(11) EP 3 042 976 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication: 13.07.2016 Bulletin 2016/28

(21) Application number: 14840842.0

(22) Date of filing: 29.08.2014

(51) Int CI.: C22C 38/00 (2006.01) C22C 38/14 (2006.01)

C21D 8/02 (2006.01) C22C 38/58 (2006.01)

(86) International application number: PCT/JP2014/072833

(87) International publication number: WO 2015/030210 (05.03.2015 Gazette 2015/09)

(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: 30.08.2013 JP 2013180663

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- (54) STEEL SHEET FOR THICK-WALLED HIGH-STRENGTH LINE PIPE HAVING EXCEPTIONAL SOURING RESISTANCE, CRUSH RESISTANCE PROPERTIES, AND LOW-TEMPERATURE DUCTILITY, AND LINE PIPE
- (57) This invention provides steel plate for thick-gauge high-strength linepipe which is excellent in sour resistance, collapse resistance, and low-temperature toughness and the method for manufacturing the same.

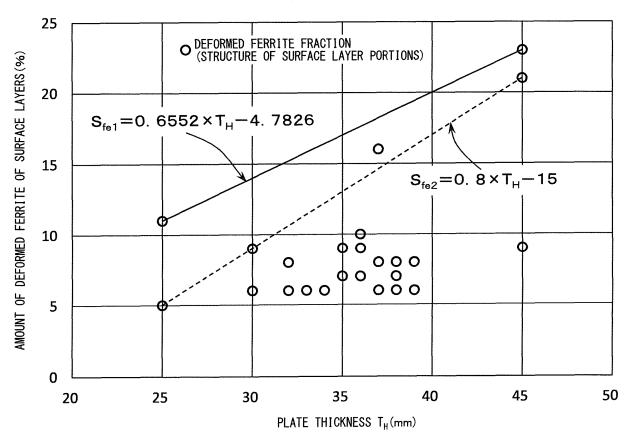
Steel plate for thick-gauge high-strength linepipe comprises steel plate having a plate thickness of 25 mm to 45 mm, wherein a microstructure of surface layer portion is restricted to, by area percentage, deformed ferrite: 5% or more and S_{fe1} % found by the following formula 1a or less and martensite-austenite mixture: 8% or less and has a balance of one or both of polygonal ferrite and bainite, and a microstructure of a mid-thickness portion is restricted to, by area percentage, deformed ferrite: 5% or less, martensite-austenite mixture: 5% or less and has a balance of one or both of acicular ferrite and bainite, and the surface layer portion and mid-thickness portion have average value of effective grain size measured by electron backscatter diffraction of 20 μ m or less.

$$S_{\text{fe1}}$$
=0. 6552× T_{H} -4.7826 ··· formula 1a

where, T_H: plate thickness of steel plate for thick-gauge high-strength linepipe

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Description

Technical Field

[0001] The present invention relates to steel plate for thick-gauge high-strength linepipe which is excellent in sour resistance, collapse resistance, and low-temperature toughness, in particular steel plate for thick-gauge high-strength linepipe which is excellent in sour resistance, collapse resistance, and low-temperature toughness which is therefore optimal for linepipe for transport of natural gas or crude oil and relates to linepipe having excellent sour resistance, collapse resistance, and low-temperature toughness.

Background Art

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[0002] In recent years, the importance of pipelines as a method of long distance transport of crude oil or natural gas has been growing. The thinking in design of trunk linepipes for long distance transport is mainly based on the standards of the American Petroleum Institute (API). In the past, linepipe excellent in tensile strength and low-temperature toughness has been developed to prevent bursting upon application of internal pressure. To raise the efficiency of transport of crude oil or natural gas, higher strength and greater thickness of linepipe have been considered necessary. Further, when laying linepipe in arctic regions, in particular low-temperature toughness has been demanded. However, in general, if making the strength higher and the thickness greater, it becomes difficult to secure the toughness of the steel material. [0003] To reduce the changes in hardness of a thick-gauge material in the plate thickness direction and improve the low-temperature toughness, PLT 1 proposes the method of rolling in a temperature region where the microstructure becomes the dual phase of austenite and ferrite (dual phase region). According to this method, it is possible to make the microstructure of a thick-gauge material into a fine acicular ferrite structure in which island martensite is mixed.

[0004] Further, recently, the characteristics required for linepipe have become more diversified. In addition to strength and low-temperature toughness, a collapse resistance enabling the pipe to not be collapsed by outside pressure or a sour resistance enabling the pipe to not crack in a sour environment which contains hydrogen sulfide etc. has sometimes been demanded. In particular, when laying a pipeline in the deep ocean, achievement of both the contrary characteristics of the collapse resistance and low-temperature toughness has been demanded. However, due to the increased thickness of linepipe, achievement of both this collapse resistance and low-temperature toughness has become extremely difficult.

Citations List

Patent Literature

35 [0005]

PLT 1: Japanese Patent Publication No. 8-041536A PLT 2: Japanese Patent Publication No. 2010-084170A

PLT 3: Japanese Patent Publication No. 2010-084171A PLT 4: Japanese Patent Publication No. 2011-132599A

PLT 5: Japanese Patent Publication No. 2011-163455A

Summary of Invention

Technical Problem

[0006] As explained above, in recent years, the characteristics required for linepipe for transport of natural gas or crude oil which is laid on the deep ocean floor have become more complicated. Greater thickness, higher strength, lowtemperature toughness, sour resistance, and further collapse resistance have been demanded.

[0007] In the case of the above-mentioned PLT 1, improvement of the sour resistance and collapse resistance is not considered at all. In particular, the island martensite becomes initiating points for fracture, so have the problem of causing a drop in the fracture toughness.

[0008] To deal with this problem, the method of suppressing the formation of hard martensite and suppressing the difference in hardness between the ferrite and bainite and the method of utilizing fine bainite so as to suppress the Bauschinger effect have been proposed (for example, see PLTs 2 to 4).

[0009] In recent years, the characteristics required for linepipe have become more diversified. Among them, in particular, the characteristics required for linepipe for deep ocean floor have become complicated. Specifically, in addition to greater thickness, yield stress (YS), tensile strength (TS), low-temperature toughness (DWTT shear area at -10°C), sour resistance and further collapse resistance (0.2% flow stress of compression in circumferential direction after aging

at 200°C) have also been demanded. However, in the prior art (for example, PLTs 2 to 5 etc.), it was extremely difficult to achieve all of these characteristics at the same time.

[0010] The invention which is disclosed in PLT 2 considers how to improve crack propagation resistance and low-temperature toughness, but does not consider how to improve sour resistance and collapse resistance. Further, the invention which is disclosed in PLT 3 considers low-temperature toughness and collapse resistance, but does not consider how to improve sour resistance. Further, the invention which is disclosed in PLT 4 attempts to achieve a balance of compressive strength and low-temperature toughness and both high compressive strength and sour resistance, but does not consider the above-mentioned collapse resistance (0.2% flow stress of compression in circumferential direction after aging at 200°C).

[0011] In PLT 5, it is discovered that in the case of steel pipe for linepipe of a plate thickness of 25 mm or more and up to the X80 standard of the American Petroleum Institute (API) (tensile strength of 620 MPa or more), making the center part in plate thickness a fine bainite structure is extremely difficult. To solve such a technical problem, PLT 5 proposes a process of production which lowers the content of C, makes the microstructure into a low temperature transformation microstructure which is formed mainly of bainite, and, based on this steel material whose toughness is improved, adds Mo to improve the hardenability and keeps down the addition of AI so as to make use of the bainite in the grains.

[0012] The invention which is disclosed in PLT 5 improves the hardenability of the base material and makes the effective grain size of the HAZ finer by composing the steel plate as a whole of uniform microstructure formed of mainly bainite. The invention which is disclosed in PLT 5 is aimed at improving the low-temperature toughness of the weld zone and does not consider how to improve the sour resistance and collapse resistance.

[0013] Further, at the center part of plate thickness, the rolling due to the controlled rolling and the cooling rate due to the controlled cooling become insufficient. Therefore, even when the hardenability is improved, along with the increase in plate thickness, it is difficult to make the steel plate as a whole a uniform microstructure.

[0014] Further, in the past, steel plate for linepipe often had a plate thickness of a thin 20 mm or less. If a strength of the X65 class or so of the API standard, it was possible to easily secure various characteristics such as the sour resistance, low-temperature toughness, and collapse resistance. This was because with hot-rolling, the reduction rate was sufficiently secured and the effective grain size became finer and, further, the difference in cooling rate between the surface layers and mid-thickness portion due to accelerated cooling was small so the microstructure became uniform. In this regard, if the plate thickness is 25 mm or more, in particular 30 mm or more, it becomes difficult to satisfy all of the requirements of sour resistance, low-temperature toughness, and collapse resistance.

[0015] In particular, securing the collapse resistance and securing the low-temperature toughness are opposite things. In the prior art, no material which can achieve both collapse resistance and low-temperature toughness has been designed.

[0016] The present invention, in consideration of this situation, has as its object the provision of thick-gauge high-strength linepipe which is optimal as a material for linepipe for transport of natural gas or crude oil and has a good balance of sour resistance, collapse resistances, and low-temperature toughness and steel plate for the thick-gauge high-strength linepipe. Solution to Problem

[0017] The inventors engaged in intensive studies focusing on the microstructure and crystal grain size in steel plate for linepipe so as to obtain steel plate for thick-gauge high-strength linepipe which is excellent in sour resistance, collapse resistance, and low-temperature toughness. As a result, they discovered that in thick-gauge linepipe (also referred to as "thick-gauge steel pipe"), the compositions, microstructures, processes of production, etc. for achieving (1) both strength and sour resistance, (2) both strength and collapse resistance of thick-gauge steel pipe, and (3) both strength and low-temperature toughness of thick-gauge steel pipe can be summarized as follows:

(1) Achievement of Both Strength and Sour Resistance

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To raise the strength of linepipe without impairing the sour resistance, it is effective to make the microstructure of the base material of the linepipe, that is, the steel plate, into a uniform structure comprised of acicular ferrite or bainite. Further, to improve the sour resistance, it is necessary to suppress hardening of the center-segregation portion. Here, the mechanism behind the cracking which occurs in a sour environment will be explained. The cracking in a sour environment, in particular, hydrogen induced cracking (HIC), is in particular due to the hydrogen which collects around the elongated MnS-based inclusions and other defects in the steel present at the center-segregation portion of the steel plate. That is, in a sour environment, the hydrogen which penetrates the steel collects around these defects to form pockets of gas. When the pressure exceeds a fracture toughness value of the steel (KIC), cracking occurs. Further, if the center-segregation portion of the steel, surroundings of inclusions, etc. harden, cracking easily propagates. Therefore, in linepipe which is used in a sour environment, it is effective to suppress the formation of elongated MnS and formation of hard phases at the center-segregation portion. Specifically, it is effective to stop the accelerated cooling at a somewhat high temperature, for example, stop the accelerated cooling after hot-rolling so that the temperature of the center-segregation portion of the steel becomes 400°C or more. Note

that, the "center-segregation portion" is the portion at the center part of plate thickness of the steel plate where Mn and other components concentrate due to solidification segregation at the time of casting.

