperature of the steel plate was raised by stopping the cooling water. The first reheating start and end temperatures and the second reheating start temperature are shown in Table 2A. The second reheating end temperature (when there is a single reheating treatment, the first reheating end temperature) is the cooling end temperature.

[0091] Each obtained steel plate was shaped into a tube by a C press, U press, or O press, the end faces were tack welded, main welding was performed from the inside and outside surfaces, then the tube was expanded to obtain steel pipe for line pipe use. Note that, for the main welding, submerged arc welding was applied.

[0092] Tensile test pieces, HIC test pieces, and macro test pieces were taken from the obtained steel plates and steel pipes and used for the respective tests. The HIC test was performed based on NACETM0284. Further, the macro test pieces were measured for segregation ratios of Mn, Nb, and Ti by EPMA. The segregation ratio was measured by EPMA by probe diameters of 50 μm and 2 μm.

[0093] Further, the Vicker's hardness of the centerline segregation and the Vicker's hardness at the surface layer region from the topmost surface of the steel plate and steel pipe down to a depth of 5 mm were measured based on JIS Z 2244. The Vicker's hardness was measured using a 25 g load at the portion of the highest Mn concentration in the distribution of concentration of Mn in the thickness direction measured by EPMA.

[0094] Furthermore, to identify the microstructure of the surface layer region from the topmost surface down to 5 mm of the steel pipe, five 200X optical micrographs were taken in the L cross-section (surfaces in plate thickness direction and rolling direction), the area ratios (fractions) of the polygonal ferrite and deformed ferrite were measured, and the total fraction of these was calculated.

[0095] Table 2A to Table 2C show the thickness of the steel plate, maximum Mn segregation ratio, Nb segregation ratio, Ti segregation ratio, length of center-porosities, maximum hardness of centerline segregation, maximum hardness of surface region, tensile strength and length ratio of HIC (CLR) found by HIC test, and total fraction of polygonal ferrite and deformed ferrite in surface layer region.

[0096] Table 3 shows the thickness of steel pipe, heat input of main welding, and length ratio of HIC (CLR) found from an HIC test. Note that, the maximum Mn segregation ratio in the steel pipe, Nb segregation ratio, Ti segregation ratio, length of center-porosities, and maximum hardness of centerline segregation are all the same as the steel plate. Further, the tensile strength of steel pipe becomes 10 to 20 MPa or more larger than steel plate.

Table 1A

	Components (mass%)									
	C	Si	Mn	P	S	Al	Ti	Nb	N	Ca
1	0.040	0.10	1.32	0.005	0.0005	0.004	0.012	0.030	0.0025	0.0015
2	0.052	0.13	1.35	0.008	0.0006	0.013	0.003	0.040	0.0030	0.0017
3	0.046	0.08	1.45	0.003	0.0008	0.008	0.012	0.030	0.0021	0.0021
4	0.060	0.07	1.48	0.004	0.0003	0.010	0.016	0.060	0.0018	0.0011
5	0.052	0.25	1.47	0.009	0.0006	0.007	0.012	0.054	0.0015	0.0017
6	0.046	0.10	1.25	0.008	0.0004	0.016	0.012	0.026	0.0023	0.0013
7	0.042	0.02	1.36	0.006	0.0006	0.005	0.013	0.030	0.0031	0.0017
8	0.035	0.15	1.38	0.007	0.0005	0.013	0.008	0.050	0.0035	0.0015
9	0.042	0.17	1.41	0.005	0.0002	0.013	0.010	0.030	0.0026	0.0009
10	0.048	0.20	1.43	0.008	0.0004	0.004	0.020	0.050	0.0025	0.0013
11	0.050	0.22	1.36	0.006	0.0003	0.004	0.024	0.032	0.0026	0.0011
12	0.046	0.25	1.29	0.004	0.0006	0.010	0.012	0.030	0.0035	0.0017
13	0.038	0.31	1.42	0.006	0.0008	0.015	0.024	0.010	0.0024	0.0021
14	0.047	0.09	1.46	0.006	0.0006	0.001	0.013	0.040	0.0034	0.0017
15	0.046	0.28	1.42	0.004	0.0004	0.006	0.012	0.012	0.0026	0.0013
16	0.047	0.32	1.39	0.007	0.0006	0.006	0.008	0.006	0.0024	0.0017
17	0.052	0.48	1.32	0.008	0.0006	0.003	0.010	0.020	0.0023	0.0017
18	0.040	0.24	1.29	0.005	0.0006	0.003	0.005	0.060	0.0023	0.0017
19	0.039	0.28	1.42	0.009	0.0003	0.016	0.026	0.013	0.0029	0.0011
20	0.046	0.12	1.45	0.010	0.0005	0.016	0.012	0.024	0.0033	0.0015

(continued)

	Components (mass%)									
	C	Si	Mn	P	S	Al	Ti	Nb	N	Ca
21	0.041	0.31	1.48	0.005	0.0008	0.003	0.017	0.030	0.0032	0.0021
22	0.050	0.26	1.45	0.007	0.0006	0.002	0.002	0.002	0.0026	0.0017
23	0.046	0.31	1.32	0.004	0.0015	0.013	0.018	0.040	0.0026	0.0035
24	0.110	0.18	1.29	0.005	0.0012	0.005	0.012	0.050	0.0029	0.0029
25	0.046	0.23	1.90	0.007	0.0015	0.016	0.013	0.030	0.0028	0.0035
26	0.042	0.12	1.35	0.015	0.0016	0.015	0.008	0.014	0.0027	0.0037
27	0.042	0.25	1.33	0.006	0.0045	0.009	0.019	0.040	0.0032	0.0045
28	0.046	0.17	1.32	0.007	0.0003	0.040	0.017	0.021	0.0031	0.0011
29	0.047	0.05	1.36	0.005	0.0006	0.010	0.045	0.030	0.0026	0.0017
30	0.049	0.09	1.40	0.009	0.0009	0.003	0.013	0.120	0.0025	0.0023
31	0.042	0.12	1.45	0.005	0.0008	0.014	0.012	0.014	0.0055	0.0021
32	0.043	0.05	1.36	0.007	0.0015	0.016	0.010	0.030	0.0031	0.00005
33	0.042	0.13	1.26	0.005	0.0025	0.008	0.012	0.025	0.0026	0.0026
34	0.046	0.23	1.32	0.008	0.0010	0.012	0.013	0.035	0.0025	0.003
35	0.046	0.23	1.32	0.008	0.0010	0.012	0.013	0.035	0.0025	0.003

