(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 026 140 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
01.06.2016 Bulletin 2016/22

(21) Application number: **14829550.4**

(22) Date of filing: **23.07.2014**

(51) Int Cl.:
C22C 38/00 *(2006.01)* ***B21B 1/38*** *(2006.01)*
B21B 3/00 *(2006.01)* ***C21D 8/02*** *(2006.01)*
C22C 38/14 *(2006.01)* ***C22C 38/58*** *(2006.01)*

(86) International application number:
PCT/JP2014/069471

(87) International publication number:
WO 2015/012317 (29.01.2015 Gazette 2015/04)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **25.07.2013 JP 2013155063**
25.07.2013 JP 2013155064

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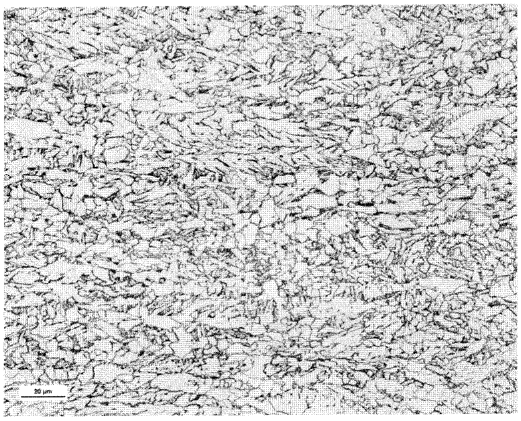
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(54) STEEL PLATE FOR LINE PIPE, AND LINE PIPE

(57) A steel plate for a line pipe, the steel plate having a plate thickness of 25 mm or more comprising in terms of mass%: 0.040 to 0.080% of C, 0.05 to 0.40% of Si, 1.60 to 2.00% of Mn, 0.020% or less of P, 0.0025% or less of S, 0.05 to 0.20% of Mo, 0.0011 to 0.0050% of Ca, 0.060% or less of Al, 0.010 to 0.030% of Nb, 0.008 to 0.020% of Ti, 0.0015 to 0.0060% of N, and 0.0040% or less of O, a remainder consisting of Fe and unavoidable impurities, wherein a content ratio of Ca to S [Ca/S] is from 0.90 to 2.70, and a content ratio of Ti to N [Ti/N] is 2.20 or higher" wherein Ceq, which is defined by the following Formula (1), is from 0.380 to 0.480: Ceq = C+Mn/6+(Ni+Cu)/15+(Cr+Mo+V)/5; and wherein: at a position of 1/4 of the plate thickness, a ferrite fraction (F1) is from 20 to 60% and a remainder is a structure of bainite; at a position of 1/2 of the plate thickness, a ferrite fraction (F2) is from 5 to 60% and a remainder is a structure of bainite or a structure of bainite and martensite; a ratio (F1/F2) of the ferrite fraction (F1) to the ferrite fraction (F2) is from 1.00 to 5.00; at a position of 1/4 of the plate thickness an average grain diameter of ferrite is from 2.0 to 15.0 μm, and at a position of 1/2 of the plate thickness the average grain diameter of ferrite is from 5.0 to 20.0 μm; and the hardness at a position of 1/2 of the plate thickness is 400 Hv or less, and the length of MnS at a position of 1/2 of the plate thickness is 1.00 mm or less.

FIG.1



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Description

Technical Field

[0001] The present invention relates to a steel plate for a line pipe, and a line pipe.

Background Art

[0002] Production areas of crude oil and natural gas have been expanding to polar regions, and a laying environment of line pipes for transporting crude oil or natural gas has been becoming severer. For example, cases of transporting a crude oil or a natural gas containing hydrogen sulfide through line pipes have been increasing. Therefore, sour resistance is apt to be demanded for a line pipe or a steel plate for a line pipe as a material for a line pipe. In this regard, the sour resistance means hydrogen-induced cracking resistance (HIC resistance) and sulfide stress cracking resistance (SSC resistance) in a corrosive environment containing hydrogen sulfide.

[0003] Meanwhile, it has been known that the sour resistance of a steel is deteriorated due to presence of MnS elongated in the rolling direction or an inclusion in a cluster shape.

[0004] In order to improve the sour resistance of a steel plate, a method by which a steel, in which contents of impurity elements, such as P, S, O, and N, are reduced and MnS is shape controlled by Ca being contained in the steel, is subjected to controlled rolling and is chilled with water has been proposed (see, for example, Patent Document 1 below).

[0005] With respect to an on-land line pipe, reduction of the wall thickness by increasing the strength of a line pipe may be occasionally demanded from viewpoints of enhancement of fluid transportation efficiency and reduction of laying costs.

[0006] In response to such a demand, a high strength steel plate, in which homogeneous and fine-grained bainite is formed in the plate thickness direction, having sour resistance of approx. X70 has been proposed (see, for example, Patent Document 2 below).

[0007] Meanwhile, with respect to a submarine line pipe, laying in the deep sea beyond the water depth of 2000 m has been tried. In the deep sea a line pipe is easily collapsed by the water pressure. Therefore, for a submarine line pipe, a steel pipe having generally a wall thickness of 25 mm or more, and having a high compressive strength in the circumferential direction may be demanded.

[0008] In response to such a demand, a welded steel pipe for a high compressive strength and sour resistant line pipe, securing a fraction of bainite of 80% or higher, and being superior in compressive strength, has been proposed (see, for example, Patent Document 3 below).

[0009] Meanwhile, in producing a thick steel plate (for example, a steel plate with a plate thickness of 25 mm or more), a favorable toughness evaluation result, especially the same by a drop weight tear test (DWTT) (this toughness evaluation result is hereinafter also referred to as "DWTT property") may not be secure easily due to insufficient rolling reduction in a recrystallization region and a non-recrystallization region.

[0010] In response thereto, a method of producing a steel plate for a thick-walled sour resistant line pipe superior in DWTT property by forming a dual phase structure of fine-grained ferrite and 70% or more bainite has been proposed (see, for example, Patent Document 4 below).

[0011]

Patent Document 1: Japanese Patent Application Laid-Open (JP-A) No. S62-112722
Patent Document 2: JP-A No. S 61-165207
Patent Document 3: JP-A No. 2011-132600
Patent Document 4: JP-A No. 2010-189722

SUMMARY OF INVENTION

Technical Problem

[0012] As described above, for obtaining sour resistance or high compressive strength, formation of a single structure as fine as possible (for example, fine-grained bainite single structure) has been proposed, meanwhile for obtaining a favorable DWTT property, formation of a dual phase structure containing fine-grained ferrite has been proposed.

[0013] However, no structure control guideline aiming at all of the sour resistance, compressive strength, and DWTT property has been proposed yet, and satisfaction of all of these have been difficult.

[0014] On the other hand, relaxation of the evaluation environment (condition) of sour resistance from a severe sour environment represented by "Solution A" (pH 2.7) according to TM0284 of NACE (National Association of Corrosion and Engineer) to a mild sour environment (for example, a sour environment of pH 5.0 or higher) closer to a real enviromnent

has been started to be discussed.

[0015] Under such a mild sour environment, a steel plate for a line pipe and a line pipe which satisfy all of sour resistance, compressive strength, and DWTT property may be possible.

[0016] The invention was made under such circumstances with an object to provide a steel plate for a line pipe which is superior in HIC resistance (especially HIC resistance in a sour environment of pH 5.0 or higher) and satisfies both compressive strength and DWTT property, as well as a line pipe produced using the steel plate for a line pipe.

Solution to Problem

[0017] The inventors diligently studied conditions to be satisfied by a steel plate for a line pipe which is superior in HIC resistance (especially HIC resistance in a sour environment of pH 5.0 or higher) and satisfies both compressive strength and DWTT property, thereby accomplishing the invention.

[0018] Namely, specific means for attaining the object are as follows.

<1> A steel plate for a line pipe, the steel plate having a plate thickness of 25 mm or more and comprising in terms of mass%:

0.040 to 0.080% of C,

0.05 to 0.40% of Si,

1.60 to 2.00% of Mn,

0.020% or less of P,

0.0025% or less of S,

0.05 to 0.20% of Mo,

0.0011 to 0.0050% of Ca,

0.060% or less of Al,

0.010 to 0.030% of Nb.

0.008 to 0.020% of Ti,

0.0015 to 0.0060% of N, and

0.0040% or less of O,

wherein a content ratio of Ca to S [Ca/S] is from 0.90 to 2.70, and a content ratio of Ti to N [Ti/N] is 2.20 or higher,

a remainder consisting of Fe and unavoidable impurities,

wherein Ceq, which is defined by the following Formula (1), is from 0.380 to 0.480:

$$Ceq = C+Mn/6+(Ni+Cu)/15+(Cr+Mo+V)/5 \qquad (1)$$

wherein, in the Formula (1), C, Mn, Ni, Cu, Cr, Mo, and V represent contents of respective elements (mass%),

and wherein:

at a position of 1/4 of the plate thickness, a ferrite fraction (F1) is from 20 to 60% and a remainder is a structure of bainite,
at a position of 1/2 of the plate thickness, a ferrite fraction (F2) is from 5 to 60% and a remainder is a

structure of bainite or a structure of bainite and martensite,
a ratio (F1/F2) of the ferrite fraction (F1) to the ferrite fraction (F2) is from 1.00 to 5.00,
at a position of 1/4 of the plate thickness an average grain diameter of ferrite is from 2.0 to 15.0 μm, and
at a position of 1/2 of the plate thickness the average grain diameter of ferrite is from 5.0 to 20.0 μm, and
a hardness at a position of 1/2 of the plate thickness is 400 Hv or less, and a length of MnS at a position of 1/2 of the plate thickness is 1.00 mm or less.