(2) Achievement of Both Strength and Collapse resistance of Thick-gauge Steel Pipe

In the case of thick-gauge steel pipe, to secure both strength and collapse resistance, it is effective to add Mo etc. to raise the hardenability and use accelerated cooling after hot-rolling to cause the formation of martensite or bainite with their high dislocation densities and promote strain aging. Specifically, if controlling the accelerated cooling stop temperature to become a somewhat low temperature, for example, so that the surface temperature of the steel plate becomes 400°C or less, martensite is produced and strain aging can be promoted at the time of coating and baking the thick-gauge steel pipe (processing for heating and holding the pipe at around 200°C at the time of coating).

(3) Achievement of Both Strength and Low-temperature toughness of Thick-gauge Steel Pipe In the case of thick-gauge steel pipe, compared with thin gauge steel pipe, the prior austenite grains (austenite grains before transformation due to accelerated cooling) become coarser and the low-temperature toughness falls. Further, compared with the structure of bainite alone, the effective grain size of the structure of acicular ferrite alone is smaller. Even so, it cannot be said that the low-temperature toughness is sufficient. For this reason, to secure low-temperature toughness, formation of polygonal ferrite is effective. However, polygonal ferrite causes the strength to fall, so to secure strength, it is effective to make the structure into a composite of bainite or acicular ferrite.

[0018] As explained above, it is learned that it is difficult to simultaneously satisfy the above (1) to (3) to secure all of the sour resistance, low-temperature toughness, and collapse resistance. For example, for the collapse resistance of (2), martensite is effective, while for the sour resistance of (1) and the low-temperature toughness of (3), martensite is harmful. Further, for the low-temperature toughness of (3), polygonal ferrite is effective, but the sour resistance of (1) falls since the production of polygonal ferrite causes the structure to become uneven. Further, polygonal ferrite, which has a low dislocation density, causes the collapse resistance to fall. Therefore, the inventors studied the method of making use of the feature of being thick-gauged, that is, using hot-rolling and subsequent accelerated cooling, to control the structure by utilizing the temperature difference between the surfaces and the center part due to the plate thickness. Further, they took note of the fact that at the center part of plate thickness, securing the sour resistance is extremely important while at the surface layers, securing the collapse resistance is extremely important. Further, to secure the low-temperature toughness, they studied refinement of the effective grain size.

[0019] First, at the mid-thickness portion, to secure the sour resistance, strength, and low-temperature toughness, it was learned that it was effective to suppress the formation of deformed ferrite and a martensite-austenite mixture (below, referred to as "MA") to hold down hardening and make a uniform structure comprised of one or both of acicular ferrite and bainite. Here, at the mid-thickness portion, Mn concentrates due to segregation. The hardenability is high and formation of ferrite is suppressed. However, to secure the low-temperature toughness, formation of ferrite is effective. It is necessary to make the microstructure so that the amount of ferrite increases toward the surface layers. On the other hand, if causing the formation of soften polygonal ferrite to secure low-temperature toughness, the compression yield strength in the circumferential direction of the surface layers falls and the collapse resistance ends up falling. To deal with such a problem, the inventors came up with the idea of causing the formation of deformed ferrite at the surface layers and raising the dislocation density of ferrite to promote strain aging and improve the collapse resistance. Therefore, they discovered that the structure of the surface layers should be made a structure in which deformed ferrite with an area percentage of 5% or more should be formed so as to satisfy the collapse resistance and should be suppressed in MA and given a balance of one or both of polygonal ferrite and bainite so as to secure low-temperature toughness.

[0020] If the amount of deformed ferrite is large, the collapse strength increases, but the low-temperature toughness deteriorates by that amount. To secure low-temperature toughness, it is necessary to control the amount of deformed ferrite to a certain extent. That is, it is necessary suitably distribute the parts bearing the collapse strength and the parts bearing the low-temperature toughness in accordance with the plate thickness. That is, the thinner the plate thickness, the smaller the allowed amount of deformed ferrite at the surface layer portion, while the thicker the plate thickness, the larger the allowed amount of deformed ferrite at the surface layer portion. Therefore, the inventors investigated the relationship between the allowed amount of deformed ferrite and plate thickness and discovered the optimum relationship. The present invention was made based on these discoveries and has as its gist the following:

[1] Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness, comprising: steel plate with a plate thickness of 25 mm to 45 mm containing, by mass%,

C: 0.04 to 0.08%, Mn: 1.2 to 2.0%,

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Nb: 0.005 to 0.05%, Ti: 0.005 to 0.03%,

Ca: 0.0005 to 0.0050%, and

N: 0.001 to 0.008%, limited to

Si: 0.5% or less,

Al: 0.05% or less.

P: 0.03% or less,

S: 0.005% or less,

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O: 0.005% or less, and

having a balance of Fe and unavoidable impurities, wherein

a microstructure of surface layer portion which is portion from the surface of steel plate down toward a plate thickness direction by 0.9 mm to 1.1 mm is restricted to, by area percentage,

deformed ferrite: 5% or more and $S_{\rm fe1}\%$ found by the following formula 1a or less and

martensite-austenite mixture: 8% or less and has a balance of one or both of polygonal ferrite and bainite, and a microstructure of a part from the center of plate thickness toward both the front and back sides of the steel plate by within 1 mm, constituting a mid-thickness portion, is restricted to, by area percentage,

deformed ferrite: 5% or less,

martensite-austenite mixture: 5% or less and has a balance of one or both of acicular ferrite and bainite, and the surface layer portion and mid-thickness portion have average value of effective grain size measured by electron backscatter diffraction of 20 μ m or less. S_{fe1} =0.6552× T_H -4.7826 ··· formula 1a where, T_H : plate thickness of steel plate for thick-gauge high-strength linepipe

[2] Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to [1], further containing, by mass%, one or more of

Cu: 0.50% or less,

Ni: 0.50% or less,

Cr: 0.50% or less.

Mo: 0.50% or less,

W: 0.50% or less,

V: 0.10% or less,

Zr: 0.050% or less,

Ta: 0.050% or less,

B: 0.0020% or less,

Mg: 0.010% or less,

REM: 0.0050% or less,

Y: 0.0050% or less,

Hf: 0.0050% or less, and

Re: 0.0050% or less

- [3] Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to [1] or [2], wherein a content of Al is 0.005% or less.
- [4] Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to any one of [1] to [3], wherein a tensile strength is 500 to 700 MPa.
- [5] Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to any one of claims 1 to 3, wherein a yield stress after pipe formation is 440 MPa or more, a tensile strength is 500 to 700 MPa, and a 0.2% flow stress of compression in the circumferential direction after aging at 200°C is 450 MPa or more.
- [6] Thick-gauge high-strength linepipe produced by shaping steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to any one of [1] to [4] into a pipe shape, then arc welding abutting ends and having a yield stress of 440 MPa or more, a tensile strength of 500 to 700 MPa, and a 0.2% flow stress of compression in the circumferential direction after aging at 200°C of 450 MPa or more. Advantageous Effects of Invention

[0021] According to the present invention, it is possible to provide steel plate for thick-gauge high-strength linepipe which is excellent in sour resistance, collapse resistance, and low-temperature toughness which is therefore optimum as a material for linepipe for transporting natural gas or crude oil. In particular, it is possible to provide steel plate for thick-gauge high-strength linepipe which is excellent in sour resistance, collapse resistance, and low-temperature toughness which has a gauge thickness of 25 to 45 mm and, after formation into pipe, a YS of 440 MPa or more, TS of 500 to 700 MPa, DWTT shear area at -10°C of 85% or more, and compressive strength in the circumferential direction after aging at 200°C (0.2% flow stress) of 450 MPa or more. The contribution to industry is extremely remarkable.

Brief Description of Drawings

[0022]

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FIG. 1 is an optical micrograph of the cross-section of a surface layer portion of steel plate for thick-gauge highstrength linepipe of the present invention.

FIG. 2 is a graph which prescribes the upper limit and lower limit of the area percentage of deformed ferrite at the surface layer portion of steel plate for thick-gauge high-strength linepipe of the present invention.

10 Description of Embodiments

[0023] Below, the steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness of the present invention (below, also simply referred to as "steel plate for linepipe" or "steel plate") and a method of production of the same will be explained. Below, the reasons for limitation of the components in the steel plate for thick-gauge high-strength linepipe of the present embodiment (base material of linepipe) will be explained. Note that, the symbols % mean mass% unless otherwise indicated.

[0024] C: C is an element which improves the strength of steel plate. In the present embodiment, 0.04% or more has to be added. Preferably, 0.05% or more, more preferably 0.055% or more of C is added. On the other hand, if over 0.08% of C is added, the low-temperature toughness falls, so the upper limit of the amount of C is made 0.08%. Preferably, the upper limit of the amount of C is made 0.07%, more preferably the upper limit is made 0.065%.

[0025] Mn: Mn is an element which contributes to improvement of the strength and toughness of steel plate. In the present embodiment, to secure the strength of the steel plate, 1.2% or more of Mn is added. Preferably, 1.4% or more, more preferably 1.5% or more of Mn is added. On the other hand, if Mn is excessively added, the mid-thickness portion rises in hardness and the sour resistance is impaired, so the upper limit of the amount of Mn is made 2.0% or less. Preferably, the upper limit of the amount of Mn is made 1.8% or less, more preferably 1.7% or less.

[0026] Nb: Nb is an element which forms carbides and nitrides and contributes to the improvement of strength. Further, it suppresses recrystallization and promotes grain refinement during hot-rolling. For that reason, the lower limit of the amount of Nb is made 0.005% or more. Preferably, the lower limit of the amount of Nb is made 0.010% or more, more preferably 0.015% or more. On the other hand, if Nb is excessively added, the strength excessively rises and the low-temperature toughness is impaired, so the upper limit of the amount of Nb is made 0.05% or less. Preferably, the upper limit of the amount of Nb is made 0.04% or less, more preferably 0.03% or less.