Table B

	Components (mass%)									
	O	B	Ni	Cu	Cr	Mo	V	Zr	Ta	Mg
1	0.0012		0.20		0.30					0.0053
2	0.0016					0.30				
3	0.0018		0.15	0.30		0.10				
4	0.0010		0.30	0.30				0.0051		
5	0.0015				0.30	0.16	0.030		0.0032	
6	0.0025	0.0002	0.20	0.35				0.0012		
7	0.0022				0.30		0.030			0.0038
8	0.0018		0.30	0.30						
9	0.0018		0.20			0.35				
10	0.0023		0.30	0.30						0.0018
11	0.0016		0.30				0.040			
12	0.0018	0.0003			0.50			0.0137		
13	0.0018					0.30				
14	0.0016		0.15	0.30						0.0033
15	0.0018		0.20	0.30						
16	0.0023		0.16	0.40						
17	0.0021				0.30			0.0008		

(continued)

	Components (mass%)									
	O	B	Ni	Cu	Cr	Mo	V	Zr	Ta	Mg
18	0.0019		0.13	0.30					0.0229	
19	0.0018		0.20		0.30					
20	0.0019		0.30	0.50						0.0025
21	0.0018					0.33				
22	0.0023									
23	0.0026		0.20							
24	0.0021		0.20	0.20						
25	0.0024					0.20				
26	0.0016					0.26				
27	0.0019	0.0005			0.30					
28	0.0023		0.16	0.16						0.0005
29	0.0021					0.30	0.040			
30	0.0016				0.30					
31	0.0018		0.13	0.20						
32	0.0013		0.13	0.20		0.30				
33	0.0080					0.10				
34	0.0025		0.20		0.30	0.10				
35	0.0023		0.20		0.30	0.10				

Table 1C

	Components (mass%)					S/Ca	Molten steel H ppm
	W	Y	Hf	Re	REM		
1						0.33	2.2
2	0.10					0.35	2.1
3					0.0008	0.38	2.3
4						0.27	1.9
5						0.35	2.1
6						0.31	1.8
7						0.35	1.6
8		0.0020				0.33	1.2
9						0.22	1.3
10						0.31	1.4
11					0.0042	0.27	1.5
12						0.35	1.6
13			0.0034			0.38	1.7
14						0.35	1.8

(continued)

	Components (mass%)					S/Ca	Molten steel H ppm
	W	Y	Hf	Re	REM		
15						0.31	1.9
16					0.0007	0.35	2.0
17						0.35	2.2
18						0.35	2.3
19					0.0006	0.27	2.1
20						0.33	1.9
21				0.0038		0.38	1.9
22						0.35	2.1
23						0.43	1.5
24						0.41	1.6
25						0.43	1.7
26					0.0012	0.43	1.9
27						1.00	1.6
28						0.27	1.7
29						0.35	1.8
30						0.39	2.1
31						0.38	2.3
32					0.0007	30.00	2.2
33						0.96	2.1
34						0.40	2.9
35						0.40	2.9

Table 2A

Steel plate	Maximum Mn segregation degree	Maximum Nb segregation degree	Maximum Ti segregation degree	Center-porosity length mm	Center segregation maximum hardness Hv (25 g)	Maximum hardness from topmost surface of steel plate down to 5 mm Hv (25 g)
1	1.35	2.1	2.5	0.020	258	255
2	1.32	2.3	2.4	0.010	261	245
3	1.26	2.6	2.0	0.030	257	238
4	1.24	2.4	2.6	0.030	262	219
5	1.32	1.6	2.4	0.050	287	227
6	1.35	2.4	1.9	0.040	222	235
7	1.24	2.6	2.3	0.020	254	258
8	1.26	2.1	2.5	0.020	238	235
9	1.23	2.3	2.4	0.030	275	265
10	1.35	2.4	2.0	0.030	251	258

(continued)

Steel plate	Maximum Mn segregation degree	Maximum Nb segregation degree	Maximum Ti segregation degree	Center-porosity length mm	Center segregation maximum hardness Hv (25 g)	Maximum hardness from topmost surface of steel plate down to 5 mm Hv (25 g)
11	1.24	2.6	1.9	0.020	237	240
12	1.23	1.9	1.7	0.040	278	245
13	1.26	1.8	2.5	0.030	257	258
14	1.34	1.9	2.6	0.030	245	238
15	1.31	2.4	2.4	0.020	239	248
16	1.35	1.9	2.2	0.040	244	259
17	1.24	1.9	1.9	0.020	258	231
18	1.25	2.0	2.4	0.001	220	241
19	1.25	1.6	2.3	0.002	270	258
20	1.29	2.1	2.1	0.003	258	241
21	1.32	1.4	2.2	0.004	273	231
22	1.25	2.4	2.3	0.011	260	238
23	1.24	1.7	2.6	0.003	212	240
24	1.26	1.9	2.4	0.002	301	318
25	2.10	2.1	1.9	0.003	335	300
26	1.28	2.3	2.2	0.004	302	285
27	1.30	2.4	1.9	0.002	275	281
28	1.32	1.9	2.8	0.003	238	260
29	1.35	1.8	4.5	0.025	286	271
30	1.45	4.2	2.4	0.060	285	300
31	1.40	2.3	2.8	0.040	258	260
32	1.30	1.6	2.7	0.020	293	270
33	2.05	2.6	2.8	0.052	268	279
34	1.32	1.6	2.7	0.160	296	263
35	1.32	1.6	2.7	0.004	296	263
36	1.50	3,4	2.6	0.020	280	270
37	1.45	2.4	2.7	0.050	290	268
38	1.49	3.6	3.0	0.070	260	280
39	1.65	3.5	3.2	0.060	270	310
40	1.45	2.7	2.9	0.030	340	350
41	1.46	2.6	3.1	0.010	280	270
42	1.53	3.5	3.2	0.030	278	320
43	1.65	3.5	3.0	0.030	285	230