<2> The steel plate for a line pipe according to <1>, wherein an A1 content is 0.008% or less in terms of mass%.
<3> The steel plate for a line pipe according to <1> or <2>, comprising, in terms of mass%, one or more of:

0.50% or less of Ni,
0.50% or less of Cr,
0.50% or less of Cu,
0.0050% or less of Mg,
0.0050% or less of REM, and
0.100% or less of V.

<4> A line pipe produced using the steel plate for a line pipe according to any one of <1> to <3>.

Advantageous Effects of Invention

[0019] According to the invention, a steel plate for a line pipe superior in HIC resistance (especially HIC resistance in a sour environment of pH 5.0 or higher) and satisfies both compressive strength and DWTT property as well as a line pipe produced with the steel plate for a line pipe can be provided.

BRIEF DESCRIPTION OF DRAWINGS

[0020] Fig. 1 is an optical micrograph (magnification 500-fold) of a cross-section of a steel plate of Inventive Example 10 at a position of 1/2 of the plate thickness (cross-section after polishing and corrosion with a LePera reagent).

DESCRIPTION OF EMBODIMENTS

[0021] A steel plate for a line pipe and a line pipe according to the invention will be described in detail below.
[0022] A numerical range expressed by "x to y" herein includes the values of x and y in the range as the minimum and maximum values, respectively.
[0023] The content of a component (element) expressed by "%" herein means "mass%".
[0024] A "position of 1/2 of the plate thickness" herein means a position corresponding to 1/2 of the plate thickness of a steel plate, namely a center part in a thickness direction of a steel plate.
[0025] A "position of 1/4 of the plate thickness" herein means a position that is apart from the center part in a thickness direction of a steel plate (position of 1/2 of the plate thickness) by a distance in the direction of the plate thickness equivalent to 1/4 of the plate thickness.
[0026] Further, the content of C (carbon) may be herein occasionally expressed as "C content". Another element may be expressed similarly.

[Steel plate for line pipe]

[0027] A steel plate for a line pipe according to the invention (hereinafter also referred to simply as "steel plate") is a steel plate for a line pipe, the steel plate having a plate thickness of 25 mm or more and containing in terms of mass%: 0.040 to 0.080% of C, 0.05 to 0.40% of Si, 1.60 to 2.00% of Mn, 0.020% or less of P, 0.0025% or less of S, 0.05 to 0.20% of Mo, 0.0011 to 0.0050% of Ca, 0.060% or less of Al, 0.010 to 0.030% ofNb, 0.008 to 0.020% ofTi, 0.0015 to 0.0060% of N, and 0.0040% or less of O, wherein a content ratio of Ca to S [Ca/S] is from 0.90 to 2.70, and a content ratio of Ti to N [Ti/N] is 2.20 or higher, a remainder consisting of Fe and unavoidable impurities, wherein Ceq, which is defined by the following Formula (1), is from 0.380 to 0.480:

$$Ceq = C+Mn/6+(Ni+Cu)/15+(Cr+Mo+V)/5 \qquad (1)$$

wherein, in the Formula (1), C, Mn, Ni, Cu, Cr, Mo, and V represent contents of respective elements (mass%),
and wherein: at a position of 1/4 of the plate thickness, a ferrite fraction (F1) is from 20 to 60% and a remainder is a structure of bainite, at a position of 1/2 of the plate thickness, a ferrite fraction (F2) is from 5 to 60% and a remainder is a structure of bainite or a structure of bainite and martensite, a ratio (F1/F2) of the ferrite fraction (F1) to the ferrite fraction (F2) is from 1.00 to 5.00, at a position of 1/4 of the plate thickness an average grain diameter of ferrite is from 2.0 to 15.0 μm, and at a position of 1/2 of the plate thickness the average grain diameter of ferrite is from 5.0 to 20.0 μm, and a hardness at a position of 1/2 of the plate thickness is 400 Hv or less, and a length of MnS at a position of 1/2 of the plate thickness is 1.00 mm or less.

[0028] The steel plate according to the invention can improve HIC resistance (especially HIC resistance in a sour environment of pH 5.0 or higher) and satisfy compressive strength and DWTT property owing to the above constitution.

[0029] The invention was made based on the following investigation results.

[0030] The inventors investigated conditions, which a steel material should fulfill in order to inhibit occurrence of hydrogen-induced cracking (HIC) in a sour environment of pH 5.0 or higher, using various steel plates with different compositions.

[0031] The sour resistance was evaluated according to the invention by examining occurrence or nonoccurrence of HIC, and a HIC crack area ratio (hereinafter referred to as "CAR in HIC test").

[0032] The evaluation was conducted by immersing a steel plate in a pH 5.0-solution saturated with a hydrogen sulfide gas (for example, "Solution B" according to NACE TM0284) and examining a HIC crack area ratio (CAR in HIC test) after 96 hours. When a HIC crack area ratio is 5% or less, the sour resistance was rated as good.

[0033] The inventors next investigated a structure of a sample in which HIC had occurred, and investigated an inclusion which was the origin of the HIC. As the result, it was discovered that any HIC originates from elongated MnS present at a position of 1/2 of the plate thickness (hereinafter referred to as "elongated MnS", or also simply as "MnS"), and that a length of the elongated MnS exceeds 1.00 mm.

[0034] Consequently, it was found that occurrence of HIC in a sour environment of pH 5.0 or higher can be suppressed by controlling the length of MnS at the position of 1/2 of the plate thickness to 1.00 mm or less.

[0035] The inventors then found that the following conditions are necessary to make the length of MnS 1.00 mm or less.

[0036] Namely, the S content should be 0.0025% or less, and the content ratio [Ca/S] should be from 0.90 to 2.70.

[0037] The inventors found that in a case in which the content ratio [Ca/S] is less than 0.90, the length of MnS may not be able to be controlled to 1.00 mm or less. Further, the inventors found that in a case in which the content ratio [Ca/S] is beyond 2.70 a coarse aggregate of Ca-based oxides is formed and HIC may occasionally occur originating from the aggregate.

[0038] The inventors then found that HIC in a sour enviromnent of pH 5.0 or higher can be suppressed by making the hardness of a steel plate at the position of 1/2 of the plate thickness to 400 Hv or less.

[0039] Further, the inventors investigated in detail a relationship at the position of 1/2 of the plate thickness between the hardness and the ferrite fraction. As a result, the inventors found that in a case in which the ferrite fraction of a structure at the position of 1/2 of the plate thickness is higher than 60%, the hardness of the steel plate may exceed 400 Hv. This is presumably because, when ferrite is formed at the position of 1/2 of the plate thickness, the C amount is concentrated in the remainder and as the result bainite or martensite with a high C content is formed.

[0040] In other words, in the steel plate according to the invention, due to the ferrite fraction at the position of 1/2 of the plate thickness being 60% or less, the hardness at the position of 1/2 of the plate thickness becomes 400 Hv or less.

[0041] It was confirmed that the position of 1/2 plate thickness in a steel plate is included in a center segregation zone of the steel plate.

[0042] In this regard, a center segregation zone means a zone where the Mn concentration is highest, in a case in which the Mn concentration distribution in the thickness direction of the steel plate is measured by an EPMA (Electron Probe Micro Analyzer).

[0043] The measuring methods of hardness at the position of 1/2 of the plate thickness, and ferrite fractions (F1, F2) are as shown in Examples below.

[0044] Next, a structure in a steel to attain satisfactory compressive strength, DWTT property, and HIC resistance was studied diligently.

[0045] As the result it was newly known that it is adequate to make a ferrite fraction (F1) at a position of 1/4 of the plate thickness from 20 to 60%, and a ferrite fraction (F2) at the position of 1/2 of the plate thickness from 5 to 60%.

[0046] A compressive strength is highly correlated with the ferrite fraction (F1), and when the fraction of soft ferrite at the position of 1/4 of the plate thickness becomes higher, the compressive strength decreases. When both the ferrite fraction (F1) and the ferrite fraction (F2) exceed 60%, the compressive strength decreases remarkably.

[0047] In other words, the steel plate according to the invention shows high compressive strength due to both the ferrite fraction (F1) and the ferrite fraction (F2) being 60% or less.

[0048] On the other hand, the DWTT property of a steel plate is enhanced, in a case in which a ferrite fraction of the steel plate becomes higher. It was found that the ferrite fraction (F1) of the steel plate is required to be 20% or higher,

and the ferrite fraction (F2) thereof is required to be 5% or higher in order to exert such an effect.

[0049] Further, the inventors found that, in order to satisfy both compressive strength and DWTT property, the ratio (F1/F2) of the ferrite fraction (F1) at the position of 1/4 of the plate thickness to the ferrite fraction (F2) at the position of 1/2 of the plate thickness is required to be 1.00 or higher.

[0050] In other words, the steel plate according to the invention satisfies both compressive strength and DWTT property due to the ratio (F1/F2) being 1.00 or higher. When the ratio (F1/F2) is less than 1.00, especially the DWTT property deteriorates (for example, refer to Comparative Example 6 below).