[0027] Ti: Ti is an element which forms nitrides and exerts an effect on the grain refinement of the microstructure. The lower limit of the amount of Ti is made 0.005% or more to make the effective grain size finer. Preferably, the lower limit of the amount of Ti is made 0.008% or more, more preferably 0.01% or more. On the other hand, if Ti is excessively added, coarse TiN grains are formed and the low-temperature toughness is impaired, so the upper limit of the amount of Ti is made 0.03% or less. Preferably, the upper limit of the amount of Ti is made 0.02% or less, more preferably 0.015%. [0028] Ca: Ca is an element which controls the form of sulfides and improves the sour resistance. In the present embodiment, to promote the formation of CaS and suppress the formation of MnS elongated in the rolling direction and secure the sour resistance, the lower limit of the amount of Ca is made 0.0005% or more. Preferably, the lower limit of the amount of Ca is made 0.0010%, more preferably 0.0015%. On the other hand, if Ca is excessively added, coarse oxides are formed and the low-temperature toughness falls, so the upper limit of the amount of Ca is made 0.0050%. Preferably, the upper limit of the amount of Ca is made 0.0040% or less, more preferably 0.0030% or less.

[0029] N: In the present embodiment, nitrides are utilized to make the microstructure of the steel finer, so the content of N is made 0.001% or more. Preferably, the amount of N is made 0.002% or more, more preferably 0.003% or more. On the other hand, if N is excessively contained, coarse nitrides will be formed and the low-temperature toughness will be impaired, so the upper limit of the amount of N is 0.007% or less, more preferably 0.006% or less.

[0030] Si and Al are deoxidizing elements. If added for the purpose of deoxidation, it is sufficient to use either one, but both may be used as well. Note that if Si and Al are excessively added, they impair the characteristics of the steel plate, so in the present embodiment, the upper limits of the contents of Si and Al are made the following:

[0031] Si: If Si is excessively added, hard MA is formed in particular at the heat affected zone (HAZ) and the toughness of the seam weld zone of the steel pipe is made to fall, so the upper limit of the amount of Si is made 0.5% or less. Preferably, the amount of Si is made 0.3% or less, more preferably 0.25% or less. Note that, as explained above, Si is an element which is used for deoxidation and is an element which contributes to the rise in strength as well, so preferably the lower limit of the amount of Si is 0.05% or more, more preferably 0.10% or more.

[0032] Al: As explained above, Al is a useful deoxidizing element. Preferably, the lower limit of the amount of Al is 0.001% or more, more preferably 0.003% or more. However, if Al is excessively added, coarse oxides are formed and the low-temperature toughness is made to fall, so the upper limit of the amount of Al is made 0.05% or less. Preferably,

the upper limit of the amount of Al is made 0.04% or less, more preferably 0.03% or less. Further, by restricting the amount of Al to 0.005% or less, the HAZ toughness can be improved.

[0033] P, S, and O (oxygen) are contained as unavoidable impurities. If excessively contained, the characteristics of the steel plate are impaired, so in the present embodiment, the upper limits of the contents of P, S, and O are set as follows:

[0034] P: P is an element which causes embrittlement of the steel. If over 0.03% is contained, the low-temperature toughness of the steel is impaired, so the upper limit is made 0.03% or less. Preferably, the upper limit of the amount of P is made 0.02% or less, more preferably 0.01% or less.

[0035] S: S is an element which forms MnS and other sulfides. If over 0.005% is contained, the low-temperature toughness and the sour resistance are made to fall, so the upper limit is made 0.005% or less. Preferably, the amount of S is made 0.003% or less, more preferably 0.002%.

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[0036] O: If O is contained in over 0.005%, coarse oxides are formed and the low-temperature toughness of the steel is made to fall, so the upper limit of the content is made 0.005% or less. Preferably, the upper limit of the amount of O is made 0.003% or less, more preferably 0.002% or less.

[0037] Furthermore, in the present invention, as elements which improve the strength or low-temperature toughness, one or more of Cu, Ni, Cr, Mo, W, V, Zr, Ta, and B can be added.

[0038] Cu: Cu is an element which is effective for making the strength rise without making the low-temperature toughness fall. Preferably, 0.01% or more of Cu is added, more preferably 0.1% or more is added. On the other hand, Cu is an element which makes cracking occur more easily at the time of heating the steel slab or at the time of seam welding the steel pipe, so the amount of Cu is preferably made 0.50% or less. More preferably, the amount of Cu is made 0.35% or less, still more preferably 0.2% or less.

[0039] Ni: Ni is an element which is effective for improving the low-temperature toughness and strength. Preferably, 0.01% or more of Ni is added, more preferably 0.1% or more is added. On the other hand, Ni is an expensive element. From the viewpoint of economy, the amount of Ni is preferably made 0.50% or less. More preferably, the amount of Ni is made 0.35% or less, still more preferably 0.2% or less.

[0040] Cr: Cr is an element which improves the strength of the steel by precipitation strengthening. Preferably, 0.01% or more of Cr is added, more preferably 0.1% or more is added. On the other hand, if Cr is excessively added, sometimes the rise in strength causes the low-temperature toughness to fall, so the upper limit of the amount of Cr is preferably made 0.50% or less. More preferably, the amount of Cr is made 0.35% or less, still more preferably 0.2% or less.

[0041] Mo: Mo is an element which improves the hardenability and which forms carbonitrides to improve the strength. Preferably, 0.01% or more of Mo is added, more preferably 0.05% or more is added. On the other hand, if Mo is excessively added, sometimes the rise in strength causes the low-temperature toughness to fall, so the upper limit of the amount of Mo is preferably made 0.50% or less. More preferably, the amount of Mo is made 0.2% or less, more preferably 0.15% or less.

[0042] W: W, like Mo, is an element which improves the hardenability and which forms carbonitrides to improve the strength. Preferably, 0.0001% or more of W is added, more preferably the amount of W is made 0.01% or more, still more preferably 0.05% or more is added. On the other hand, if W is excessively added, sometimes the rise in strength causes the low-temperature toughness to fall, so the upper limit of the amount of W is preferably made 0.50% or less. More preferably, the amount of W is made 0.2% or less, more preferably 0.15% or less.

[0043] V: V is an element which forms carbides or nitrides and which contributes to the improvement of strength. Preferably, 0.001% or more of V is added, more preferably 0.005% or more is added. On the other hand, if over 0.10% of V is added, sometimes this causes the low-temperature toughness to fall, so the amount of V is preferably made 0.10% or less. More preferably, the amount of V is made 0.05% or less, more preferably 0.03% or less.

[0044] Zr and Ta: Zr and Ta, like V, are elements which form carbides or nitrides and contribute to the improvement of strength. Zr and Ta are preferably added in 0.0001% or more, more preferably 0.0005% or more, still more preferably 0.001% or more is added. On the other hand, if over 0.050% of Zr or Ta is added, sometimes the low-temperature toughness falls, so the upper limits of the amount of Zr and the amount of Ta are preferably 0.050% or less. More preferably, the amounts are 0.030% or less.

[0045] B: B is an element which can cause an improvement in the hardenability by addition in a fine amount. To raise the strength, 0.0001% or more of B is preferably added. Preferably, 0.0003% or more of B is added. On the other hand, if B is excessively added, precipitates of B are sometimes formed and the low-temperature toughness is sometimes degraded, so the amount of B is preferably made 0.0020% or less. More preferably, the amount of B is made 0.0010% or less.

[0046] Furthermore, in the present invention, to control the form of inclusions such as sulfides and oxides and to improve the low-temperature toughness and sour resistance, one or more of Mg, REM, Y, Hf, and Re may be added.

[0047] Mg: Mg is an element which contributes to improvement of the sour resistance or low-temperature toughness by control of the form of the sulfides or formation of fine oxides. Preferably, 0.0001% or more of Mg is added, more preferably 0.0005% or more, still more preferably 0.001% or more is added. On the other hand, if over 0.010% of Mg is added, sometimes coarse oxides easily form and the toughness of the HAZ is impaired, so the amount of Mg is preferably

made 0.010% or less. More preferably, the amount of Mg is made 0.005% or less, still more preferably 0.003% or less. **[0048]** REM, Y, Hf, and Re: REM, Y, Hf, and Re form sulfides and suppress the formation of MnS elongated in the rolling direction, in particular, contribute to the improvement of the sour resistance. REM, Y, Hf, and Re are all preferably added in 0.0001% or more, more preferably 0.0005% or more, still more preferably 0.0010% or more. On the other hand, if REM, Y, Hf, or Re is added in over 0.0050%, the oxides increase and sometimes the toughness is impaired, so the upper limit is preferably made 0.0050% or less. More preferably, the amount is made 0.0030% or less.

[0049] Further, in the present embodiment, the balance besides the above elements is substantially comprised of Fe. Unavoidable impurities and other elements which do not harm the action or effect of the present invention may also be added in trace amounts. "Unavoidable impurities" mean components which are contained in the raw materials or which enter in the process of production and refer to components which are not deliberately included in the steel.

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[0050] Specifically, Si, Al, P, S, O, N, Sb, Sn, Co, As, Pb, Bi, and H may be mentioned. Among these, P, S, O, and N, as explained above, have to be controlled to Si: 0.5% or less, Al: 0.05% or less, P: 0.03% or less, S: 0.005% or less, O: 0.005% or less, and N: 0.008% or less.

[0051] Regarding other elements, usually Sb, Sn, Co, and As can be contained in amounts of 0.1% or less, Pb and Bi in 0.005% or less, and H in 0.0005% or less as unavoidable impurities. However, if in the usual ranges, do not particularly have to be controlled.

[0052] Further, the optionally added elements of Cu, Ni, Cr, Mo, W, V, Zr, Ta, B, Mg, REM, Y, Hf, and Re in the steel plate for thick-gauge high-strength linepipe according to the present invention can be contained as unavoidable impurities even if not deliberately included. However, these elements do not have a detrimental effect on the present invention even if the amounts of the added elements are below the lower limit so long as the amounts of the added elements are below the upper limit of the content in the case of deliberate inclusion explained above, so do not pose problems.

[0053] Furthermore, in the present invention, to secure the hardenability to raise the strength and low-temperature toughness, the carbon equivalent Ceq of the following (formula 2), which is calculated from the contents of the C, Mn, Ni, Cu, Cr, Mo, and V (mass%), is preferably made 0.30 to 0.50. The lower limit of Ceq is more preferably 0.32 or more, still more preferably 0.35 or more, to raise the strength. Further, the upper limit of the Ceq is more preferably 0.45 or less, still more preferably 0.43 or less, to raise the low-temperature toughness.

[0054] Further, to secure the low-temperature toughness of the steel plate and HAZ, the cracking susceptibility parameter Pcm of the following (formula 3), which is calculated from the contents of the C, Si, Mn, Cu, Cr, Ni, Mo, and V (mass%), is preferably 0.10 to 0.20. The lower limit of Pcm raises the strength, so is more preferably 0.12 or more, still more preferably 0.14 or more. Further, the upper limit of the Pcm raises the low-temperature toughness, so is more preferably 0.19 or less, still more preferably 0.18 or less.

[0055] Note that, in the case of not deliberately adding the selectively contained elements of Ni, Cu, Cr, Mo, and V, they are calculated as 0 in the above (formula 2) and (formula 3).