Table 2B

Steel plate	Chem. comp.	Plate thickness mm	t/D	Heating temperature °C	Recrcrystallization reduction ratio	Non-recrystallization reduction ratio	Cooling start temperature °C	Cooling stop temperature °C	First recuperation start temperature °C	First recuperation end temperature °C	Second recuperation start temperature °C	No. of recuperations
1	1	25	0.036	1200	3.4	3.5	780	400	350	550	300	2
2	2	30	0.040	1150	3.0	3.3	800	450	400	600	350	2
3	3	26	0.043	1180	3.0	3.8	810	480	450	650	400	2
4	4	30	0.036	1120	2.5	4.0	810	500	500	700	450	2
5	5	35	0.048	1150	2.6	3.3	790	400	350	550	300	2
6	6	38	0.050	1200	2.5	3.2	820	430	400	600	350	2
7	7	27	0.043	1180	2.8	4.0	800	520	500	700	450	2
8	8	28	0.046	1210	3.1	3.5	770	550	430	630	380	2
9	9	29	0.056	1230	2.3	4.5	760	400	420	620	370	2
10	10	26	0.055	1200	2.3	5.0	790	560	440	640	380	2
11	11	25	0.045	1150	3.8	3.2	750	590	350	550	300	2
12	12	37	0.035	1100	2.1	3.8	780	600	320	520	270	2
13	13	33	0.038	1150	2.2	4.2	790	430	530	730	450	2
14	14	36	0.040	1200	2.2	3.8	810	450	480	680	430	2
15	15	34	0.041	1180	2.5	3.5	800	420	300	500	270	2
16	16	33	0.052	1210	2.7	3.4	780	400	360	560	320	2
17	17	39	0.055	1150	2.1	3.7	770	430	350	550	300	2
18	18	36	0.059	1200	2.4	3.5	750	420	340	540	300	2
19	19	33	0.039	1100	2.7	3.4	780	440	430	630	400	2
20	20	31	0.043	1130	2.4	4.0	790	450	440	640	400	2
21	21	25	0.056	1200	3.8	3.2	810	500	450	650	400	2
22	22	39	0.045	1200	2.2	3.5	800	520	320	520	280	2
23	23	34	0.038	1150	2.5	3.6	790	430	390	590	340	2

(continued)

Steel plate	Chem. comp.	Plate thickness mm	t/D	Heating temperature °C	Recrcrystallization reduction ratio	Non-recrystallization reduction ratio	Cooling start temperature °C	Cooling stop temperature °C	First recuperation start temperature °C	First recuperation end temperature °C	Second recuperation start temperature °C	No. of recuperations
24	24	26	0.036	1200	3.2	3.6	770	450	350	550	320	2
25	25	30	0.043	1100	2.8	3.6	790	440	430	630	400	2
26	26	34	0.060	1130	2.1	4.3	800	480	450	650	400	2
27	27	39	0.048	1190	2.0	3.8	810	420	480	680	420	2
28	28	31	0.050	1100	2.9	3.3	790	430	500	700	450	2
29	29	34	0.052	1100	2.5	3.5	810	450	500	700	450	2
30	30	33	0.047	1200	2.5	3.6	760	500	480	680	430	2
31	31	36	0.048	1250	2.1	3.9	770	430	520	720	450	2
32	32	39	0.048	1100	2.3	3.4	830	480	500	700	450	2
33	33	30	0.056	1150	2.4	4.2	850	420	360	560	320	2
34	34	31	0.046	1180	2.4	4.0	760	520	320	520	300	2
35	35	31	0.045	1130	2.3	4.3	750	500	500	700	450	2
36	1	35	0.035	900	2.0	4.3	780	430	540	740	500	2
37	1	35	0.037	1200	1.5	4.6	790	480	480	680	430	2
38	1	35	0.039	1250	4.3	2.0	810	430	350	550	300	2
39	1	35	0.043	1200	2.4	3.5	700	400	380	580	330	2
40	1	35	0.043	1210	2.3	3.7	750	400	300	-	-	1
41	1	35	0.045	1180	2.4	3.5	790	650	400	600	350	2
42	1	35	0.039	1150	2.2	3.9	750	400	200	430	150	2
43	1	35	0.043	1180	2.7	3.2	820	460	600	800	500	2

Table 2C

Steel plate	Fraction of total of polygonal ferrite and deformed ferrite %	Tensile strength MPa	CLR %
1	10	604	0.0
2	8	610	0.0
3	12	601	0.0
4	10	613	0.0
5	7	628	0.0
6	5	518	0.0
7	4	593	0.0
8	0	558	0.0
9	16	613	0.0
10	13	587	0.0
11	12	554	0.0
12	14	642	0.0
13	13	601	0.0
14	9	573	0.0
15	7	560	0.0
16	15	571	0.0
17	10	603	0.0
18	8	543	0.0
19	13	562	0.0
20	12	605	0.0
21	14	638	0.0
22	16	608	0.0
23	13	542	0.0
24	0	651	20.6
25	0	723	15.4
26	10	569	5.3
27	15	593	4.5
28	13	540	5.6
29	8	617	7.3
30	5	616	18.1
31	4	557	6.2
32	3	633	6.3
33	2	555	5.2
34	6	640	5.3
35	26	640	9.8
36	10	490	4.5
37	14	580	0.0

(continued)

Steel plate	Fraction of total of polygonal ferrite and deformed ferrite %	Tensile strength MPa	CLR %
38	23	590	0.0
39	40	600	3.5
40	17	556	15.0
41	13	495	0.0
42	10	570	12.0
43	17	499	0.0

Table 3

Steel plate	Thickness mm	TS MPa	Maximum hardness from topmost layer of steel pipe down to 5 mm Hv(25 g)	Average heat input of inside and outside surfaces kJ/mm	CLR %	DWTT ductile fracture rate at 0°C %
1	25	605	260	5.6	0	100
2	30	620	250	6.7	0	100
3	26	600	243	5.8	0	100
4	30	610	224	6.7	0	95
5	35	630	232	7.8	0	90
6	38	519	240	8.4	0	85
7	27	596	263	6.0	0	100
8	28	554	240	6.2	0	100
9	29	610	270	6.4	0	100
10	26	590	263	5.8	0	100
11	25	555	245	5.6	0	100
12	37	646	250	8.2	0	85
13	33	598	263	7.3	0	90
14	36	575	243	8.0	0	90
15	34	562	253	7.6	0	95
16	33	573	264	7.3	0	90
17	39	606	236	8.7	0	90
18	36	544	246	8.0	0	85
19	33	563	263	7.3	0	90
20	31	608	246	6.9	0	96
21	25	642	236	5.6	0	100
22	39	605	243	8.7	0	85
23	34	552	245	7.6	0	90
24	26	655	323	5.8	25.6	100
25	30	722	305	6.7	20.4	90
26	34	575	290	7.6	4.6	85
27	39	589	286	8.7	5.1	85