[0051] From the above investigation, the ratio (F1/F2) is decided to be 1.00 or higher in the invention.

[0052] Further, since it is difficult to make the ratio (F1/F2) exceed 5.00 from a standpoint of production, the ratio (F1/F2) was decided to be 5.00 or less in the invention.

[0053] With respect to the ratio (F1/F2) of an ordinary steel plate, the ratio (F1/F2) is less than 1.00 due to the following reason.

[0054] Namely, the cooling rate in a cooling process after rolling for obtaining a steel plate is ordinarily slowest at the position of 1/2 of the plate thickness (center part in the thickness direction of the plate). Therefore, in an ordinary steel plate the ferrite fraction is highest at the position of 1/2 of the plate thickness in the plate thickness direction. Consequently, in an ordinary steel plate, the ratio (F1/F2) is less than 1.00 (for example, refer to Comparative Example 6 below).

[0055] However, the inventors succeeded in making the ratio (F1/F2) to 1.00 or higher, by making a cooling rate (V1) at the position of 1/4 of the plate thickness slower than a cooling rate (V2) at the position of 1/2 of the plate thickness in a temperature range between 600 to 700°C, where ferrite is formed.

[0056] Meanwhile, the ratio (F1/F2) of the steel plate according to the invention is required to be from 1.00 to 5.00, and there is no particular restriction on a production method thereof (for example, cooling method after rolling).

[0057] The remainder at the position of 1/4 of the plate thickness of the steel plate according to the invention is a structure of bainite. As the result, occurrence of HIC is suppressed. In a case in which the remainder at the position of 1/4 of the plate thickness is pearlite, HIC occurs.

[0058] Meanwhile, the remainder at the position of 1/2 of the plate thickness of the steel plate according to the invention is a structure of bainite or a structure of bainite and martensite. As the result, occurrence of HIC is suppressed. In a case in which the remainder at the position of 1/2 of the plate thickness is pearlite, HIC occurs.

[0059] With respect to the compressive strength of the steel plate according to the invention; the steel plate is formed into a steel pipe (line pipe) (pipe making), the steel pipe is then subjected to heating in coating for anti-corrosion, and then the compressive strength in the circumferential direction of the steel pipe is measured for evaluation; or the steel plate is subjected to treatments corresponding to the pipe making and the heating in coating, and then the compressive strength of the steel plate is measured for evaluation as in Examples below.

[0060] This is because collapse of a steel pipe such as a line pipe has the highest correlation with the compressive strength in the circumferential direction of a steel pipe.

[0061] Further, although the compressive strength in the circumferential direction of a steel pipe decreases remarkably by a Bauschinger effect due to pipe making, the compressive strength recovers during the heating in coating. The recovery occurs due to a so-called static strain aging, by which C (carbon) diffuses during the heating in coating into a dislocation formed during pipe making to form a Cottrell atmosphere.

[0062] The inventors diligently investigated alloy elements, which exhibit sufficiently static strain aging, so as to enhance the compressive strength of a steel plate. As the result, it was found that Mo is effective as such an alloy element.

[0063] The reason why Mo is effective as the alloy element is considered as follows.

[0064] Namely, there is a weak interaction between Mo and C, and in a steel plate containing Mo, Mo fixes many C atoms. With heating, however, the interaction weakens further and a C atom is released from a Mo atom and migrates to a dislocation. Through such migration, static strain aging is presumably sufficiently exhibited.

[0065] For exhibiting the effect, the Mo content is set at 0.05% or higher in the invention.

[0066] The inventors further found that the upper limit of the Mo content is preferably 0.20%, because when the Mo content is too high, the hardness at the position of 1/2 of the plate thickness (center part in the thickness direction of the plate) becomes extremely high.

[0067] The invention made based on the investigation results will be described in detail below.

[0068] Firstly, the components (composition) of the steel plate according to the invention will be described.

[0069] The steel plate for a line pipe according to the invention contains 0.040 to 0.080% of C (carbon), 0.05 to 0.40% of Si (silicon), 1.60 to 2.00% of Mn (manganese), 0.020% or less of P (phosphorus), 0.0025% or less of S (sulfur), 0.05 to 0.20% of Mo (molybdenum), 0.0011 to 0.0050% of Ca (calcium), 0.060% or less of Al (aluminum), 0.010 to 0.030% of Nb (niobium), 0.008 to 0.020% of Ti (titanium), 0.0015 to 0.0060% ofN (nitrogen), and 0.0040% or less of O (oxygen); wherein the content ratio of Ca to S [Ca/S] is from 0.90 to 2.70, and the content ratio of Ti to N [Ti/N] is 2.20 or higher; the remainder consists of Fe (iron) and unavoidable impurities; and the Ceq is from 0.380 to 0.480.

C: 0.040 to 0.080%

[0070] C is an element to improve the steel strength. From a viewpoint of such an effect, the lower limit of the C content is 0.040%. Meanwhile, when the C content exceeds 0.080%, generation of a carbide is promoted and the HIC resistance is impaired. Therefore, the upper limit of the C content is set at 0.080%. Further, for suppression of decrease in HIC resistance, weldability, and toughness, a preferable upper limit of the C content is 0.060%.

Si: 0.05 to 0.40%

[0071] Si is a deoxidizing element. From a viewpoint of such an effect, the lower limit of the Si content is 0.05%. Meanwhile, when the Si content exceeds 0.40%, the toughness of a heat affected zone (HAZ) (hereinafter also referred to as "HAZ toughness") decreases. Therefore, the upper limit of the Si content is set at 0.40%.

Mn: 1.60 to 2.00%

[0072] Mn is an element to improve strength and toughness. From a viewpoint of such effects, the lower limit of the Mn content is 1.60%. Meanwhile, when the Mn content exceeds 2.00%, the HAZ toughness decreases. Therefore, the upper limit of the Mn content is set at 2.00%. For suppressing HIC, the Mn content is preferably less than 1.75%.

P: 0.020% or less

[0073] P is an impurity, and when the content exceeds 0.020%, the HIC resistance is impaired, and the HAZ toughness decreases. Therefore, the P content is limited to 0.020% or less.

[0074] Meanwhile, the P content is preferably as low as possible, and there is no particular restriction on the lower limit of the P content. However, from a viewpoint of the production cost, the P content is preferably 0.001 % or higher.

S: 0.0025% or less

[0075] S is an element to form MnS elongating during hot rolling in the rolling direction, which decreases the HIC resistance. Therefore, in the invention, it is necessary to reduce the S content, and the S content is limited to 0.0025% or less. Since the S content is preferably as low as possible, and there is no particular restriction on the lower limit of the S content. However, from viewpoints of the production cost for secondary refining and production constraint, the S content may be 0.0008% or higher.

Mo: 0.05 to 0.20%

[0076] Mo is an element to improve hardenability and at the same time to improve strength by forming a carbonitride. Further, in the invention, Mo is contained from a viewpoint of securing a high compressive strength by promoting static strain aging during the heating in coating after making a steel pipe (line pipe), as described above. For obtaining such effects, in the invention, the lower limit of the Mo content is set at 0.05%.

[0077] On the other hand, in a case in which the Mo content is too high, the strength of a steel is increased, and the HIC resistance and the toughness (for example, DWTT property) may be occasionally decreased. Therefore, the upper limit of the Mo content is set at 0.20%.

Ca: 0.0011 to 0.0050%

[0078] Ca is an element, which forms a sulfide CaS to suppress formation of MnS elongating in the rolling direction, and contributes remarkably to improvement of the HIC resistance. When the Ca content is less than 0.0011% the above effects cannot be obtained, and therefore the lower limit of the Ca content is set at 0.0011 % in the invention. Meanwhile, when the Ca content exceeds 0.0050%, an oxide accumulates to impair the HIC resistance, and therefore the upper limit of the Ca content is set at 0.0050% or less.

Content ratio [Ca/S]: 0.90 to 2.70

[0079] In the invention, Ca is contained in the steel plate to form CaS. Thereby, S is immobilized. Therefore the content ratio of Ca to S [Ca/S] is an important index in the invention. When the content ratio [Ca/S] is less than 0.90, MnS is formed and elongated MnS is formed during rolling. As the result, the HIC resistance is deteriorated. On the other hand, when the content ratio [Ca/S] exceeds 2.70, Ca-based oxides aggregate to deteriorate the HIC resistance.

[0080] Therefore, the content ratio [Ca/S] is limited to from 0.90 to 2.70 according to the invention.

Al: 0.060% or less

[0081] Al is an element contained ordinarily as a deoxidizing element.

[0082] However, when the Al content is too high, an inclusion increases to impair the ductility or the toughness. Therefore, the upper limit of the Al content is 0.060%.

[0083] Al is further an element to promote formation of a mixed structure of martensite-austenite (MA). From a viewpoint of reduction of the MA fraction, the Al content is preferably 0.008% or less. When the Al content is 0.008% or less, it is advantageous for enhancement of the HAZ toughness.

[0084] Meanwhile, from a viewpoint of obtaining more efficiently the effect as a deoxidizing element, the Al content is preferably 0.0002% or higher.

[0085] Al is not only contained intentionally in a steel, but may also be mixed into a steel as an impurity. In a case in which Al is mixed into a steel as an impurity, the Al content is preferably as low as possible, and therefore there is no particular restriction on the lower limit of the Al content.