[0056] Next, the microstructure of the steel plate of the present invention will be explained. The steel plate of the present invention has a plate thickness of 25 mm or more, more preferably a 30 mm or more thickness, and is suitable as steel plate for thick-gauge linepipe (25 mm to 45 mm). Further, the steel plate of the present invention utilizes the temperature difference of hot-rolling or difference of cooling rate of the accelerated cooling at the surface layers and the mid-thickness portion to control the structure and differs in microstructure at the surface layers and the mid-thickness portion. Note that, in the present invention, the surface layer portion of the steel plate is the portion of 0.9 mm to 1.1 mm from the surface of the steel plate in the thickness direction (that is, the region within 0.1 mm in the directions to both the front and back surfaces centered at the positions of 1 mm in the thickness directions from the surfaces of the steel plate is the region within 1 mm in the directions to both the front and back surfaces from the center of plate thickness.

[0057] At the surface layer portion, to raise the collapse resistance, an area percentage of 5% or more of deformed ferrite is formed. "Deformed ferrite" is ferrite which is elongated by hot-rolling in the rolling direction. Compared with polygonal ferrite which is formed by cooling after rolling, the dislocation density is higher. This is effective for improvement of the collapse resistance. An optical micrograph of the cross-section of a surface layer portion of the steel plate of the present invention is shown in FIG. 1. Further, the dark gray parts are deformed ferrite. Such a part is shown by the arrow mark. The surface layer portion which is shown in FIG. 1 contains deformed ferrite in 9.3%.

[0058] Further, if the deformed ferrite is large in amount, the collapse strength increases, but the low-temperature toughness deteriorates by that amount. Therefore, the inventors discovered that it is possible to suppress the deformed ferrite at the center part to raise the low-temperature toughness. As the thickness of the steel plate becomes greater,

the temperature difference between the surface layers and the center in wall thickness becomes larger. For this reason, as the gauge thickness of the steel plate becomes greater, the amount of deformed ferrite which can be produced at the center part of plate thickness becomes smaller, while the amount of deformed ferrite which can be produced at the surface layer portion becomes greater. Therefore, the inventors investigated the relationship of the gauge thickness of the steel plate and the amount of deformed ferrite at the surface layer portion and discovered the optimal range.

[0059] FIG. 2 shows the relationship between plate thickness of steel plate with a plate thickness of 25 mm to 45 mm and the upper limit S_{fe1} of the area percentage of deformed ferrite at the surface layer portion.

[0060] From FIG. 2, it was learned that to obtain the collapse resistance and low-temperature toughness which are optimal for linepipe for transport of natural gas and crude oil, the area percentage of the deformed ferrite at the surface layer portion of the steel plate has to be the following lower limit value or more and the upper limit value or less.

Lower limit value of area percentage of deformed ferrite at surface layer portion of steel plate: 5% Upper limit value of area percentage of deformed ferrite at surface layer portion of steel plate:

$$S_{fe1} = 0.6552 \times T_H - 4.7826$$
 formula 1a

(where, T_H: plate thickness of steel plate for thick-gauge high-strength linepipe)

[0061] Further, if the area percentage of the deformed ferrite exceeds the S_{fe1} %, the surface layers harden and the low-temperature toughness is impaired, so the area percentage of the deformed ferrite is made S_{fe1} % or less. Further, preferably, the upper limit of the area percentage of deformed ferrite at the surface layer portion of the steel plate satisfies the following formula 1b.

More preferable upper limit value:

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$$S_{fe2}$$
=0.8× T_H -15 formula 1b

[0062] As shown in the above formula 1a and formula 1b, the area percentage of the deformed ferrite for obtaining a sour resistance, collapse resistance, and low-temperature toughness optimal for a material of linepipe for transporting natural gas or crude oil depends on the plate thickness. The temperature difference in hot-rolling between the surface layers and the mid-thickness portion and the difference in cooling rates at accelerated cooling are easily affected by the plate thickness, so the area percentage of the deformed ferrite is considered to have dependency on the plate thickness. [0063] At the surface layer portion, to raise the collapse resistance, it is preferable to form the MA having high dislocation density by an area percentage of 0.1% or more. However, MA forms initiating points of fracture and if excessively formed, impairs the low-temperature toughness. For this reason, the MA at the surface layer portion is restricted to an area percentage of 8% or less. Preferably, the area percentage of the MA at the surface layer portion is made 5% or less, more preferably 3% or less.

[0064] At the surface layer portion, the balance besides the above deformed ferrite and MA is a microstructure composed of one or both of polygonal ferrite and bainite. Polygonal ferrite is effective for improvement of the low-temperature toughness. It is easily formed at the surface layer portion and gradually decreases toward the mid-thickness portion. Bainite is effective for improvement of the strength. Unlike polygonal ferrite, the amount of it is minor at the surface layer portion and gradually increases toward the mid-thickness portion. This is because at the mid-thickness portion, compared with the surface layers, the rolling temperature in hot-rolling and the start temperature of accelerated cooling become higher.

[0065] At the mid-thickness portion, to secure low-temperature toughness and sour resistance, it is necessary to suppress the formation of deformed ferrite. The area percentage of deformed ferrite is restricted to 5% or less. The area percentage of deformed ferrite is preferably made 3% or less, more preferably 0%. At the mid-thickness portion, it is preferable to suppress the formation of MA which act as initiating points of fracture and suppress the hardening of the mid-thickness portion. To secure the low-temperature toughness, the area percentage of MA is restricted to 5% or less. Preferably, the area percentage of MA at the mid-thickness portion is made 4% or less, more preferably is made 2% or less. [0066] At the mid-thickness portion, the balance besides the deformed ferrite and MA is a microstructure comprised of one or both of acicular ferrite and bainite. Polygonal ferrite is effective for improving the low-temperature toughness, but impairs the sour resistance, so at the mid-thickness portion, the microstructure is preferably a uniform one comprised of one or both of acicular ferrite and bainite.

[0067] Here, the microstructures of the above-mentioned surface layer portion and mid-thickness portion can be observed by an optical microscope. Specifically, the area percentages of the deformed ferrite and MA can be found by image analysis of the optical micrographs of the structures. Note that, at the MA, repeller etching is performed and the area percentage of the non-colored structures is found by image analysis. Further, the polygonal ferrite which is produced at the time of accelerated cooling is granular. The deformed ferrite is elongated in the rolling direction. Further, the deformed ferrite is high in dislocation density, so is hardened more compared with the polygonal ferrite. Therefore, the deformed ferrite and polygonal ferrite can be differentiated by the ratio of the long axis and short axis (aspect ratio) or

the hardness. Acicular ferrite and bainite are lath structures and can be differentiated by the deformed ferrite and polygonal ferrite

[0068] To secure the low-temperature toughness of steel plate, it is effective to increase the crystal grain boundaries which provide the resistance to propagation of cracks, that is, make the crystal grain sizes smaller. In the present invention, the size of the region surrounded by high angle grain boundaries of a difference of orientation of 15° or more, that is, the effective grain size, is made smaller to improve the low-temperature toughness. By making the average value of the effective grain sizes of the surface layer portion and the mid-thickness portion which are measured by electron backscatter diffraction (EBSD) 20 μ m or less, it is possible to secure the low-temperature toughness. The smaller the effective grain size, the more stable the high toughness which is obtained. Preferably, the value is 10 μ m or less.

[0069] Note that, the low-temperature toughness of steel plate is evaluated by measuring the effective grain size at the mid-thickness portion and finding the average value. Further, as the means for measuring the effective grain size of different microstructures, electron backscatter diffraction is employed. The effective grain size is defined as the circle equivalent diameter found by analyzing the structure in the longitudinal direction of the steel plate after rolling by EBSD. Note that, at the surface layer portion, the size can be made smaller by utilizing deformed ferrite or polygonal ferrite, but at the mid-thickness portion, formation of deformed ferrite or polygonal ferrite ends up being suppressed, so the prior austenite grains can be made finer by hot-rolling.

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[0070] Next, the characteristics of the steel plate of the present invention will be explained. If raising the pressure of the crude oil or natural gas which is transported so as to improve the transport efficiency of pipelines, the linepipe has to be raised in strength and increased in gauge thickness to prevent the pipe from bursting due to internal pressure. From these viewpoints, to avoid bursting of linepipe due to internal pressure, the steel plate which is used for the linepipe is preferably made a plate thickness of 25 mm or more. Further, the steel plate preferably has a 500 MPa or more tensile strength. Further, the steel plate after pipe formation, that is, the part of the steel pipe other than the weld zone and HAZ, for example, the part of the steel pipe from the seam part to 90° to 180° positions (positions at 3 o'clock to 6 o'clock from seam part) also similarly preferably has a 440 MPa or more yield stress and a 500 to 700 MPa or more tensile strength. Note that, to avoid bursting, the plate thickness of the steel plate is more preferably 30 mm or more, still more preferably 35 mm or more.

[0071] When laying pipeline at arctic regions, low-temperature toughness of the linepipe is considered required. The low-temperature toughness can be evaluated by the drop weight tear test (DWT test). In the present invention, the DWTT shear area at -10°C of steel plate before pipe formation is preferably 85% or more. Further, along with the increased thickness and higher strength of the linepipe, securing low-temperature toughness becomes difficult, so the plate thickness of the steel plate is preferably made 45 mm or less and the tensile strength of the steel plate is preferably 700 MPa or less. When producing steel pipe by cold-working, the strength of the steel plate after pipe formation tends to become higher than the strength of the steel plate before pipe formation, but the tensile strength of the steel pipe after formation is also preferably made 700 MPa or less.

[0072] When laying pipeline at the ocean floor, resistance of the linepipe to outside pressure (collapse resistance) is considered necessary. The collapse resistance is evaluated by a compression test using test pieces which are taken from the steel pipe since there is the effect of strain which is introduced when cold-working steel plate into steel pipe. To prevent the linepipe from being collapsed by outside pressure, the compressive strength in the circumferential direction after aging at 200°C (0.2% flow stress) is preferably 450 MPa or more.

[0073] Next, the method of production of the steel plate of the present invention will be explained.

[0074] The steel plate according to the present invention is given structures which differ at the surface layers and the mid-thickness portion by performing one or more passes of hot-rolling in the temperature region where the microstructure of the surface layers become dual phase of ferrite and austenite (dual phase region) and further performing the accelerated cooling after the hot-rolling by water cooling or other means under conditions whereby the temperature of the surfaces of the steel plate becomes 400°C or less and heat is recuperated after stopping thereof. If the steel plate is thick in gauge, the temperature of the surface layers at the time of hot-rolling falls from the temperature at the mid-thickness portion. At the mid-thickness portion, formation of ferrite is suppressed compared with the surface layers. Further, the stopping temperature of accelerated cooling becomes higher at the mid-thickness portion than at the surfaces. If setting a condition of accelerated cooling so that the temperature of the surfaces is recuperated after the accelerated cooling, the temperature of the center part of the steel plate after stopping the accelerated cooling can be made 400°C or more, hardening of the mid-thickness portion can be suppressed, and the sour resistance can be secured.