(continued)

Steel plate	Thickness mm	TS MPa	Maximum hardness from topmost layer of steel pipe down to 5 mm Hv(25 g)	Average heat input of inside and outside surfaces kJ/mm	CLR %	DWTT ductile fracture rate at 0°C %
28	31	541	265	6.9	6.6	90
29	34	621	276	7.6	5.2	85
30	33	619	305	7.3	24.8	90
31	36	558	265	8.0	5.6	90
32	39	636	275	8.7	6.5	85
33	30	551	284	6.7	4.8	100
34	31	644	268	6.9	4.9	95
35	31	644	268	6.9	10.6	95
36	35	493	285	7.8	9.5	90
37	35	583	283	7.9	0.0	56
38	35	593	295	7.8	0.0	45
39	35	603	325	7.8	8.5	90
40	35	559	312	7.8	20.0	90
41	35	498	285	7.8	0.0	85
42	35	573	335	7.8	17.0	85
43	35	499	245	7.8	0.0	90

[0097] Steel Plates 1 to 23 are invention examples. As shown in Table 2A to Table 2C, these steel plates had a maximum Mn segregation ratio of 1.6 or less, Nb segregation ratio of 4.0 or less, and Ti segregation ratio of 4.0 or less. Further, the maximum hardness from the topmost layers of the top and bottom surfaces of the steel plate and the inside and outside surfaces of the steel pipe down to 5 mm are 300Hv or less, while the maximum hardness of the centerline segregation was 300Hv or less. Furthermore, the total fraction of the polygonal ferrite and the deformed ferrite was 20% or less. Therefore, no HIC occurred due to the HIC test. The steel pipes made using these Steel Plates 1 to 23 as materials also gave similar results as shown in Table 3.

[0098] Steel Plates 24 to 43 are comparative examples outside the scope of the present invention. Steel Plates 24 to 35 have one of the elements among the basic components or optional added elements outside the scope of the present invention. Steel Plates 36 to 43 do not satisfy the production conditions of the present invention. As a result, in both the steel plates (see Table 2A to Table 2C) and steel pipes (see Table 3), HIC occurred in HIC tests, the CLR exceeded 3%, or the ductile fracture rate of DWTT at 0°C was less than 85%.

[0099] FIG. 4A shows the hardness distribution from the topmost layer down to 5 mm of the Steel 11 produced by the method of production of the present invention, while FIG. 4B shows a photo of the structure of the surface layer of the Steel 11. Further, FIG. 5A shows the hardness distribution from the topmost layer down to 5 mm of the Steel 40 produced by the conventional method of production of the present invention, while FIG. 5B shows a photo of the structure of the surface layer of the Steel 40.

[0100] The hardness distribution of the steel plate of the present invention which is shown in FIG. 4A has a maximum hardness of a low 245Hv, but the hardness distribution of the steel plate which was produced by the conventional method which is shown in FIG. 5A has a part where the hardness locally exceeds 300Hv. This can become the starting point of HIC. The steel plate which was produced by the conventional method which is shown in FIG. 5B was treated for reheating one time, so the base material was not sufficiently tempered and a hard structure was formed.

Reference Signs List

[0101]

1 self-reheating treatment

2 reheating start temperature
3 reheating end temperature
4 water cooling stop temperature

Claims

1. A steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance,

   a steel plate composing a base material of the steel pipe;
   the steel plate containing, by mass%,
   C: 0.02 to 0.08%,
   Si: 0.01 to 0.5%,
   Mn: 1.2 to 1.8%,
   Nb: 0.001 to 0.10%,
   Ca: 0.0005 to 0.0050%,
   N: 0.0010 to 0.0060%,
   O: 0.0001 to 0.0035%, and
   a balance consisting of Fe and unavoidable impurities, wherein
   contents are restricted to
   P: 0.01% or less,
   S: 0.0020% or less,
   Al: 0.030% or less, and
   Ti: 0.030% or less, and
   contents of S and Ca satisfy S/Ca<0.5;
   the steel plate satisfying:
   maximum Mn segregation ratio: 2.0 or less,
   Nb segregation ratio: 4.0 or less,
   Ti segregation ratio: 4.0 or less,
   length of center-porosities at centerline segregation: 0.1 mm or less,
   maximum hardness of centerline segregation: 300 Hv or less,
   maximum hardness of surface layer region from topmost surface of two front and back plate surfaces down to depth of 5 mm: 300Hv or less, and
   a total fraction of polygonal ferrite and deformed ferrite with an aspect ratio of 3 or more at surface layer region from topmost surface of two front and back plate surfaces down to depth of 5 mm: 0.1 to 20%; and
   thickness "t" [mm] of the steel plate and outside diameter D [mm] of the steel pipe after pipemaking satisfying
   $t \geq 25$ and
   $t/D \geq 0.035$.

2. The steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance according to claim 1, the steel plate further containing, by mass%, one or more of

   Ni: 0.01 to 2.0%,
   Cu: 0.01 to 1.0%,
   Cr: 0.01 to 1.0%,
   Mo: 0.01 to 0.60%,
   W: 0.01 to 1.0%,
   V: 0.01 to 0.10%,
   Zr: 0.0001 to 0.050%,
   Ta: 0.0001 to 0.050%,
   B: 0.0001 to 0.0020%,
   REM: 0.0001 to 0.01%,
   Mg: 0.0001 to 0.01%,
   Y: 0.0001 to 0.005%,
   Hf: 0.0001 to 0.005%, and
   Re: 0.0001 to 0.005%.

3. The steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance according to claim 1

or 2, wherein there is no deformed ferrite with an aspect ratio of 3 or more at surface layer region from topmost surface of two front and back plate surfaces down to depth of 5 mm.

4. A steel plate for high strength line pipe use excellent in hydrogen induced crack resistance, the steel plate used for the steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance according to claim 1 or 2.

5. A steel plate for high strength line pipe use excellent in hydrogen induced crack resistance , the steel plate used for the steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance according to claim 3.