Nb: 0.010 to 0.030%

[0086] Nb is an element to form a carbide or a nitride contributing to improvement of the strength. For obtaining the effects, the Nb content is 0.010% or higher in the invention. However, when the Nb content is too high, a coarse carbonitride of Nb accumulates to decrease the toughness. Therefore, the Nb content is set at 0.030% or less in the invention. Further, the Nb content is preferably 0.020% or less.

Ti: 0.008 to 0.020%

[0087] Ti is an element, which is utilized ordinarily as a deoxidizing agent or a nitride forming element for micronizing a crystal grain. For obtaining the effect, the Ti content is set at 0.008% or higher according to the invention. However, Ti is also an element to decrease the toughness by forming a coarse carbonitride, when Ti is contained excessively. Therefore, the Ti content is limited to 0.020% or less in the invention.

N: 0.0015 to 0.0060%

[0088] N (nitrogen) is an element to form a nitride, such as TiN, and NbN. In order to micronize the grain size of austenite during heating by utilizing a nitride, the N content is set at 0.0015% or higher in the invention. However, when the N content exceeds 0.0060%, carbonitrides of Ti and Nb are apt to accumulate to impair the toughness. Therefore, the upper limit of the N content is set at 0.0060% in the invention.

Content ratio [Ti/N]: 2.20 or higher

[0089] In the invention, for micronizing the grain size of austenite during heating, the content ratio of Ti to N [Ti/N] is important. When the content ratio [Ti/N] is less than 2.20, sufficient TiN precipitation does not occur, and micronization of austenite cannot be achieved. Therefore, the content ratio [Ti/N] is 2.20 or higher in the invention. The content ratio [Ti/N] is preferably 3.00 or higher.

[0090] Meanwhile, from a viewpoint of further suppression of deterioration of the toughness caused by an excessive Ti carbide, the content ratio [Ti/N] is preferably 5.00 or less, and more preferably 4.00 or less.

O: 0.0040% or less

[0091] O is an impurity element. The O content is limited to 0.0040% or less in the invention. Since O is preferably as low level as possible, there is no particular restriction on the lower limit of the O content. However, from viewpoints of production cost and production constraint, the O content may be also 0.0010% or higher.

Ceq: 0.380 to 0.480

[0092] Ceq is an amount defined by the following formula (1).

$$Ceq = C+Mn/6+(Ni+Cu)/15+(Cr+Mo+V)/5 \qquad (1)$$

[0093] In the Formula (1), C, Mn, Ni, Cu, Cr, Mo, and V represent respectively the contents (mass%) of elements of C (carbon), Mn (manganese), Ni (nickel), Cu (copper), Cr (chromium), Mo (molybdenum), and V (vanadium).

[0094] Among the elements, Ni, Cu, Cr, and V are optional elements, and each of them may be also 0%. Preferable contents of the optional elements are described below.

[0095] Ceq defined by the Formula (1) is limited to from 0.380 to 0.480 in the invention. When Ceq is less than 0.380, the strength of a line pipe to be obtained by the steel plate in the invention decreases. For example, when Ceq is less than 0.380, the line pipe cannot satisfy a required tensile strength (520 MPa or higher) corresponding to the strength grade X60 or higher. Meanwhile, when Ceq exceeds 0.480, the toughness (for example, DWTT property) and the sour resistance (for example, HIC resistance) deteriorate.

[0096] Therefore, Ceq is limited to from 0.380 to 0.480 in the invention.

[0097] With respect to the steel plate according to the invention, an unavoidable impurity means a component contained in a source material or a component mixed into a steel in a production process, and not a component contained intentionally in a steel.

[0098] Specific examples of an unavoidable impurity include Sb (antimony), Sn (tin), W (tungsten), Co (cobalt), As (arsenic), Pb (lead), Bi (bismuth), B (boron), and H (hydrogen).

[0099] Ordinarily, with respect to Sb, Sn, W, Co, and As, mix up to a content of 0.1% or less, with respect to Pb and Bi mix up to a content of 0.005% or less, and with respect to B and H mix up to a content of 0.0004% or less are possible, however with respect to another element, no particular control is required insofar as the content is within an ordinary range.

[0100] Further, the steel plate according to the invention may contain one or more of 0.50% or less of Ni (nickel), 0.50% or less of Cr (chromium), 0.50% or less of Cu (copper), 0.0050% or less of Mg (magnesium), 0.0050% or less of REM (rare earth element), and 0.100% or less of V (vanadium).

[0101] For example, the steel plate according to the invention may contain one or more of 0.50% or less of Ni, 0.50% or less of Cr, and 0.50% or less of Cu. Further, it may contain one or more of 0.0050% or less of Mg, 0.0050% or less of REM, and 0.100% or less of V.

[0102] These elements may be mixed into a steel as unavoidable impurities besides intentional containing in a steel. Therefore, there is no particular restriction on the lower limits of the contents of the elements.

[0103] The elements and preferable contents thereof in case in which the steel plate according to the invention contains the elements, will be described below.

Ni: 0.50% or less

[0104] Ni (nickel) is an element effective for improving toughness and strength.

[0105] However, when the Ni content is too high, the HIC resistance and the weldability may sometimes decrease. Therefore, the Ni content is preferably 0.50% or less.

[0106] Meanwhile, the Ni content is preferably 0.05% or higher.

Cr: 0.50% or less

[0107] Cr (chromium) is an element effective for enhancing the strength of a steel by means of precipitation strengthening.

[0108] However, when the Cr content is too high, the hardenability may be increased, and bainite may become excessive to decrease the toughness. Therefore, the Cr content is preferably 0.50% or less.

[0109] Meanwhile, the Cr content is preferably 0.05% or higher.

Cu: 0.50% or less

[0110] Cu is an element effective for enhancing the strength without decreasing the toughness.

[0111] However, when the Cu content is too high, cracking is apt to occur during slab heating or welding. Therefore, the Cu content is preferably 0.50% or less.

[0112] Meanwhile, the Cu content is preferably 0.05% or higher.

Mg: 0.0050% or less

[0113] Mg is an element effective as a deoxidizing agent and a desulfurization agent, and especially an element which

contributes also to improvement of the HAZ toughness by generating a fine oxide.

[0114] However, when the Mg content is too high, an oxide is apt to aggregate and coarsen, which may lead to deterioration of the HIC resistance, or decrease in the toughness of a base material and HAZ. Therefore, the Mg content is preferably 0.0050% or less.

[0115] Meanwhile, the Mg content is preferably 0.0001 % or higher.

REM: 0.0050% or less

[0116] "REM" means herein a rare earth element, and a general term for 17 kinds of elements of Sc (scandium), Y (yttrium), La (lanthanum), Ce (cerium), Pr (praseodymium), Nd (neodymium), Pm (promethium), Sm (samarium), Eu (europium), Gd (gadolinium), Tb (terbium), Dy (dysprosium), Ho (holmium), Er (erbium), Tm (thulium), Yb (ytterbium), and Lu (lutetium). Further, "0.0050% or less of REM" means that the total content of the 17 kinds of elements is 0.0050% or less.

[0117] REM is elements effective as a deoxidizing agent and a desulfurization agent.

[0118] However, when the Mg content is too high, a coarse oxide is generated, which may lead to deterioration of the HIC resistance, or decrease in the toughness of a base material and HAZ. Therefore, the REM content is preferably 0.0050% or less.

[0119] Meanwhile, the REM content is preferably 0.0001% or higher.

V: 0.100% or less

[0120] V is an element to form a carbide or a nitride contributing to enhancement of the strength.

[0121] However, when the V content is too high, the toughness may be decreased. Therefore, the V content is preferably 0.100% or less.

[0122] Meanwhile, the V content is preferably 0.010% or higher.

[0123] A form of structure, *etc.* of the steel plate according to the invention will be described below.

[0124] As described above, in the steel plate according to the invention, due to the ferrite fraction (F1) in a structure at the position of 1/4 of the plate thickness being 20% or higher, and the ferrite fraction (F2) in a structure at the position of 1/2 of the plate thickness being 5% or higher, DWTT property is improved. In at least one of a case in which the ferrite fraction (F1) is less than 20%, and a case in which the ferrite fraction (F2) is less than 5%, (DWTT property deteriorates.

[0125] Further, as described above, in the steel plate according to the invention, due to the ferrite fraction (F1) being 60% or less, and the ferrite fraction (F2) is 60% or less, compressive strength is improved. In at least one of a case in which the ferrite fraction (F1) is beyond 60%, and a case in which the ferrite fraction (F2) is beyond 60%, the compressive strength decreases.

[0126] Further, as described above, in the steel plate according to the invention, due to the ratio (F1/F2) being 1.00 or higher, both compressive strength and DWTT property are satisfied. In a case in which the ratio (F1/F2) is less than 1.00, especially, the DWTT property deteriorates.

[0127] Further, it is difficult to make the ratio (F1/F2) beyond 5.00 from a production standpoint.

[0128] Although the ratio (F1/F2) is from 1.00 to 5.00, it is preferably more than 1.00 but 5.00 or less, and more preferably from 1.05 to 5.00.

[0129] Further, in the steel plate according to the invention, the hardness at the position of 1/2 of the plate thickness is 400 Hv or less, and the length of MnS at the position of 1/2 of the plate thickness is 1.00 mm or less.

[0130] By the above, the HIC resistance is improved. Further, the above is favorable for the DWTT property.