[0075] Further, to secure low-temperature toughness, the average effective grain size of the surface layers and midthickness portion is made $20~\mu m$ or less. At the surface layer, due to formation of deformed ferrite and polygonal ferrite, the effective grain size becomes smaller. On the other hand, at the mid-thickness portion, formation of deformed ferrite and polygonal ferrite ends up being suppressed, so the prior austenite grains have to be made smaller in size. By refining the average value of the effective grain size which is measured at the surface layers and the effective grain size which is measured at the mid-thickness portion, the effective grain size of the plate thickness as a whole becomes finer and the low-temperature toughness can be secured. For this reason, in hot-rolling, the reduction ratio in the recrystallization

region has to be made 2.0 or more and the reduction ratio in the non-recrystallization region has to be made 3.0 or more. **[0076]** As explained above, by suitably controlling the conditions of the hot-rolling and the subsequent accelerated cooling, it is possible to make not only the strength and low-temperature toughness of thick-gauge steel plate, but also the composite characteristics of the sour resistance and collapse resistance after pipe formation satisfactory.

[0077] The process of production of the steel plate according to the present invention will be explained in order. First, steel containing the above components is smelted in the steelmaking process, then is cast to obtain a steel slab. The casting can be performed by an ordinary method, but from the viewpoint of productivity, continuous casting is preferable. Next, the obtained steel slab is heated, hot rolled, and cooled by accelerated cooling to produce steel plate. Note that, in the present embodiment, the heating of the steel slab which is performed for hot-rolling is also referred to as "reheating" and the heating temperature of the steel slab at this time is also called the "reheating temperature".

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[0078] The reheating temperature of hot-rolling is made 1000°C or more so as to dissolve the carbides, nitrides, etc. which is formed in the steel slab in the steel. Further, by making the reheating temperature 1000°C or more, hot-rolling in the recrystallization region that is over 900°C (recrystallization rolling) is possible and the structure of the steel can be made finer. Note that, the upper limit of the reheating temperature is not prescribed, but to suppress coarsening of the effective grain size, the reheating temperature is preferably made 1250°C or less. Further, the reheating temperature is more preferably made 1200°C to secure the low-temperature toughness, more preferably 1150°C or less.

[0079] The hot-rolling according to the present embodiment is comprised of a rolling process in the recrystallization region that is over 900°C, rolling in the non-recrystallization region that is 900°C or less, and rolling in the temperature region where the temperature at the surface of the steel plate becomes a temperature resulting in a dual phase of austenite and ferrite (dual phase region) in that order. Note that, the hot-rolling may be started right after extraction from the heating furnace performing the reheating, so the start temperature of the hot-rolling is not particularly prescribed.

[0080] To refine the effective grain size of the mid-thickness portion of the steel plate, it is necessary to set the reduction ratio at the recrystallization region that is over 900°C to 2.0 or more and promote recrystallization. Here, the reduction ratio at the recrystallization region is the ratio of the plate thickness of the steel slab and the plate thickness at 900°C.

[0081] Next, hot-rolling is performed at the non-recrystallization region that is 900°C or less (non-recrystallization region rolling). To refine the effective grain size of the surface layer portion of the steel plate after accelerated cooling after hot-rolling, it is necessary to set the reduction ratio at the non-recrystallization region rolling to 3.0 or more and promote the transformation by accelerated cooling. More preferably, the reduction ratio at non-recrystallization rolling is set to 4.0 or more. Note that, in the present invention, the reduction ratio of non-recrystallization rolling is the ratio of the plate thickness at 900°C divided by the plate thickness after the end of non-recrystallization rolling.

[0082] In the hot-rolling, the rolling (dual phase rolling) is performed in the temperature region (dual phase region) of the temperature of the surfaces of the steel plate wherein dual phase of austenite and ferrite are formed. In dual phase rolling, the surface temperature of the steel plate becomes the beginning temperature of ferrite transformation Ar_3 or less, but during the period of the start to the end of the dual phase rolling, the temperature of the mid-thickness portion of the steel plate is maintained so as to be higher than the temperature of the surfaces of the steel plate and over Ar_3 . Such a temperature distribution can be realized by, for example, performing accelerated cooling for a short time and lowering the temperature at only the surface layers. In this dual phase rolling, the number of passes is set to 1 or more and the reduction rate is set to from 0.1 to 40%. As a result of dual phase rolling, the start temperature of the later performed accelerated cooling also becomes the dual phase region, so hardening of the mid-thickness portion can be suppressed and the low-temperature toughness can be improved. Further, the "reduction rate" is the amount of reduction of the steel plate due to rolling, that is, the value which is obtained by dividing the difference between the thickness of the steel plate before rolling and the thickness of the steel plate after rolling by the thickness of the steel plate before rolling and can be expressed by a percent (%) etc. Further, at the portions between the surface layers and the mid-thickness portion, formation of polygonal ferrite is promoted. This contributes to improvement of the low-temperature toughness. Further, the Ar_3 can be calculated from the contents of C, Si, Mn, Ni, Cr, Cu, ad Mo (mass%).

$Ar_3 = 905-305C+33Si-92(Mn+Ni/2+Cr/2+Cu/2+Mo/2)$

[0083] Here, the C, Si, Mn, Ni, Cr, Cu, and Mo in the above formula show the contents (mass%) of the elements. Further, Ni, Cu, Cr, and Mo are elements which are selectively added in the present invention. When not deliberately added, the content is calculated as "0" in the formula.

[0084] The lower limit of the reduction rate in dual phase rolling is set to 0.1% or more so as to cause the formation of deformed ferrite elongated in the rolling direction. Preferably, the reduction rate of the dual phase rolling is set to 1% or more, more preferably 2% or more. On the other hand, the upper limit of the reduction rate in dual phase rolling is set to 40% or less since it is difficult to secure a reduction rate at a low temperature where the deformation resistance becomes higher. Preferably, the reduction rate in dual phase rolling is made 30% or less, more preferably 20% or less, still more preferably less than 10%.

[0085] The end temperature of the dual phase rolling, that is, the hot-rolling end temperature, is set to 700°C or more

as a temperature of the surfaces of the steel plate so that the deformed ferrite is not excessively formed. If the hot-rolling end temperature becomes less than 700°C, ferrite transformation occurs at the mid-thickness portion and, due to the deformed ferrite, the low-temperature toughness and sour resistance sometimes fall. Further, if the hot-rolling end temperature falls, sometimes the formation of ferrite causes C to concentrate at the austenite and the formation of MA to be promoted. On the other hand, when the hot-rolling end temperature is too high, if the accelerated cooling stop temperature is lowered, the mid-thickness portion sometimes hardens and the low-temperature toughness falls.

[0086] Next, after the end of hot-rolling, accelerated cooling is immediately started. However, after hot-rolling, air-cooling is allowed while the steel is transported from the exit side of the rolling mill to the accelerated cooling apparatus. The accelerated cooling stop temperature is set to a temperature within temperature range of 200 to 400°C at the surfaces of the steel plate. If stopping the accelerated cooling at a temperature where the surface of the steel plate exceeds 400°C, polygonal ferrite is formed at the mid-thickness portion and the sour resistance falls. On the other hand, if performing accelerated cooling until the temperature of the surfaces of the steel plate becomes less than 200°C, the mid-thickness portion hardens and the low-temperature toughness falls. After accelerated cooling, air-cooling is performed in that state. If stopping the accelerated cooling when the surface temperature of the steel plate reaches 200 to 400°C in temperature range, after that, the temperature of the surface layers of the steel plate recovers at the time of air cooling. Therefore, the temperature of the mid-thickness portion reaches 400°C or more, the hardness falls, and the low-temperature toughness and sour resistance can be improved.

[0087] The above process of production can be used to produce the steel plate for high-strength linepipe according to the present invention. Further, when using the steel plate for high-strength linepipe according to the present invention as a material, it is possible to produce steel pipe for thick-gauge high-strength linepipe which is excellent in sour resistance, collapse resistance, and low-temperature toughness. Note that, when producing steel pipe, it is preferable to employ the UOE process of shaping the steel plate for high-strength linepipe according to the present invention by C-pressing, U-pressing, and O-pressing. Alternatively, the JCOE process can be used to produce steel pipe using the steel plate for high-strength linepipe according to the present invention. The thick-gauge high-strength linepipe according to the present invention into a pipe shape, then arc welding the abutting ends. For the arc welding, submerged arc welding is preferably employed from the viewpoints of the toughness of the weld metal and the productivity. Note that, the collapse resistance of the thick-gauge, high-strength linepipe according to the present invention can be evaluated by taking compression test pieces in the circumferential direction from the steel pipes produced by the above-mentioned methods.

Examples

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[0088] Next, examples of the present invention will be explained, but the present invention is not limited to the conditions which are used in the following examples.

[0089] Steels comprised of the chemical compositions of Table 1-1, Table 1-2, Table 2-1, and Table 2-2 were smelted and cast to obtain steel slabs. The "slab thickness" of Table 3-1 and Table 3-2 shows the thicknesses of the obtained steel slabs (mm). The steel slabs were reheated and hot-rolled in the recrystallization region that is over 900°C. Further, the "heating temperature" of Table 3-1 and Table 3-2 shows that reheating temperature, while the "transport thickness" of Table 3-1 and Table 3-2 shows the plate thickness at 900°C after hot-rolling in the recrystallization region and before the hot-rolling in the later explained non-recrystallization region that is 900°C or less. Further, the "reduction ratio in recrystallization region" of Table 3-1 and Table 3-2 shows the ratio of the slab thickness divided by the transport thickness. [0090] Next, the steel plate having the transport thickness was hot-rolled in the non-recrystallization region that is 900°C or less. The "plate thickness" of Table 3-1 and Table 3-2 shows the plate thickness after hot-rolling in the non-recrystallization region and before the later explained dual phase rolling, while the "non-recrystallization reduction ratio" of Table 3-1 and Table 3-2 is the value obtained by dividing the value of the transport thickness by the plate thickness after the end of the non-recrystallization rolling.

[0091] After the hot-rolling in the non-recrystallization region, the final hot-rolling process before accelerated cooling was performed. The surface temperature of the steel plate at the time of end of the final hot-rolling process is shown by the "finishing end temperature (°C)" in Table 3-1 and Table 3-2. Further, the number of rolling operations performed at the time of the final hot-rolling process, that is, the number of passes, is shown by the "no. of α + γ reduction passes" in Table 3-1 and Table 3-2, while the reduction rate of the steel plate by the final hot-rolling process is shown by the " α + γ reduction rate (%)" in Table 3-1 and Table 3-2.