6. A method of production of a steel plate for high strength line pipe use excellent in hydrogen induced crack resistance comprising the steps of:

a step of producing molten steel containing, by mass%,
C: 0.02 to 0.08%,
Si: 0.01 to 0.5%,
Mn: 1.2 to 1.8%,
Nb: 0.001 to 0.10%,
Ca: 0.0005 to 0.0050%,
N: 0.0010 to 0.0060%,
O: 0.0001 to 0.0035%, and
a balance consisting of Fe and unavoidable impurities, wherein
contents are restricted to
P: 0.01% or less,
S: 0.0020% or less,
Al: 0.030% or less, and
Ti: 0.030% or less,
contents of S and Ca satisfy S/Ca<0.5, and
a content of hydrogen after secondary refining is 2.5 ppm or less;
a step of making the molten steel a steel slab by continuous cast;
a step of heating the steel slab to 1000°C or more;
a step of hot rolling the heated steel slab by a reduction ratio in a recrystallization temperature region of 2 or more and a reduction ratio in the non-recrystallization temperature region of 3 or more to obtain a steel plate; and
a cooling step of cooling the steel plate from a 750°C or more to 400 to 600°C, the cooling step including at least two self-reheating treatments making the steel plate rise in temperature, and
in the self-reheating treatment, a start temperature of a first self-reheating treatment being 300°C or more, and an end temperature of all self-reheating treatments being less than 750°C.

7. The method of production of a steel plate for high strength line pipe use excellent in hydrogen induced crack resistance according to claim 6, the molten steel further containing, by mass%, one or more of

Ni: 0.01 to 2.0%,
Cu: 0.01 to 1.0%,
Cr: 0.01 to 1.0%,
Mo: 0.01 to 0.60%,
W: 0.01 to 1.0%,
V: 0.01 to 0.10%,
Zr: 0.0001 to 0.050%,
Ta: 0.0001 to 0.050%,
B: 0.0001 to 0.0020%,
REM: 0.0001 to 0.01%,
Mg: 0.0001 to 0.01%,
Y: 0.0001 to 0.005%,
Hf: 0.0001 to 0.005%, and
Re: 0.0001 to 0.005%.

8. A method of production of a steel pipe for high strength line pipe use excellent in hydrogen induced crack resistance, the steel pipe made from the steel plate obtained by the method of production of a steel plate for high strength line pipe use excellent in hydrogen induced crack resistance according to claim 6 or 7, comprising the steps of:

a step of shaping the steel plate into a tube shape; and
a step of welding both plate edge beveled;
wherein a thickness "t" [mm] of the steel plate and an outside diameter D [mm] of the steel pipe after pipemaking pipe satisfy
$t \geq 25$ and
$t/D \geq 0.035$.

FIG. 1

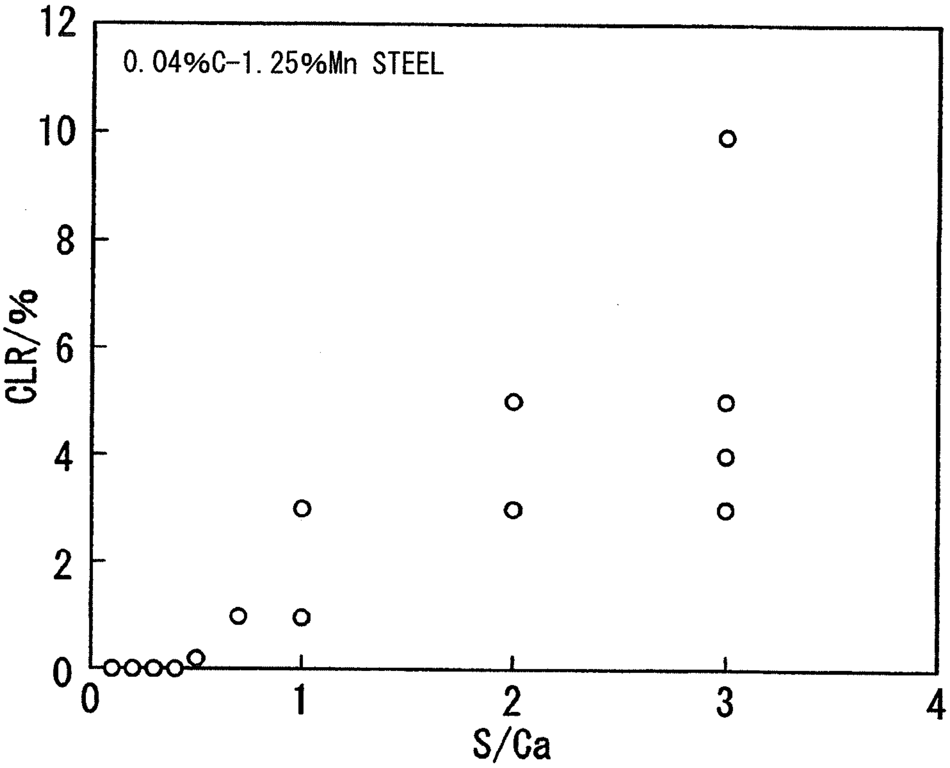

0.04%C-1.25%Mn STEEL
CLR/%
12
10
8
6
4
2
0
0
1
2
3
4
S/Ca

FIG. 2

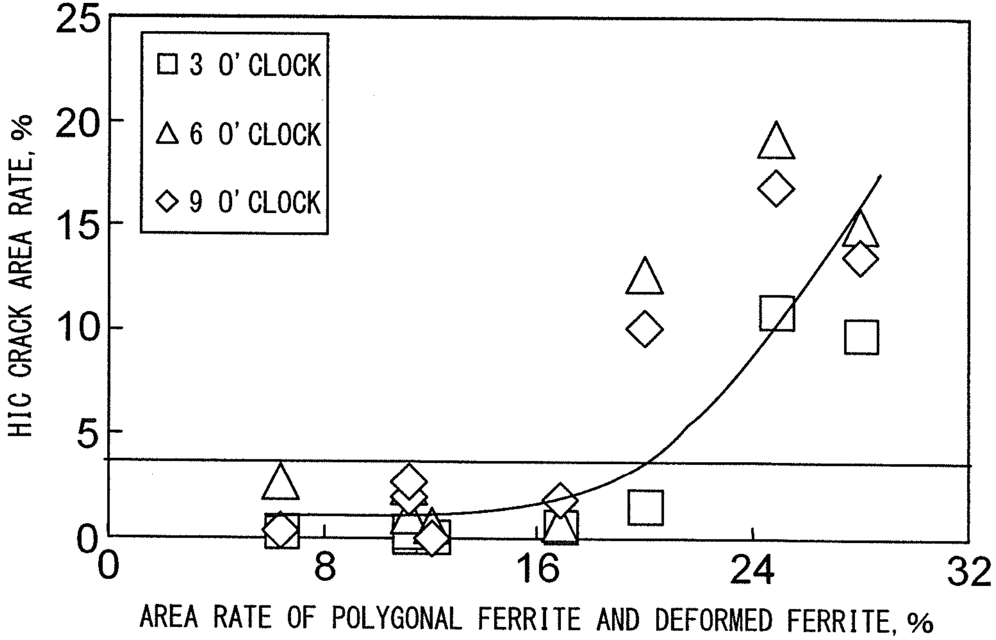

□ 3 O'CLOCK
△ 6 O'CLOCK
◇ 9 O'CLOCK
HIC CRACK AREA RATE, %
25
20
15
10
5
0
0
8
16
24
32
AREA RATE OF POLYGONAL FERRITE AND DEFORMED FERRITE, %