[0131] Although the length of MnS at the position of 1/2 of the plate thickness is 1.00 mm or less as described above, the same is more preferably within a range satisfying the following Formula (2) from a viewpoint of improvement of the HIC resistance.

$$\text{Length of MnS at the position of 1/2 of the plate thickness} \leq 10^{[(1350-X)/350]}/1000 \quad (2)$$

wherein, in Formula (2), X is a hardness (Hv) at the position of 1/2 of the plate thickness, having a value of 400 (Hv) or less.

[0132] Examples of a method for making the length of MnS at the position of 1/2 of the plate thickness satisfy the Formula (2) include a method by which a slab with a maximum Mn segregation degree in a center segregation zone of the slab of 2.2 or less and a thickness of the center segregation zone of 1.0 mm or less is subjected successively to processings of reheating, heavy plate rolling (rough rolling and finish rolling), and cooling to produce the steel plate. Preferable embodiments of respective processings will be described below.

[0133] In the steel plate according to the invention, the average grain diameter of ferrite at the position of 1/4 of the plate thickness is from 2.0 to 15.0 μm.

[0134] When the average grain diameter of ferrite at the position of 1/4 of the plate thickness is 15.0 μm or less, the DWTT property is improved.

[0135] When the average grain diameter of ferrite at the position of 1/4 of the plate thickness is 2.0 μm or more, increase in a rolling load is suppressed, which is advantageous in terms of a production cost.

[0136] Further, in the steel plate according to the invention, the average grain diameter of ferrite at the position of 1/2 of the plate thickness is from 5.0 to 20.0 μm.

[0137] When the average grain diameter of ferrite at the position of 1/2 of the plate thickness is 20.0 μm or less, the DWTT property is improved.

[0138] When the average grain diameter of ferrite at the position of 1/2 of the plate thickness is 5.0 μm or more, increase in a rolling load is suppressed, which is advantageous in terms of a production cost.

[0139] Further, the plate thickness of the steel plate according to the invention is 25 mm or more.

[0140] By this, a high compressive strength can be secured.

[0141] The plate thickness is preferably beyond 25 mm, more preferably 30 mm or more, further preferably 32 mm or more, and especially preferably 35 mm or more.

[0142] There is no particular restriction on the upper limit of the plate thickness, and the plate thickness may be for example 45 mm or less.

[0143] The steel plate according to the invention can be produced by producing a slab in a steelmaking process by melting followed by continuous casting, and thereafter subjecting the slab to reheating, heavy plate rolling, and cooling successively.

[0144] The thickness of the slab is preferably 300 mm or more, because a steel plate with a plate thickness of 25 mm or more can be obtained easily.

[0145] The reheating temperature in reheating the slab is preferably 950°C or more from a viewpoint of further improvement of the HIC resistance.

[0146] Further, the reheating temperature is preferably 1150°C or less, from a viewpoint of further suppression of deterioration of the DWTT property.

[0147] Further, in the heavy plate rolling, rough rolling with an average rolling reduction of 10% or more per 1 pass to 120 mm or more in a recrystallization temperature range (for example, a temperature range beyond 900°C) is preferable. The average rolling reduction of 10% or more per 1 pass is advantageous, because recrystallization of austenite is promoted so that the grain size can be made fine. Further, rough rolling only to 120 mm or more is advantageous, because a cumulative rolling reduction can be enlarged in the succeeding rolling in the non-recrystallization region. Namely, in a case in which a cumulative rolling reduction in the rolling in the non-recrystallization region is enlarged, many dislocations can be introduced in austenite grains. Since the dislocations introduced in austenite grains can constitute nucleation sites for transformation to ferrite in the succeeding cooling process, they contribute to micronization of the grain size.

[0148] Meanwhile, in the heavy plate rolling, after the rough rolling, a rolling (finish rolling) is performed preferably in a non-recrystallization region (for example, a temperature range between 750 and 900°C) down to a final plate thickness of 25 mm or more.

[0149] Cooling after the heavy plate rolling (for example, water cooling) is preferably performed with a cooling start temperature of 700 to 820°C. The cooling start temperature of 700°C or more is advantageous, because the ferrite fraction (F2) at the position of 1/2 of the plate thickness can be easily made to 60% or less, and the maximum hardness at the position of 1/2 of the plate thickness can be easily made to 400 Hv or less. The cooling start temperature of 820°C or less is advantageous, because the ferrite fraction (F2) can be easily adjusted to 5% or higher, and the DWTT property can be easily improved.

[0150] The cooling rate during the cooling is preferably 10°C/s or more from a viewpoint of further improvement of the strength.

[0151] The cooling stop temperature is preferably 200°C or more from a viewpoint of further suppression of HIC at the position of 1/2 of the plate thickness so as to further suppress deterioration of the toughness. The cooling stop temperature is preferably 450°C or less from a viewpoint of further improvement of the strength.

[0152] In the cooling, the cooling rate (V1) at the position of 1/4 of the plate thickness is preferably slower than the cooling rate (V2) at the position of 1/2 of the plate thickness (V2) in a temperature range between 600 and 700°C. By this, the ferrite formation amount at the position of 1/4 of the plate thickness can be made higher than the ferrite formation amount at the position of 1/2 of the plate thickness, and therefore the ratio (F1/F2) can be easily adjusted to 1.00 or higher.

[0153] Meanwhile, in an ordinary steel plate production the cooling rate (V1) is higher than the cooling rate (V2) as described above, and therefore the ratio (F1/F2) of the obtained steel plate is less than 1.00.

[0154] Further, with respect to the cooling, the cooling rate in a temperature range of 600°C or less (V3) is preferably 15°C/s or more. By this, formation of a pearlite structure in remainder structures at the position of 1/4 of the plate thickness

and at the position of 1/2 of the plate thickness can be suppressed so as to suppress HIC.

[Line pipe]

[0155] A line pipe according to the invention is a steel pipe produced using the steel plate for a line pipe according to the invention.

[0156] Therefore, similar to the steel plate according to the invention, the line pipe according to the invention is superior in HIC resistance (especially HIC resistance in a sour environment of pH 5.0 or higher) and satisfies both compressive strength and DWTT property.

[0157] The line pipe according to the invention can be produced using the steel plate for a line pipe according to the invention as a source material by a publicly known pipe making method.

[0158] Examples of a publicly known pipe making method include UOE forming method, and JCOE forming method.

EXAMPLES

[0159] Next, the invention will be described in more detail by way of Examples, provided that the invention be not limited to the following Examples.

[0160] [Inventive Examples 1 to 10, and Comparative Examples 1 to 12]

<Production of steel plate>

[0161] Steels having a chemical composition set forth in the following Table 1 (steel No. 1 to steel No. 15) were produced by melting, and slabs with a thickness (slab thickness) shown in the following Table 2 were produced by continuous casting. In continuous casting, soft reduction was conducted during the final solidification so as to suppress segregation of Mn in a center segregation zone.

[0162] In this regard, components of a steel (the remainder) other than the components shown in the following Table 1 are Fe and unavoidable impurities.

[0163] Further, "REM" in steel No. 6 is specifically Ce, and "REM" in steel No. 9 is specifically La.

[0164] The thus obtained slab was heated to from 950 to 1150°C (exceptionally 1180°C in Comparative Example 2), then rough rolling was conducted above 900°C with an average rolling reduction of 10% or higher (exceptionally 8% in Comparative Example 3) down to a thickness of 120 mm or more (exceptionally 100 mm in Comparative Example 4), and thereafter finish rolling was conducted in a non-recrystallization temperature range of 900°C or less (exceptionally 930°C in Comparative Example 5) down to the final plate thickness.

[0165] After hot rolling accelerated cooling (water cooling) was started in a temperature range between 700 and 820°C and the accelerated cooling (water cooling) was stopped at a temperature of from 200 to 450°C to produce steel plates with various different plate thicknesses (final plate thicknesses) shown in the following Table 2.

[0166] Detailed conditions of respective examples are as shown in the following Table 2.

[0167] Especially, with respect to accelerated cooling (water cooling) in Inventive Examples 1 to 10 and Comparative Examples 1 to 5 and 7 to 13, the accelerated cooling (water cooling) was regulated such that the cooling rate (V1) at the position of 1/4 of the plate thickness was slower than the cooling rate (V2) at a position of 1/2 of the plate thickness in a temperature range of from 600 to 700°C where ferrite is formed. Specifically, a water cooling zone, where a steel plate after finish rolling passed, was segmented to sprinkling zones and non-sprinkling zones, so that a steel plate could be cooled with water intermittently. By this, cooling and heat-recuperation of a surface of the steel plate are regulated properly such that the V1 was made slower than the V2

[0168] In the case of accelerated cooling (water cooling) in Comparative Example 6, the V1 was made faster than the V2 by cooling the steel plate continuously with water similarly as an ordinary production method for a steel plate.

<Measurement and evaluation>

[0169] The following measurements and evaluations were performed on the thus obtained steel plates. The results are shown in the following Table 3.

- Ferrite fractions (F1, F2), ferrite grain size, and remainder structure -

[0170] With respect to each of a cross-section of the steel plate cut at the position of 1/2 of the plate thickness and a cross-section of the steel plate cut at the position of 1/4 of the plate thickness, the ferrite fraction (ferrite area ratio) and the ferrite grain size (average grain diameter of ferrite) were measured, and further the remainder structure was identified.