[0092] After the final hot-rolling process, accelerated cooling was performed by water cooling immediately after transporting the steel plate to the cooling zone. The start temperature and end temperature of the accelerated cooling which was performed in the process of production of steel plates of Steel Nos. 1 to 46 are shown in the "water cooling start temperature (°C)" and "water cooling stop temperature (°C)" of Table 3-1 and Table 3-2. The following process of production was used to obtain steel plates of Steel Nos. 1 to 46.

[0093] Test pieces were taken from the surface layer portion and mid-thickness portions of the steel plates of the

obtained Nos. 1 to 46. These were examined for structure by an optical microscope to find the area percentage of deformed ferrite and the area percentage of MA and confirm the structure of the balance. The structure of the balance, in all of the steel plates of Nos. 1 to 46, was a microstructure comprised of one or both of polygonal ferrite and bainite at the surface layer portion and a microstructure comprised of one or both of acicular ferrite and bainite at the midthickness portion. Note that, the area percentage of MA was measured using a test piece etched by repeller etching. Further, the average values of the effective grain sizes at the surface layers and mid-thickness portion were found by EBSD.

[0094] Measurement of Strength of Steel Plate Further, two full-thickness test pieces each based on the American Petroleum Institute Standard API 5L (below, simply referred to as "API 5L") having the length direction corresponding to the width direction of the steel plate were taken from the center part of plate width of the steel plate of each of the obtained Nos. 1 to 46. The full-thickness test pieces were subjected to tensile tests based on the API Standard 2000 at room temperature to find the yield stresses and tensile strengths. The maximum loads at the tensile tests were used as the basis to find the tensile strengths.

[0095] Measurement of DWTT shear area of Steel Plate Further, a full-thickness DWT test piece having the length direction corresponding to the width direction of the steel plate was taken from the center part of plate width of the steel plate of each of the obtained Nos. 1 to 46. The DWT test was also performed based on the API standard 2000 at -10°C to measure the DWTT shear area.

Measurement of Strength of Steel Pipe and Compression Test

[0096] The obtained Nos. 1 to 46 steel plates were used to form pipes by the UOE process and were welded at the inside and outside surfaces by the heat inputs shown in Table 5-1 and Table 5-2 by submerged arc welding so as to produce outside diameter 30 to 36 inch steel pipes (the steel plate numbers and steel pipe numbers correspond to each other). Next, test pieces were taken from the steel pipes and were measured for strength and subjected to compression tests. The test pieces were processed from the 3 o'clock positions of the steel pipes, in which the seam weld zones was defined as 0 o'clock, so that the longitudinal directions of the tensile test pieces matched the longitudinal directions of the steel pipes. The strengths of the steel pipes were measured based on ASTM E9-09 so as to measure the yield strengths and tensile strengths in the longitudinal directions of the linepipes. Here, the 0.5% underload yield strength was defined as the yield strength. The compression test pieces which were used for the compression test of steel pipe were obtained by taking parts which has 22 mm diameter and 66 mm length below 3 mm from the inside surfaces of the steel pipes at the 6 o'clock positions of the steel pipes when defining the seam weld zone of the steel pipes as 0 o'clock. The compression test was conducted based on ASTM E9-09. The compressive strength after aging at 200°C for 10 minutes (0.2% flow stress) was found.

HIC Test of Steel Pipes

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[0097] Further, defining the seam weld zone of the steel pipe as 0 o'clock, HIC test samples of 20 mm width and 100 mm length were taken from the 3 o'clock and 6 o'clock positions of the steel pipe. The HIC test pieces were taken so that the center parts of gauge thickness of the steel pipes became the test positions. The HIC test was based on TM0284 of the NACE (National Association of Corrosion and Engineer) and was performed using as the test solution the Solution B. The crack length ratio (CLR) was used for evaluation.

[0098] The characteristics of the steel plates are shown in Table 4-1 and Table 4-2, while the characteristics of the steel pipes are shown in Tables 5-1 and 5-2. The steel plates of Nos. 1 to 28 show examples of the present invention. As clear from Tables 4-1 and 4-2 and Tables 5-1 and 5-2, the steel pipes which were produced using these steel plates have yield stresses of 440 MPa or more and tensile strengths of 500 to 700 MPa in range. Further, as shown in Tables 4-1 and 4-2, the steel plates had tensile strengths of 500 MPa or more and had DWTT shear areas at -10°C of 85% or more. Further, as shown in Tables 5-1 and 5-2, the steel pipes produced by forming these steel plates into pipe shapes and then butt welding them were good ones with CLR of 10% or less after HIC tests and results of compression tests of 450 MPa or more after strain aging at 200°C.

[0099] On the other hand, Steel Nos. 29 to 46 are comparative examples. Steel Nos. 29 to 40 have contents of chemical components outside the range of the present invention, while Steel Nos. 41 to 46 have microstructures outside the range of the present invention and have at least one of the strength, low-temperature toughness, collapse resistance, and sour resistance of an inferior level. Steel No. 29 has a small amount of C and falls in strength and collapse resistance. On the other hand, Steel No. 30 has a large amount of C, Steel No. 31 has a large amount of Si, and Steel No. 32 has a large amount of Mn. In each comparative example, the tensile strength excessively rises and the low-temperature toughness falls. Further, the Ar₃ of Steel No. 30 is less than 700°C, and the steel plate of Steel No. 30 is not rolled in the dual phase region in the present invention. However, the amount of C which is contained is large, so C concentrates at the austenite at the mid-thickness portion of Steel No. 30, the formation of MA is promoted, and the sour resistance

falls. Further, Steel No. 32 has a large amount of Mn of 3%, so the sour resistance falls. Steel Nos. 33, 34, and 40 have large contents of impurities (P, S, and O) and fall in low-temperature toughness. Steel Nos. 35 to 39 are examples which have large contents of elements which contribute to the formation of carbides, nitrides, oxides, and sulfides and which fall in low-temperature toughness due to precipitates and inclusions. Steel Nos. 41 and 42 are examples which respectively are insufficient in reduction rate in the recrystallization region and reduction rate in the non-recrystallization region, become large in effective grain size, and fall in low-temperature toughness. Steel No. 43 has an end temperature of hotrolling of 700°C or more, but is low in Ar_3 and is not rolled in the dual phase region in the present invention, so deformed ferrite is not formed at the surface layer, the mid-thickness portion hardens, and the low-temperature toughness falls. Steel No. 44 is an example where the accelerated cooling stop temperature is high, deformed ferrite and MA are excessively formed at the mid-thickness portion, and the strength falls. Further, the accelerated cooling is stopped at the temperature where the temperature of the surface of the steel plate exceeds 400°C, so polygonal ferrite is formed at the mid-thickness portion and the sour resistance falls. Steel Nos. 45 and 46 are examples where the rolling end temperatures are low, deformed ferrite and MA are excessively formed at the surface layer portion and mid-thickness portions, and the low-temperature toughnesses and sour resistances fall.

Table 1-1

| | | | | | Chemical | | sition (ma | nss%) | | | |
|-----------------|-------|------|------|-------|----------|------|------------|--------|--------|---------|-------|
| Steel Plate No. | С | Si | Mn | Р | S | Nb | Ti | Al | Ca | N | 0 |
| 1 | 0.065 | 0.25 | 1.65 | 0.005 | 0.0005 | 0.02 | 0.012 | 0.004 | 0.0023 | 0.0025 | 0.001 |
| 2 | 0.055 | 0.13 | 1.81 | 0.008 | 0.0006 | 0.04 | 0.003 | 0.013 | 0.0012 | 0.0034 | 0.001 |
| 3 | 0.060 | 0.08 | 1.70 | 0.003 | 0.0008 | 0.03 | 0.012 | 0.008 | 0.0024 | 0.0045 | 0.002 |
| 4 | 0.056 | 0.07 | 1.60 | 0.004 | 0.0003 | 0.01 | 0.016 | 0.010 | 0.003 | 0.0023 | 0.002 |
| 5 | 0.060 | 0.25 | 1.60 | 0.009 | 0.0006 | 0.01 | 0.012 | 0.007 | 0.0015 | 0.0037 | 0.001 |
| 6 | 0.045 | 0.10 | 1.85 | 0.026 | 0.0004 | 0.03 | 0.012 | 0.016 | 0.0021 | 0.0047 | 0.00 |
| 7 | 0.046 | 0.02 | 1.70 | 0.003 | 0.0006 | 0.03 | 0.013 | 0.005 | 0.0024 | 0.0034 | 0.001 |
| 8 | 0.055 | 0.15 | 1.80 | 0.007 | 0.0005 | 0.05 | 0.008 | 0.013 | 0.0022 | 0.0043 | 0.001 |
| 9 | 0.046 | 0.17 | 1.90 | 0.005 | 0.0002 | 0.03 | 0.010 | 0.013 | 0.0016 | 0.0045 | 0.001 |
| 10 | 0.050 | 0.20 | 1.56 | 0.008 | 0.0004 | 0.05 | 0.030 | 0.004 | 0.0024 | 0.0024 | 0.002 |
| 11 | 0.056 | 0.22 | 1.65 | 0.002 | 0.0003 | 0.04 | 0.024 | 0.004 | 0.0023 | 0.0017 | 0.001 |
| 12 | 0.048 | 0.25 | 1.65 | 0.004 | 0.0006 | 0.03 | 0.012 | 0.010 | 0.0035 | 0.0045 | 0.00 |
| 13 | 0.065 | 0.31 | 1.76 | 0.006 | 0.0008 | 0.01 | 0.024 | 0.015 | 0.0034 | 0.0023 | 0.00 |
| 14 | 0.066 | 0.09 | 1.56 | 0.006 | 0.0006 | 0.04 | 0.013 | 0.001 | 0.0035 | 0.0024 | 0.000 |
| 15 | 0.045 | 0.28 | 1.80 | 0.004 | 0.0004 | 0.01 | 0.012 | 0.006 | 0.0025 | 0.0034 | 0.000 |
| 16 | 0.050 | 0.32 | 1.65 | 0.003 | 0.0006 | 0.01 | 0.008 | 0.006 | 0.0034 | 0.0045 | 0.00 |
| 17 | 0.060 | 0.48 | 1.85 | 0.002 | 0.0006 | 0.02 | 0.010 | 0. 003 | 0.0015 | 0.0045 | 0.00 |
| 18 | 0.055 | 0.24 | 1.67 | 0.004 | 0.0006 | 0.04 | 0.005 | 0.003 | 0.0023 | 0.0056 | 0.00 |
| 19 | 0.065 | 0.28 | 1.75 | 0.017 | 0.0003 | 0.01 | 0.026 | 0.016 | 0.0017 | 0.0016 | 0.002 |
| 20 | 0.045 | 0.12 | 1.70 | 0.003 | 0.0005 | 0.02 | 0. 012 | 0.022 | 0.0017 | 0. 0024 | 0.001 |
| 21 | 0.066 | 0.31 | 1.60 | 0.002 | 0.0008 | 0.03 | 0.017 | 0.003 | 0.0026 | 0.0034 | 0.00 |
| 22 | 0.054 | 0.31 | 1.55 | 0.004 | 0.0025 | 0.05 | 0.018 | 0.025 | 0.0021 | 0.0045 | 0.00 |
| 23 | 0.050 | 0.25 | 1.60 | 0.007 | 0.0020 | 0.04 | 0.015 | 0.005 | 0.0028 | 0.0035 | 0.00 |
| 24 | 0.050 | 0.23 | 1.77 | 0.005 | 0.0012 | 0.03 | 0.014 | 0.004 | 0.0018 | 0. 0038 | 0.002 |
| 25 | 0.050 | 0.24 | 1.71 | 0.005 | 0.0015 | 0.03 | 0.012 | 0.003 | 0.0015 | 0.0035 | 0.00 |
| 26 | 0.056 | 0.25 | 1.73 | 0.005 | 0.0013 | 0.03 | 0.012 | 0.003 | 0.0015 | 0.0036 | 0.00 |
| 27 | 0.055 | 0.24 | 1.75 | 0.005 | 0.0012 | 0.03 | 0.012 | 0.003 | 0.0015 | 0.0034 | 0.001 |