FIG. 3A

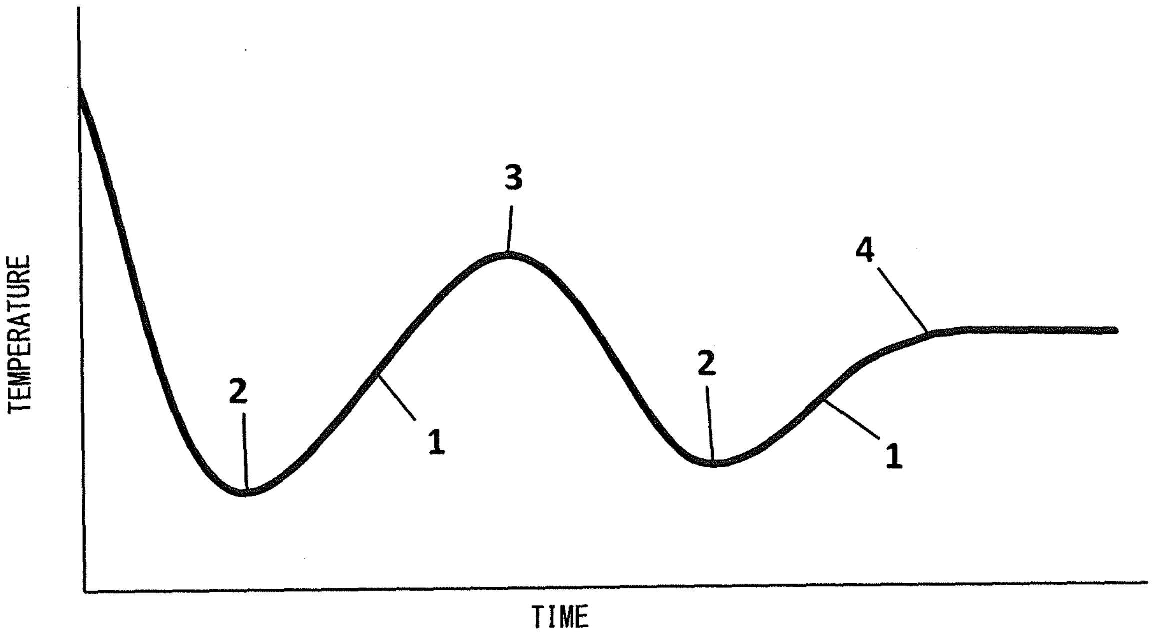


FIG. 3B

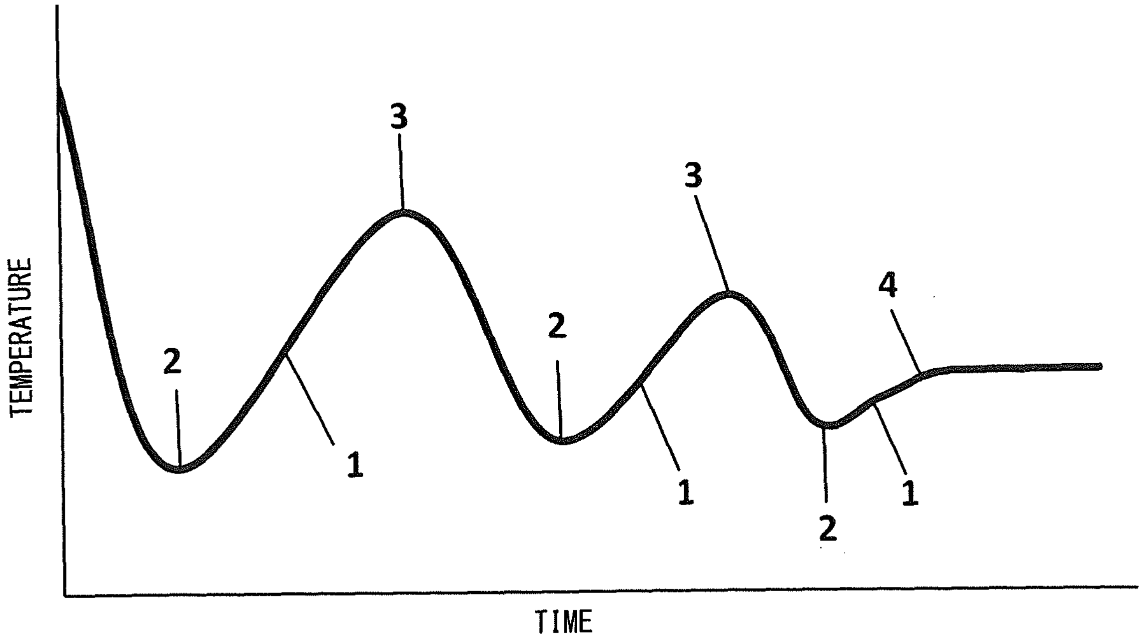


FIG. 3C