[0171] More particularly, a cross-section of the steel plate was polished, and corroded with a LePera reagent, and a

photograph of a structure of the same was taken using an optical microscope at a magnification of 500-fold. Through image processing of the obtained optical micrograph (magnification 500-fold), the ferrite fraction (ferrite area ratio) and the ferrite grain size (average grain diameter of ferrite) were determined, and further the remainder structure was identified.

[0172] The image processing was carried out using a small size multi-purpose image analyzer LUZEX AP (produced by Nireco Corporation).

[0173] In this regard, an average grain diameter of ferrite was determined by measuring equivalent circle diameters for 30 grains of ferrite, and calculating a simple average of the 30 equivalent circle diameters.

[0174] As above, the ferrite fraction at 1/4 of plate thickness F1, the ferrite fraction at 1/2 of plate thickness F2, the ferrite grain size at 1/4 of plate thickness, and the ferrite grain size at 1/2 of plate thickness as shown in the following Table 3 were determined respectively, and the remainder structure at 1/4 of plate thickness and the remainder structure at 1/2 of plate thickness as shown in the following Table 3 were identified respectively.

[0175] For example, an optical micrograph (magnification 500-fold) of a cross-section (cross-section after polishing and corrosion with a LePera reagent) at the position of 1/2 of the plate thickness of the steel plate of Inventive Example 10 is shown in Fig. 1.

- Calculation of ratio [F1/F2] -

[0176] A ratio [F1/F2] was determined based on a ferrite fraction at the position of 1/4 of the plate thickness (F1), and a ferrite fraction at the position of 1/2 of the plate thickness (F2) measured as above.

- Hardness at position of 1/2 of plate thickness -

[0177] The steel plate obtained as above was cut along the plate thickness direction, and the appeared cross-section was mirror polished. According to JIS Z 2244 (2009), a Vickers hardness test was conducted on the mirror polished cross-section with a 25 g load.

[0178] The Vickers hardness test was performed for 400 points at the position of 1/2 of the plate thickness. The maximum value among the 400 measurement results was defined as the "Hardness at 1/2 of plate thickness" (the following Table 3).

- MnS length at position of 1/2 of plate thickness -

[0179] A macro-specimen was sampled from the steel plate, and a corrosion test was conducted on the sampled macro-specimen according to NACE TM0284. By this, cracking caused by elongated MnS was forcibly induced on the macro-specimen, which was then forcibly fractured in liquid nitrogen. By this, elongated MnS were exposed on the fractured surface. The fractured surface was observed with a scanning electron microscope, and the lengths of all the recognized elongated MnS were measured. From the length measurement results, the lengths of elongated MnS existing at the position of 1/2 of the plate thickness were selected, and the maximum value among the selected values (lengths) was defined as "MnS length at 1/2 of plate thickness" (the following Table 3).

- Tensile strength -

[0180] A specimen for a tensile test was sampled from the steel plate such that the longitudinal direction of the specimen is parallel to the width direction of the steel plate. In this regard, the shape of a specimen was a flat plate shape according to the American Petroleum Institute specification: API 5L (hereinafter referred to simply as "API 5L").

[0181] A tensile test was conducted on the sampled specimen at room temperature according to API 5L. The tensile strength was determined based on the maximum load in the tensile test.

- Compressive strength -

[0182] Compressive strength was measured by the following method in order to evaluate a property in the circumferential direction of a steel pipe, the steel pipe being made of the steel plate as a line pipe followed by being subjected to the heating in coating for anti-corrosion.

[0183] A large width specimen (full thickness specimen) was sampled from the steel plate such that the longitudinal direction of the specimen was parallel to the width direction of the steel plate. In order to apply a strain correspond to pipe making, a 2% pre-strain was applied to the sampled large width specimen.

[0184] Next, a compression test specimen was taken from the pre-strained large width specimen.

[0185] In this case, the compression test specimen was in a cylindrical shape with diameter 22 mm $\times$ length 66 mm, and taken such that the center part in the direction of the steel plate was included and the longitudinal direction of the

compression test specimen (test direction of the compression test) was parallel to the width direction of the steel plate.

[0186] The taken compression test specimen was heat-treated at 220°C for 5 min in a salt bath, and then the heat-treated compression test specimen was subjected to a compression test according to ASTM E9-09. A 0.5% offset yield strength in the compression test was defined as a yield strength (compressive strength).

- Evaluation of DWTT property (DWTT fracture area ratio (-20°C)) -

[0187] A DWTT specimen was taken out from the steel plate such that the longitudinal direction of the DWTT specimen was parallel to the width direction of the steel plate.

[0188] In this case, the DWTT specimen was a full thickness specimen with a pressed notch.

[0189] A DWTT test was conducted on the taken out DWTT specimen at -20°C according to API 5L to measure the ratio of a ductile fracture area to the total fracture area (DWTT fracture area ratio (%)).

[0190] According to this evaluation, the higher (most preferably 100%) a value of the DWTT fracture area ratio (%) exhibits, the superior the DWTT property is.

- Evaluation of HIC resistance (CAR in HIC test) -

[0191] A specimen (full thickness specimen) for a HIC resistance evaluation was taken out of the steel plate.

[0192] The taken specimen was immersed in a "Solution B" according to NACE TM0284 for 96 hours, and the specimen after the immersion was analyzed with an ultrasonic flaw detector for existence or nonexistence of occurrence of HIC. Based on the analysis results, a crack area ratio (CAR) was determined.

[0193] According to this evaluation, the smaller the CAR (most preferably 0%) exhibits, the superior the HIC resistance is.

[Table 1]

	Steel	Component (mass%)																				Ca/S	Ti/N	Ceq
		C	Si	Mn	P	S	Mo	Ca	Al	Nb	Ti	N	Ni	Cu	Cr	Mg	REM	V	O			
Inventive Example	1	0.078	0.06	1.98	0.006	0.0022	0.18	0.0023	0.007	0.012	0.016	0.0043							0.0018	1.05	3.72	0.444
	2	0.065	0.37	1.65	0.013	0.0023	0.20	0.0028	0.032	0.029	0.011	0.0030							0.0021	1.22	3.67	0.380
	3	0.080	0.10	1.61	0.005	0.0008	0.19	0.0011	0.005	0.011	0.008	0.0023							0.0016	1.38	3.48	0.386
	4	0.062	0.12	1.70	0.018	0.0020	0.05	0.0050	0.020	0.010	0.020	0.0050	0.50						0.0025	2.50	4.00	0.389
	5	0.040	0.17	1.95	0.005	0.0019	0.10	0.0021	0.005	0.020	0.010	0.0029	0.20	0.20					0.0023	1.11	3.45	0.412
	6	0.052	0.12	1.92	0.013	0.0024	0.17	0.0024	0.006	0.021	0.011	0.0049			0.35		0.0023		0.0021	1.00	2.24	0.476
	7	0.057	0.24	1.63	0.008	0.0022	0.08	0.0028	0.007	0.018	0.012	0.0032	0.10	0.10	0.25			0.050	0.0017	1.27	3.75	0.418
	8	0.042	0.19	1.69	0.013	0.0018	0.13	0.0028	0.005	0.025	0.014	0.0042	0.17	0.17	0.17	0.0023		0.040	0.0023	1.56	3.33	0.414
	9	0.063	0.21	1.62	0.009	0.0012	0.13	0.0025	0.005	0.018	0.012	0.0033	0.13	0.13	0.30		0.0032		0.0021	2.08	3.64	0.436
	10	0.050	0.17	1.63	0.013	0.0020	0.10	0.0021	0.005	0.020	0.010	0.0029	0.16	0.18	0.13	0.0020			0.0023	1.05	3.45	0.390
Comparative Example	11	0.035	0.22	1.55	0.012	0.0011	0.02	0.0022	0.006	0.028	0.010	0.0030	0.30		0.20				0.0027	2.00	3.33	0.357
	12	0.062	0.43	2.10	0.018	0.0013	0.12	0.0023	0.012	0.012	0.013	0.0063	0.30	0.30	0.10				0.0019	1.77	2.06	0.496
	13	0.085	0.11	1.62	0.008	0.0017	0.15	0.0009	0.006	0.022	0.020	0.0044							0.0023	0.53	4.55	0.385
	14	0.066	0.08	1.75	0.009	0.0030	0.08	0.0023	0.006	0.035	0.015	0.0025			0.25				0.0021	0.77	6.00	0.424
	15	0.061	0.23	1.78	0.022	0.0020	0.25	0.0060	0.006	0.022	0.011	0.0020	0.10	0.10					0.0018	3.00	5.50	0.421

[Table 2]