(continued)

| Steel Plate No. | | | | | Chemical | compos | sition (ma | iss%) | | | |
|-----------------|-------|------|------|-------|----------|--------|------------|-------|--------|--------|--------|
| Steel Flate No. | С | Si | Mn | Р | S | Nb | Ti | Al | Ca | N | 0 |
| 28 | 0.058 | 0.23 | 1.72 | 0.005 | 0.0014 | 0.03 | 0.012 | 0.003 | 0.0015 | 0.0033 | 0.0018 |

Table 1-2

| | | | | | | Table | _ | | | | | |
|----|-----------------|-------|------|-------|-------|----------|--------|------------|--------|--------|--------|--------|
| 10 | Steel plate No. | | | | | Chemical | compos | sition (ma | ıss%) | | | |
| | Steel plate No. | С | Si | Mn | Р | S | Nb | Ti | Al | Ca | N | 0 |
| | 29 | 0.001 | 0.18 | 1.67 | 0.005 | 0.0026 | 0.05 | 0.012 | 0.005 | 0.0023 | 0.0045 | 0.0013 |
| 15 | 30 | 0.150 | 0.45 | 1.75 | 0.007 | 0.0015 | 0.03 | 0.013 | 0.016 | 0.0013 | 0.0034 | 0.0014 |
| | 31 | 0.056 | 1.50 | 1.45 | 0.005 | 0.0005 | 0.03 | 0.010 | 0.025 | 0.0024 | 0.0023 | 0.0014 |
| | 32 | 0.060 | 0.01 | 3.00 | 0.015 | 0.0021 | 0.01 | 0.008 | 0.017 | 0.0024 | 0.0034 | 0.0019 |
| | 33 | 0.060 | 0.25 | 1. 93 | 0.040 | 0.0026 | 0.04 | 0.019 | 0.009 | 0.0034 | 0.0023 | 0.0023 |
| 20 | 34 | 0.045 | 0.17 | 1.86 | 0.003 | 0.0351 | 0.02 | 0.017 | 0.005 | 0.0025 | 0.0034 | 0.0017 |
| | 35 | 0.067 | 0.24 | 1.56 | 0.008 | 0.0023 | 0.10 | 0.015 | 0.030 | 0.0015 | 0.0035 | 0.0013 |
| | 36 | 0.060 | 0.05 | 1.70 | 0.005 | 0.0030 | 0.03 | 0.064 | 0.030 | 0.0011 | 0.0023 | 0.0014 |
| 25 | 37 | 0.059 | 0.09 | 1.60 | 0.003 | 0.0009 | 0.03 | 0.023 | 0.100 | 0.0017 | 0.0034 | 0.0013 |
| | 38 | 0.064 | 0.25 | 1.35 | 0.005 | 0.0034 | 0.02 | 0.010 | 0.040 | 0.01 | 0.0023 | 0.0014 |
| | 39 | 0.057 | 0.23 | 1.67 | 0.005 | 0.0015 | 0.02 | 0.010 | 0.030 | 0.0023 | 0.01 | 0.0014 |
| 00 | 40 | 0.056 | 0.45 | 1.56 | 0.009 | 0.0023 | 0.03 | 0.018 | 0.020 | 0.0024 | 0.0034 | 0.05 |
| 30 | 41 | 0.04 | 0.12 | 1.85 | 001 | 0.0008 | 0.01 | 0.015 | 0.014 | 0.0034 | 0.0014 | 0.0013 |
| | 42 | 0.060 | 0.05 | 1.96 | 0.002 | 0.0015 | 0.03 | 0.010 | 0.016 | 0.0023 | 0.0023 | 0.0006 |
| | 43 | 0.055 | 0.12 | 1.70 | 0.007 | 0.0021 | 0.02 | 0.015 | 0.020 | 0.0027 | 0.0025 | 0.0015 |
| 35 | 44 | 0.045 | 0.15 | 1.65 | 0.009 | 0.0015 | 0.03 | 0.012 | 0. 015 | 0.0015 | 0.0034 | 0.0023 |
| | 45 | 0.052 | 0.20 | 1.60 | 0.010 | 0.0013 | 0.04 | 0.010 | 0.013 | 0.0019 | 0.0025 | 0.0024 |
| | 46 | 0.056 | 0.15 | 1.55 | 0.006 | 0.0009 | 0.03 | 0.009 | 0.025 | 0.0029 | 0.0035 | 0.0017 |

| | | | Ar_3 | 742 | 710 | 719 | 734 | 725 | 717 | 721 | 714 | 708 | 753 | 720 | 705 | 902 | 714 | 721 | 739 | 723 | 724 | 701 | 707 | 748 | 719 | 732 | 709 |
|----|-----------|------------------------------|-----------------|-------|--------|--------|--------|--------|--------|--------|-------|-------|--------|--------|--------|-------|--------|-------|--------|--------|--------|--------|--------|-------|-------|-------|-------|
| 5 | | | Pcm | 0.156 | 0.170 | 0.162 | 0.152 | 0.163 | 0.143 | 0.145 | 0.165 | 0.162 | 0.135 | 0.170 | 0.171 | 0.189 | 0.168 | 0.164 | 0.147 | 0.180 | 0.158 | 0.184 | 0.162 | 0.156 | 0.170 | 0.150 | 0.174 |
| | | | Ceq | 0.340 | 0.405 | 0.385 | 0.363 | 0.360 | 0.363 | 0.353 | 0.415 | 0.423 | 0.310 | 0.403 | 0.450 | 0.456 | 0.409 | 0.405 | 0.338 | 0.408 | 0.373 | 0.443 | 0.375 | 0.333 | 0.419 | 0.357 | 0.427 |
| 10 | | | H | | | | | | | | | | | | | | | | | | | | | 0.001 | | | |
| 15 | | | Re | | | | | | | | | | | | | | | | | | 0.001 | | | | | | |
| | | | Υ | | | | | | | | | | | | | 0.001 | | | | | | | | | | | |
| 20 | | (0 | REM | | | 0.0008 | | | | | | | | 0.0042 | | | | | 0.0007 | | | 0.0006 | | | | | |
| 25 | | Chemical composition (mass%) | Mg | | | | | | | 0.0038 | | | 0.0018 | | | | 0.0033 | | | | | | 0.0025 | | | | |
| | 2-1 | compositi | Та | | | | | 0.0032 | | | | | | | | | | | | | 0.0029 | | | | | | |
| 30 | Table 2-1 | Chemical | Zr | | | | 0.0051 | | 0.0012 | | | | | | 0.0034 | | | | | 0.0008 | | | | | | | |
| 35 | | | M | | | | | 0.050 | | | | | | | | | | | | | | | | | | | |
| | | | В | | 0.0008 | | | | | | | | | | | | | | | | | | | | | | |
| 40 | | | ^ | | 90.0 | 0.04 | | | | 0.02 | | | | 90.0 | | 0.02 | | | | | | | | | | | 90.0 |
| | | | Мо | | 0.10 | 0.10 | 0.20 | | | | | | | 0.20 | | | | 08.0 | | 0.10 | 0.10 | | | | 0.10 | 0.10 | 0.25 |
| 45 | | | Cr | | | | | | | | 08.0 | 08.0 | | | 0.50 | 0.40 | 08.0 | | | 0.10 | | 0.30 | | | 08.0 | | |
| 50 | | | Cn | | 0.10 | | | 0.20 | | 0.20 | | | | | | | | | | | | | 0.50 | | | | |
| 30 | | | Ē | | 0.15 | 0.20 | | 0:30 | 0.15 | 0.10 | | | | 0:30 | 0.40 | 0.20 | 0.35 | | 0.20 | | 0:30 | 0.40 | 0.20 | | 0.40 | 0:30 | 0.30 |
| 55 | | Steel plate No | oteol plate No. | 1 | 2 | 8 | 4 | 5 | 9 | 7 | 8 | 6 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |

| | | | Ar_3 | 722 | 712 | 715 | 718 |
|----|-------------|------------------------------|-----------------|-------------|-------------|-------------|-------------|
| 5 | | | Pcm | 0.378 0.156 | 0.408 0.170 | 0.391 0.163 | 0.388 0.165 |
| | | | Ced | 0.378 | 0.408 | 0.391 | 0.388 |
| 10 | | | Ŧ | | | | |
| 15 | | | Re | | | | |
| | | | λ | | | | |
| 20 | | (%) | REM | | | | |
| 25 | | Chemical composition (mass%) | Mg | | | | |
| | (pai | compos | Та | | | | |
| 30 | (continued) | Chemica | Zr | | | | |
| 35 | | | Μ | | | | |
| | | | В | | | | |
| 40 | | | > | | | | |
| 45 | | | Мо | 0.12 | 0.20 | 0.11 | 0.12 |
| 45 | | | Ö | | | | |
| 50 | | | Cu | | | | |
| 50 | | | Ë | 0.28 | 0.35 | 0.33 | 0.29 |
| 55 | | Stole loots | oteel plate No. | 25 | 26 | 27 | 28 |
| | | | | | | | |