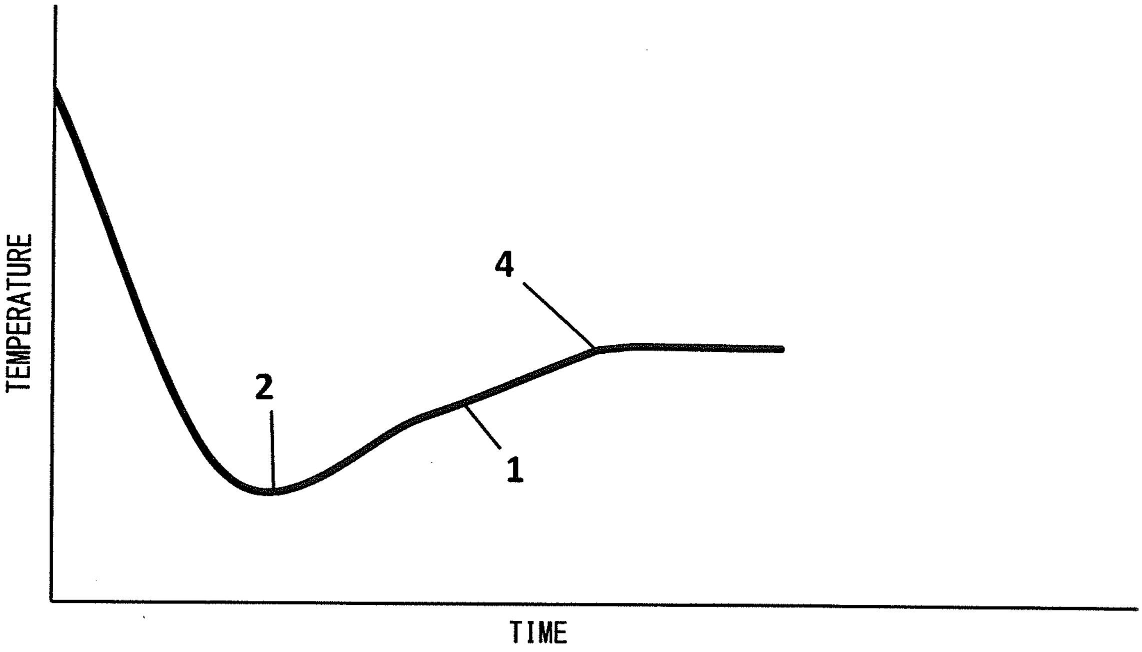


FIG. 4A

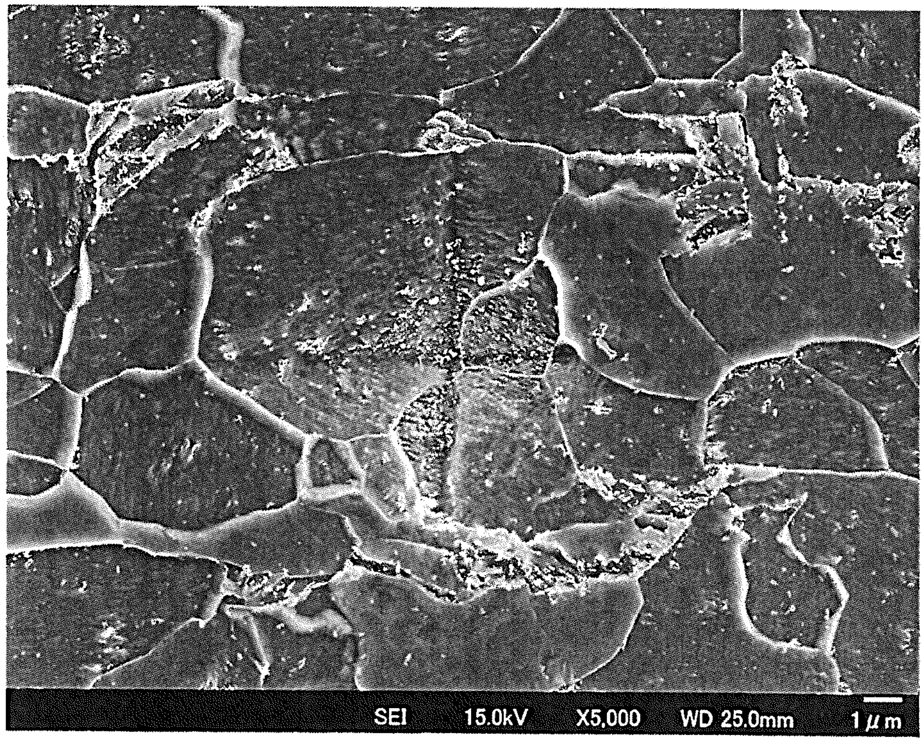
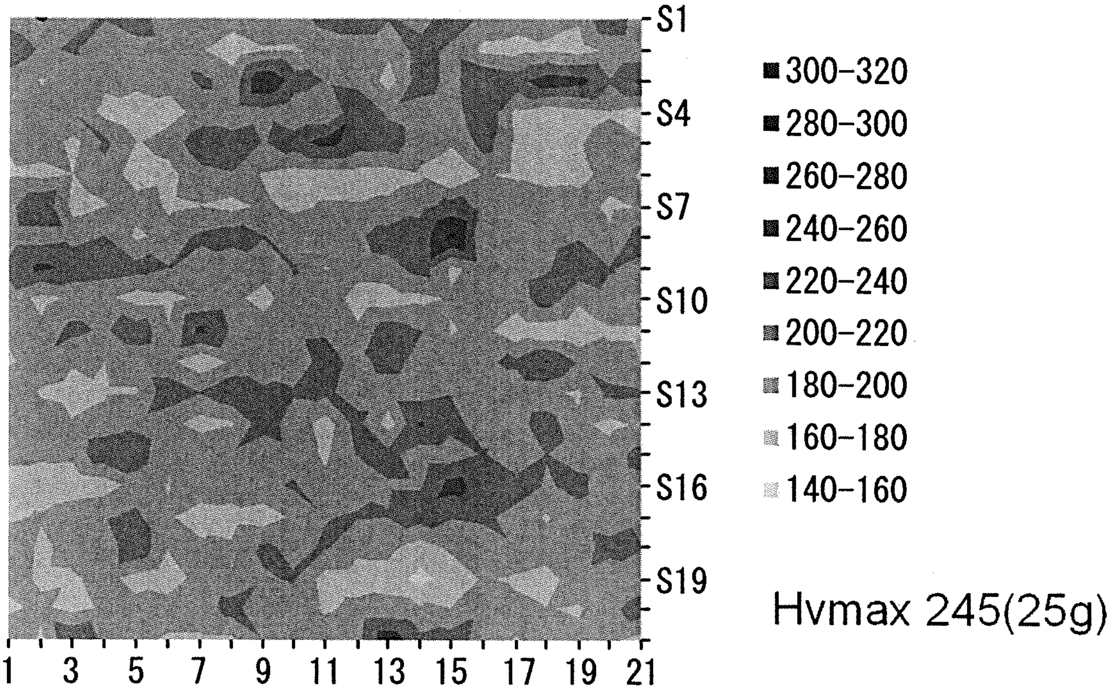