	Steel	Slab thickness	Heating temperature	Average rolling reduction per 1 pass at 900°C or higher	Thickness at end of rough rolling	Start temperature of finish rolling	Final plate thickness	Accelerated cooling start temperature	Cooling rate from 700°C to 600°C		Cooling rate below 600°C	Stop temperature of accelerated cooling
									at 1/4 of plate thickness V1	at 1/2 of plate thickness V2	at 1/2 of plate thickness V3	
		mm	°C	%	mm	°C	mm	°C	°C/s	°C/s	°C/s	°C
Inventive Example 1	1	400	950	10	140	880	35	740	14	16	20	450
Inventive Example 2	2	400	950	10	150	800	45	740	12	13	20	300
Inventive Example 3	3	360	950	13	160	840	40	820	12	15	20	440
Inventive Example 4	4	360	1150	10	150	820	35	780	13	16	20	420
Inventive Example 5	5	320	1150	15	120	900	25	700	10	12	20	280
Inventive Example 6	6	320	1000	10	160	830	32	750	10	13	15	300
Inventive Example 7	7	320	1080	13	160	830	32	750	12	15	20	400
Inventive Example 8	8	300	1100	20	150	850	39	760	14	15	30	200
Inventive Example 9	9	300	1050	13	150	850	39	770	13	14	25	350
Inventive Example 10	10	300	1080	18	120	850	39	780	10	12	20	350
Comparative Example 1	8	240	1050	12	150	830	36	800	11	14	25	400
Comparative Example 2	9	320	1180	12	150	870	36	800	12	14	20	250

(continued)

	Steel	Slab thickness	Heating temperature	Average rolling reduction per 1 pass at 900°C or higher	Thickness at end of rough rolling	Start temperature of finish rolling	Final plate thickness	Accelerated cooling start temperature	Cooling rate from 700°C to 600°C		Cooling rate below 600°C	Stop temperature of accelerated cooling
									at 1/4 of plate thickness V1	at 1/2 of plate thickness V2	at 1/2 of plate thickness V3	
		mm	°C	%	mm	°C	mm	°C	°C/s	°C/s	°C/s	°C
Comparative Example 3	10	320	1100	8	150	830	36	750	14	15	20	350
Comparative Example 4	9	300	1100	12	100	830	36	750	13	14	20	350
Comparative Example 5	8	300	1100	10	150	930	36	750	12	14	20	300
Comparative Example 6	10	300	1080	18	120	850	39	750	16	12	20	350
Comparative Example 7	9	400	1100	12	150	800	36	780	12	13	7	250
Comparative Example 8	11	300	1100	12	150	800	36	750	12	14	20	400
Comparative Example 9	12	300	1100	12	150	800	36	750	12	14	20	400
Comparative Example 10	13	300	1100	12	150	800	36	750	12	14	20	400
Comparative Example 11	14	360	1100	12	150	800	36	750	12	14	20	400
Comparative Example 12	15	360	1100	12	150	800	36	750	12	14	20	400

[Table 3]

	Steel	Ferrite fraction at 1/4 of plate thickness F1	Remainder structure at 1/4 of plate thickness	Ferrite fraction at 1/2 of plate thickness F2	Remainder structure at 1/2 of plate thickness	Ferrite grain size at 1/4 of plate thickness	Ferrite grain size at 1/2 of plate thickness	F1/F2	Hardness at 1/2 of plate thickness	MnS length at 1/2 of plate thickness	Tensile strength	Compressive strength *	DWTT fracture area ratio (-20°C)	CAR in HIC test
		%		%		μm	μm		Hv	mm	MPa	MPa	%	%
Inventive Example 1	1	45	bainite	38	bainite	3.4	5.3	1.18	340	0.95	622	519	100	0
Inventive Example 2	2	58	bainite	42	bainite + martensite	4.3	5.5	1.38	312	0.85	623	523	100	0
Inventive Example 3	3	22	bainite	5	bainite	7.8	7.6	4.40	348	0.92	605	510	100	0
Inventive Example 4	4	25	bainite	18	bainite	13.7	12.3	1.39	250	0.67	608	501	100	0
Inventive Example 5	5	51	bainite	42	bainite + martensite	13.5	16.2	1.21	310	0.98	648	534	100	0
Inventive Example 6	6	51	bainite	21	bainite + martensite	5.8	6.3	2.43	333	0.88	675	555	100	0
Inventive Example 7	7	48	bainite	28	bainite	7.7	7.8	1.71	278	0.88	622	512	100	0
Inventive Example 8	8	55	bainite	52	bainite + martensite	6.4	7.4	1.06	292	0.81	638	522	100	0
Inventive Example 9	9	52	bainite	45	bainite + martensite	8.5	8.2	1.16	278	0.19	650	536	100	0
Inventive Example 10	10	40	bainite	35	bainite + martensite	6.4	6.4	1.14	255	0.98	642	532	100	0
Comparative Example 1	8	35	bainite	25	bainite	16.8	18.2	1.40	288	0.83	632	512	10	0
Comparative Example 2	9	12	bainite	5	bainite + martensite	17.8	17.3	2.40	322	0.80	642	555	25	0

(continued)

	Steel	Ferrite fraction at 1/4 of plate thickness F1	Remainder structure at 1/4 of plate thickness	Ferrite fraction at 1/2 of plate thickness F2	Remainder structure at 1/2 of plate thickness	Ferrite grain size at 1/4 of plate thickness	Ferrite grain size at 1/2 of plate thickness	F1/F2	Hardness at 1/2 of plate thickness	MnS length at 1/2 of plate thickness	Tensile strength	Compressive strength *	DWTT fracture area ratio (-20°C)	CAR in HIC test
		%		%		μm	μm		Hv	mm	MPa	MPa	%	%
Comparative Example 3	10	35	bainite	32	bainite + martensite	16.5	16.2	1.09	292	0.88	640	529	40	0
Comparative Example 4	9	48	bainite	42	bainite + martensite	17.8	18.2	1.14	266	0.22	652	519	38	0
Comparative Example 5	8	12	bainite	12	bainite+ martensite	16.9	19.1	1.00	322	0.82	544	540	25	0
Comparative Example 6	10	18	bainite	35	bainite + martensite	7.1	6.6	0.51	261	0.31	661	574	40	0
Comparative Example 7	9	50	pearlite	45	pearlite	8.5	7.8	1.11	265	0.28	525	440	100	12
Comparative Example 8	11	75	bainite	80	bainite	9.2	19.0	0.94	198	0.12	495	450	100	0
Comparative Example 9	12	7	bainite	3	bainite + martensite	7.8	5.7	2.33	353	0.65	732	645	35	28.5
Comparative Example 10	13	46	bainite	34	bainite + martensite	8.8	9.3	1.35	415	1.45	712	623	55	48.5
Comparative Example 11	14	48	bainite	42	bainite	9.4	7.9	1.14	288	2.41	634	521	75	34.5
Comparative Example 12	15	16	bainite	15	bainite	7.8	8.8	1.07	341	0.88	677	578	45	14.2

* The compressive strength in the Table 3 is a compressive strength after application of a 2% pre-strain followed by a heat treatment at 220°C.

[0194] As shown in Table 1 to Table 3, the steel plates of Inventive Examples 1 to 10 having compositions of Steel No. 1 to Steel No. 10, which are Inventive Examples, and in which the ferrite fraction (F1), the ferrite fraction (F2), the ratio [F1/F2], the remainder structure at 1/4 of the plate thickness, the remainder structure at 1/2 of the plate thickness, the ferrite grain size at 1/4 of the plate thickness, the ferrite grain size at 1/2 of the plate thickness, the hardness at 1/2 of the plate thickness and the MnS length at 1/2 of the plate thickness were within the scope of the invention, were superior in compressive strength, DWTT property, and HIC resistance.

[0195] In contrast thereto, the steel plates of Comparative Examples 1 to 7 having compositions of Steel No. 8 to Steel No. 10, which are Inventive Examples, but in which at least one of the ferrite fraction (F1), the ferrite fraction (F2), the ratio [F1/F2], the remainder structure at 1/4 of the plate thickness, the remainder structure at 1/2 of the plate thickness, the ferrite grain size at 1/4 of the plate thickness, the ferrite grain size at 1/2 of the plate thickness, the hardness at 1/2 of the plate thickness and the MnS length at 1/2 of the plate thickness was outside the scope of the invention, were inferior in at least one of compressive strength, DWTT properties, and HIC resistance.

[0196] Further, the steel plates of Comparative Examples 8 to 12 having compositions of Steel No. 11 to Steel No. 15, which are Comparative Examples, were inferior in at least one of compressive strength, DWTT property, and HIC resistance.

[Production of line pipe]

<Production and evaluation of line pipe 1>

[0197] The steel plate of Inventive Example 10 was subjected to pipe making by the UOE forming method to yield a line pipe 1 with the outer diameter and the wall thickness set forth in Table 4.

[0198] With respect to the yielded line pipe 1, tensile strength, yield strength, compressive strength, DWTT fracture area ratio (-20°C), CAR in a HIC test, HAZ toughness, and WM (Weld Metal) toughness were measured.

[0199] The measurement results are shown in Table 4.

[0200] Among them, tensile strength, DWTT fracture area ratio (-20°C), and CAR in a HIC test were measured similarly as the respective measurements with respect to the steel plates above.

[0201] Yield strength, compressive strength, HAZ toughness, and WM toughness were measured as follows.

- Measurement of yield strength -

[0202] The yield strength in the longitudinal direction of the line pipe was measured according to ASTM E9-09. In this regard, a 0.5% under load proof strength was defined as a yield strength.

- Measurement of compressive strength -

[0203] The compressive strength in the circumferential direction of a line pipe was measured according to ASTM E9-09. In this regard, a 0.5% extension under load yield strength was defined as a compressive strength.

- Measurement of HAZ toughness -

[0204] A Charpy test specimen with a V-notch was taken from a position 2 mm-deep from the outer peripheral surface of the line pipe. The V-notch of the specimen was provided such that a fracture after a Charpy impact test includes HAZ and WM at an area ratio of 50%/50%.

[0205] Using the obtained Charpy test specimen with a V-notch, a Charpy impact test was conducted according to JIS Z2242 (2005) under the temperature condition of -20°C, and a Charpy absorbed energy (J) was defined as a HAZ toughness (J).

- Measurement ofWM toughness -

[0206] A Charpy test specimen with a V-notch was taken from a position 2 mm-deep from the outer peripheral surface of a line pipe. The V-notch of the specimen was provided such that the center of the V-notch was positioned at the center of a WM.

[0207] Using the obtained Charpy test specimen with a V-notch, a Charpy impact test was conducted according to JIS Z2242 (2005) under the temperature condition of -20°C, and a Charpy absorbed energy (J) was defined as a WM toughness (J).

<Production and evaluation of line pipe 2>

[0208] A steel plate was prepared identically with the steel plate of Inventive Example 10 except that the plate thickness was changed to 45 mm.

[0209] The prepared 45 mm-thick steel plate was subjected to pipe making by the JCOE forming method to obtain a line pipe 2 with the outer diameter and the wall thickness set forth in Table 4.

[0210] For the line pipe 2 measurements were conducted similarly as for the line pipe 1. The results are shown in Table 4.

[Table 4]

Line pipe	Pipe making method	Steel	Outer diameter	Wall thickness	Tensile strength	Yield strength	Compressive strength	DWTT fracture area ratio (-20°C)	CAR in HIC test	HAZ toughness (-20°C)	WM toughness (-20°C)
			mm	mm	MPa	MPa	MPa	%	%	J	J
1	UOE	10	813	39	651	553	539	95	0	194	210
2	JCOE	10	813	45	659	555	541	97	0	165	226

[0211] As is obvious from Table 4, the line pipes 1 and 2 produced by using the steel plates of the Inventive Examples were superior in compressive strength, DWTT property, and HIC resistance, in a similar manner to the steel plates of the Inventive Examples.

[0212] Further, also with respect to HAZ toughness and WM toughness, the line pipes 1 and 2 exhibited favorable results.

[0213] The entire disclosure of Japanese Patent Applications No. 2013-155063, and Japanese Patent Applications No. 2013-155064 are incorporated herein by reference.

[0214] All documents, patent applications, and technical standards described in this specification are herein incorporated by reference to the same extent as if each individual document, patent application, or technical standard was specifically and individually indicated to be incorporated by reference.

Claims

1. A steel plate for a line pipe, the steel plate having a plate thickness of 25 mm or more and comprising in terms of mass%:

0.040 to 0.080% of C,
0.05 to 0.40% of Si,
1.60 to 2.00% of Mn,
0.020% or less of P,
0.0025% or less of S,
0.05 to 0.20% of Mo,
0.0011 to 0.0050% of Ca,
0.060% or less of Al,
0.010 to 0.030% of Nb,
0.008 to 0.020% of Ti,
0.0015 to 0.0060% of N, and
0.0040% or less of O,
wherein a content ratio of Ca to S [Ca/S] is from 0.90 to 2.70, and a content ratio of Ti to N [Ti/N] is 2.20 or higher,
a remainder consisting of Fe and unavoidable impurities,
wherein Ceq, which is defined by the following Formula (1), is from 0.380 to 0.480:

$$Ceq = C+Mn/6+(Ni+Cu)/15+(Cr+Mo+V)/5 \quad (1)$$

wherein, in the Formula (1), C, Mn, Ni, Cu, Cr, Mo, and V represent contents of respective elements (mass%), and wherein:

at a position of 1/4 of the plate thickness, a ferrite fraction (F1) is from 20 to 60% and a remainder is a structure of bainite,
at a position of 1/2 of the plate thickness, a ferrite fraction (F2) is from 5 to 60% and a remainder is a structure of bainite or a structure of bainite and martensite,
a ratio (F1/F2) of the ferrite fraction (F1) to the ferrite fraction (F2) is from 1.00 to 5.00,
at a position of 1/4 of the plate thickness an average grain diameter of ferrite is from 2.0 to 15.0 μm, and
at a position of 1/2 of the plate thickness the average grain diameter of ferrite is from 5.0 to 20.0 μm, and
a hardness at a position of 1/2 of the plate thickness is 400 Hv or less, and a length of MnS at a position of 1/2 of the plate thickness is 1.00 mm or less.

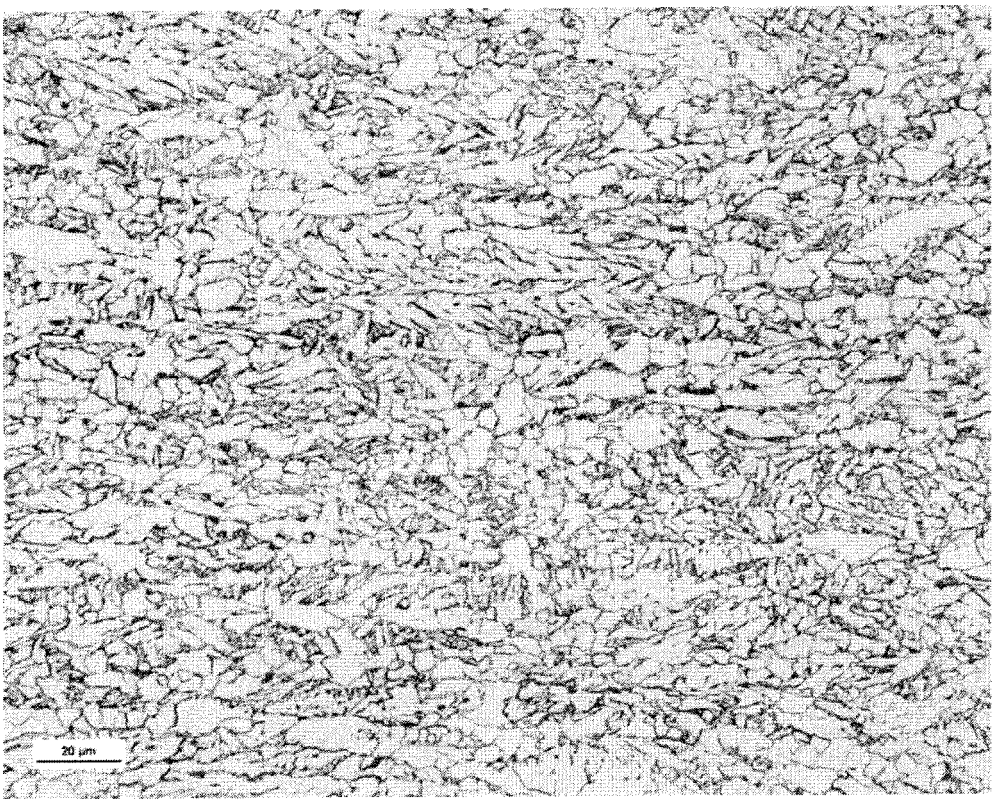
2. The steel plate for a line pipe according to claim 1, wherein an A1 content is 0.008% or less in terms of mass%.

3. The steel plate for a line pipe according to claim 1 or 2, comprising, in terms of mass%, one or more of:

0.50% or less of Ni,
0.50% or less of Cr,
0.50% or less of Cu,
0.0050% or less of Mg,
0.0050% or less of REM, and
0.100% or less of V.

4. A line pipe produced using the steel plate for a line pipe according to any one of claims 1 to 3.

FIG.1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/069471

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *B21B1/38*(2006.01)i, *B21B3/00*(2006.01)i, *C21D8/02*(2006.01)i, *C22C38/14*(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, B21B1/38, B21B3/00, C21D8/02, C22C38/14, 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 2012-241272 A (JFE Steel Corp.), 10 December 2012 (10.12.2012), entire text; all drawings (Family: none)	1-4
A	JP 2011-132599 A (JFE Steel Corp.), 07 July 2011 (07.07.2011), entire text; all drawings & US 2012/0285576 A1 & EP 2505682 A1 & WO 2011/065579 A1 & KR 10-2012-0083935 A & CN 102666898 A	1-4
A	WO 2011/030768 A1 (Nippon Steel Corp.), 17 March 2011 (17.03.2011), entire text; all drawings & JP 5131715 B & WO 2011/030768 A1 & CN 102482744 A	1-4

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

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Date of the actual completion of the international search	Date of mailing of the international search report
08 September, 2014 (08.09.14)	07 October, 2014 (07.10.14)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/069471

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 2008-101242 A (JFE Steel Corp.), 01 May 2008 (01.05.2008), entire text; all drawings (Family: none)	1-4
A	JP 11-80833 A (NKK Corp.), 26 March 1999 (26.03.1999), entire text; all drawings (Family: none)	1-4
A	JP 63-38520 A (Sumitomo Metal Industries, Ltd.), 19 February 1988 (19.02.1988), entire text; all drawings (Family: none)	1-4
A	WO 2009/072753 A1 (Posco), 11 June 2009 (11.06.2009), entire text; all drawings & US 2010/0258219 A1 & EP 2240618 A1 & KR 10-2009-0058058 A & KR 10-2009-0119263 A & CN 101883875 A & ES 2402548 T3	1-4

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REFERENCES CITED IN THE DESCRIPTION

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- JP S61165207 A **[0011]**
- JP 2011132600 A **[0011]**
- JP 2010189722 A **[0011]**
- JP 2013155063 A **[0213]**
- JP 2013155064 A **[0213]**