FIG. 4B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S7
S10
S13
S16
S19
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3
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9
11
13
15
17
19
21
■300-320
■280-300
■260-280
■240-260
■220-240
■200-220
■180-200
■160-180
■140-160
Hvmax 245(25g)

FIG. 5A

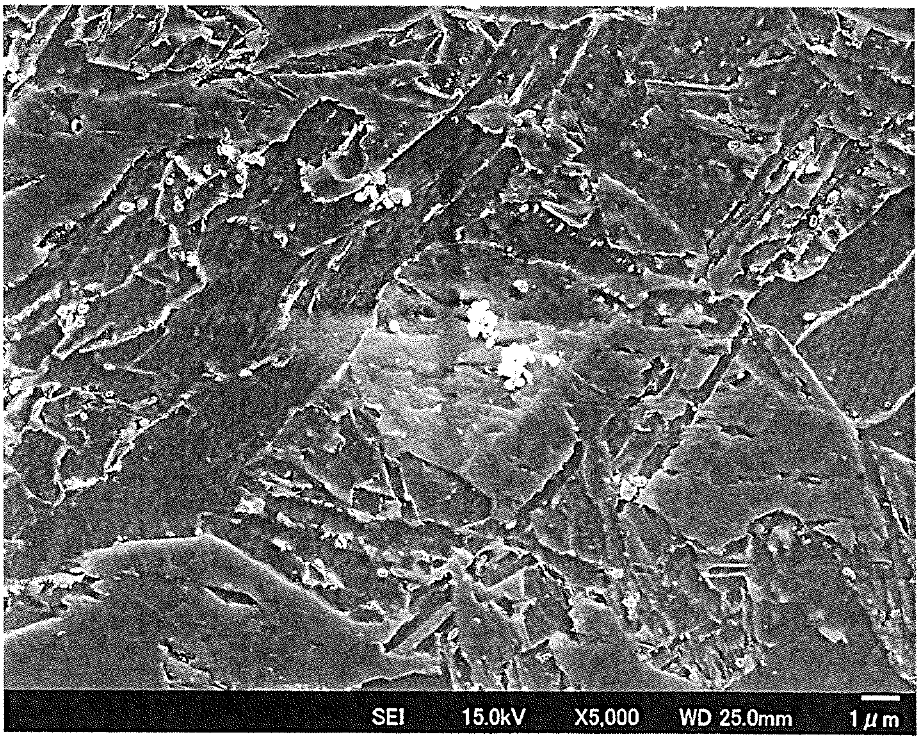
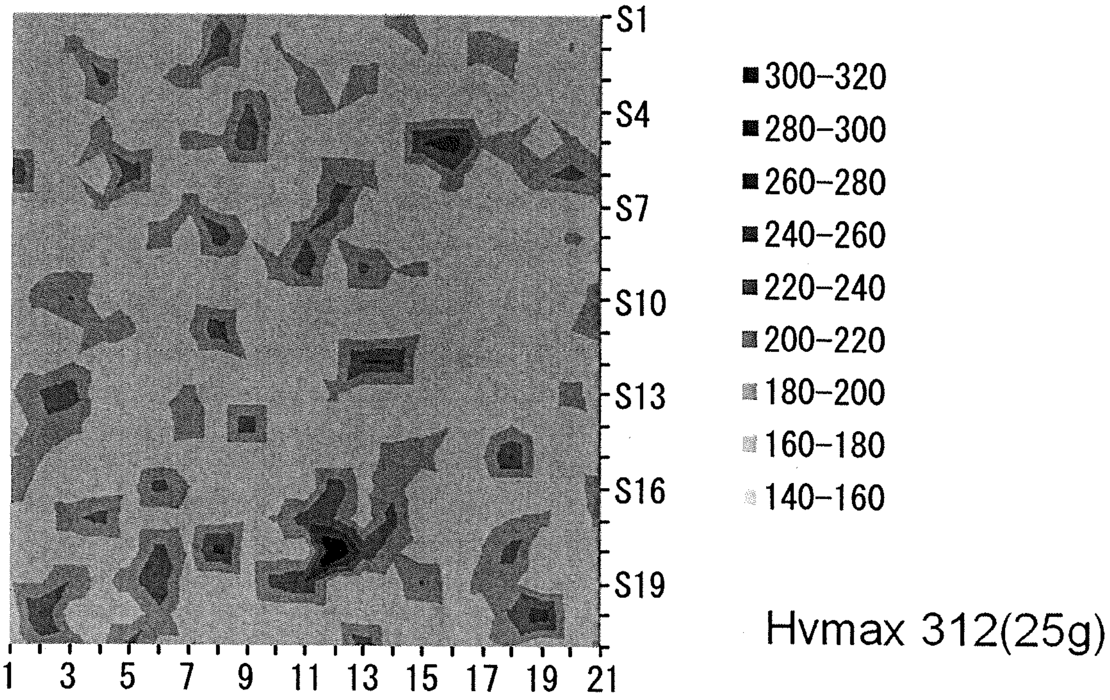

SEI
15.0kV
X5,000
WD 25.0mm
1 μm

FIG. 5B


S1
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S10
S13
S16
S19
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3
5
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11
13
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17
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21
■300-320
■280-300
■260-280
■240-260
■220-240
■200-220
■180-200
■160-180
■140-160
Hvmax 312(25g)

INTERNATIONAL SEARCH REPORT	International application No. PCT/JP2013/059617

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D8/02*(2006.01)i, *C22C38/12*(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)
C22C1/00-49/14, 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	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

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	WO 2010/052928 A1 (Nippon Steel Corp.), 14 May 2010 (14.05.2010), & JP 4819186 B & CN 102203303 A & RU 2459875 C	1-8
A	WO 2009/123292 A1 (JFE Steel Corp.), 08 October 2009 (08.10.2009), & JP 2009-263777 A & EP 2272994 A1 & CN 102124133 A & KR 10-2010-0116701 A	1-8
A	JP 2009-174020 A (JFE Steel Corp.), 06 August 2009 (06.08.2009), (Family: none)	1-8

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search 13 June, 2013 (13.06.13)	Date of mailing of the international search report 25 June, 2013 (25.06.13)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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

REFERENCES CITED IN THE DESCRIPTION

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