| 5 | | | Ar ₃ | 743 | 069 | 740 | 611 | 717 | 712 | 749 | 718 | 729 | 751 | 742 | 759 | 719 | 708 | 685 | 726 | 714 | 602 |
|-----|-----------|------------------------------|-----------------|-------|-------|-------|--------|-------|--------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|
| 10 | | | Pcm | 0.111 | 0.293 | 0.240 | 0.210 | 0.165 | 0.164 | 0.153 | 0.170 | 0.162 | 0.167 | 0.148 | 0.149 | 0.145 | 0.160 | 0.184 | 0.154 | 0.172 | 0.171 |
| , 0 | | | Ced | 0.349 | 0.528 | 0.471 | 0.560 | 0.382 | 0.415 | 0.327 | 0.419 | 0.386 | 0.369 | 0.335 | 0.316 | 0.363 | 0.387 | 0.492 | 998.0 | 0.389 | 0.436 |
| 15 | | | ¥ | | | | | | | | | | | | | | | | | | |
| 70 | | | Re | | | | | | | | | | | | | | | | | | |
| | | | <u>+</u> | | | | | | | | | | | | | | | | | | |
| 20 | | (%ss | REM | | | | 0.0012 | | | | | | | | | | 0.0007 | | | | |
| 25 | | Chemical composition (mass%) | Mg | | | | | | 0.0005 | | | | | | | | | | | | |
| | 2-5 | comp | Та | | | | | | | | | | | | | | | | | | |
| 30 | Table 2-2 | emical | Zr | | | | | | | | | | | | | | | | | | |
| | _ | Š | > | | | | | | | | | | | | | | | | | | |
| 0.5 | | | В | | | | | | | | | | | | | | | | | | |
| 35 | | | > | 0.05 | 0.20 | | | | | | 0.08 | | | | | 00.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.04 |
| 40 | | | Mo | | 0.10 | 0.30 | | | 0.30 | | | 0:30 | 0.40 | | | | | 0.10 | 0.10 | 0.15 | |
| | | | ပ် | 0:30 | | 0:30 | | | | | 0:30 | | | | | | | 0.50 | | | 0.40 |
| 45 | | | Cu | | 0.20 | 0.40 | | | | | | | | | | | | | 0.20 | 0.40 | |
| | | | Ē | | 0.20 | 0.40 | | | | | | | | | | 0.13 | | 0.50 | 0.10 | 0.20 | 09.0 |
| 50 | | 010010 | oteel plate No. | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 |

| | | Water cooling end temp. | 350 | 400 | 300 | 300 | 375 | 380 | 350 | 380 | 300 | 370 | 320 | 330 | 370 | 320 | 300 | 325 | 320 | 400 | 320 | 380 | 320 | 370 |
|----------|-----------|--|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 5 | | Water cooling start temp. (°C) | 736 | 202 | 711 | 726 | 716 | 902 | 716 | 902 | 701 | 746 | 711 | 200 | 701 | 902 | 716 | 731 | 716 | 716 | 969 | 701 | 736 | 711 |
| 45 | | α + γ reduction rate (%) | 3 | 5 | 2 | 2 | 9 | 2 | 4 | 2 | 7 | 2 | 9 | 3 | 7 | 4 | 7 | 2 | 2 | 7 | 3 | 9 | 7 | 8 |
| 15 | | No. of $\alpha+\gamma$ rolling passes | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | _ |
| 20 | | Finishing end temp. (°C) | 740 | 602 | 715 | 730 | 720 | 710 | 720 | 710 | 705 | 750 | 715 | 704 | 202 | 710 | 720 | 735 | 720 | 720 | 700 | 202 | 740 | 715 |
| 25 | Table 3-1 | Non- recrystallization draft | 3.1 | 4.0 | 3.1 | 3.1 | 3.1 | 3.1 | 3.5 | 3.1 | 3.1 | 3.1 | 3.1 | 3.5 | 3.1 | 3.5 | 3.7 | 3.1 | 3.1 | 3.1 | 3.1 | 3.8 | 3.4 | 3.1 |
| 30 35 | Tabl | Recrystallization draft | 2.3 | 2.0 | 2.2 | 2.2 | 2.0 | 2.0 | 2.0 | 2.2 | 2.0 | 2.0 | 2.2 | 2.1 | 2.1 | 2.1 | 2.2 | 2.2 | 2.0 | 2.0 | 2.2 | 2.1 | 2.1 | 2.1 |
| 40 | | Heating temp. (°C) | 1100 | 1150 | 1150 | 1200 | 1100 | 1150 | 1200 | 1150 | 1200 | 1100 | 1150 | 1200 | 1100 | 1150 | 1200 | 1100 | 1150 | 1100 | 1200 | 1150 | 1100 | 1150 |
| 45 | | Plate thickness (mm) | 34 | 30 | 35 | 32 | 39 | 38 | 35 | 36 | 38 | 38 | 35 | 32 | 37 | 32 | 30 | 36 | 39 | 39 | 36 | 30 | 33 | 37 |
| 50 | | Transport thickness (mm) | 105 | 120 | 109 | 109 | 121 | 118 | 123 | 112 | 118 | 118 | 109 | 112 | 115 | 112 | 111 | 112 | 121 | 121 | 112 | 114 | 112 | 115 |
| 55 | | Slab thickness (mm) | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 |
| | | Steel plate no. | 1 | 2 | 3 | 4 | 2 | 9 | 7 | 8 | 6 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |

| | Water cooling end temp. | 390 | 320 | 350 | 320 | 300 | 300 |
|----------------|---------------------------------------|------|------|------|------|------|------|
| 5 10 | Water cooling start temp. (°C) | 726 | 701 | 715 | 707 | 202 | 700 |
| | α+γ reduction rate (%) | - | 10 | 10 | 10 | 7 | 10 |
| 15 | No. of $\alpha+\gamma$ rolling passes | - | - | - | - | 2 | 2 |
| 20 | Finishing end temp. (°C) | 730 | 705 | 730 | 202 | 202 | 202 |
| 25 (penu | Non- recrystallization draft | 4.0 | 3.0 | 4.0 | 3.1 | 3.0 | 3.0 |
| 30 (panuiuneo) | Recrystallization draft | 2.0 | 2.0 | 2.0 | 2.1 | 2.0 | 2.0 |
| 40 | Heating temp. | 1180 | 1100 | 1180 | 1100 | 1100 | 1100 |
| 45 | Plate thickness (mm) | 25 | 45 | 25 | 37 | 45 | 45 |
| 50 | Transport thickness (mm) | 100 | 135 | 100 | 115 | 135 | 135 |
| 55 | Slab thickness (mm) | 240 | 240 | 240 | 240 | 240 | 240 |
| | Steel plate no. | 23 | 24 | 25 | 26 | 27 | 28 |

| | | Water cooling end temp. | 380 | 370 | 350 | 320 | 400 | 400 | 370 | 400 | 350 | 350 | 320 | 330 | 370 | 350 | 400 | 220 | 380 | 400 |
|----|-----------|--------------------------------------|--------|------|------|------|------|------|------|------|------|------|------|------|-------|------|------|------|------|------|
| 5 | | Water cooling start temp. (°C) | 710 | 200 | 200 | 009 | 200 | 200 | 720 | 200 | 200 | 750 | 720 | 730 | 200 | 200 | 750 | 200 | 650 | 099 |
| | | α+γ reduction rate (%) | 3 | 2 | 4 | 2 | 2 | 7 | 5 | 8 | 3 | 5 | 7 | 4 | 7 | 5 | 0 | 7 | 9 | 7 |
| 15 | | No. of α+γ rolling passes | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 2 | 3 |
| 20 | | Finishing end temp. (°C) | 012 | 002 | 002 | 009 | 002 | 002 | 720 | 002 | 002 | 092 | 720 | 082 | 002 | 002 | 092 | 002 | 059 | 099 |
| 25 | Table 3-2 | Non- recrystallization draft | 3.1 | 3.5 | 3.3 | 3.1 | 3.1 | 3.1 | 3.5 | 3.1 | 3.1 | 3.6 | 3.7 | 3.1 | 4.0 1 | 2.0 | 3.1 | 3.1 | 3.1 | 3.1 |
| 35 | Table | Recrystallization draft | 2.2 | 2.1 | 2.1 | 2.0 | 2.0 | 2.2 | 2.1 | 2.1 | 2.0 | 2.1 | 2.0 | 2.2 | 1.6 | 3.1 | 2.2 | 2.3 | 2.1 | 2.2 |
| 40 | | Heating temp. (°C) | 1100 . | 1200 | 1150 | 1100 | 1200 | 1100 | 1160 | 1150 | 1150 | 1130 | 1150 | 1100 | 1100 | 1150 | 1150 | 1150 | 1150 | 1100 |
| 45 | | Plate thickness (mm) | 35 | 32 | 34 | 39 | 38 | 35 | 33 | 37 | 39 | 32 | 32 | 35 | 38 | 39 | 36 | 34 | 37 | 36 |
| 50 | | Transport thickness (mm) | 109 | 112 | 112 | 121 | 118 | 109 | 116 | 115 | 121 | 115 | 118 | 109 | 152 | 82 | 112 | 105 | 115 | 112 |
| 55 | | Slab thickness (mm) | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 | 240 |
| | | Steel plate no. | 59 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 |

Table 4-1

| - | Steel | Composition o | | Composition of part in plate the | | Effective | Steel plate | DVACTT I CI |
|----|-------------|---------------------------|----|----------------------------------|-----|----------------------------|---------------------------|------------------------------|
| 5 | pipe No. | Deformed ferrite fraction | MA | Deformed ferrite fraction | MA | crystal grain size (μm) | tensile strength (MPa) | DWTT ductile fracture (%) |
| 10 | 1 | 6 | 4 | <5 | 2 | 3 | 540 | 90 |
| 10 | 2 | 6 | 4 | <5 | 2 | 4 | 586 | 85 |
| | 3 | 7 | 5 | <5 | 3 | 5 | 558 | 85 |
| | 4 | 7 | 5 | <5 | 3 | 3 | 525 | 88 |
| 15 | 5 | 6 | 4 | <5 | 2 | 4 | 567 | 92 |
| | 6 | 7 | 5 | <5 | 3 | 5 | 596 | 85 |
| | 7 | 9 | 7 | <5 | 5 | 4 | 502 | 88 |
| 20 | 8 | 7 | 5 | <5 | 3 | 5 | 571 | 98 |
| 20 | 9 | 8 | 6 | <5 | 4 | 3 | 551 | 96 |
| | 10 | 6 | 4 | <5 | 2 | 5 | 534 | 91 |
| | 11 | 7 | 5 | <5 | 3 | 6 | 530 | 100 |
| 25 | 12 | 6 | 4 | <5 | 2 | 4 | 584 | 98 |
| | 13 | 6 | 4 | <5 | 2 | 5 | 632 | 97 |
| | 14 | 8 | 6 | <5 | 4 | 3 | 580 | 89 |
| 30 | 15 | 9 | 7 | <5 | 5 | 4 | 567 | 91 |
| 00 | 16 | 10 | 5 | <5 | 3 | 5 | 508 | 90 |
| | 17 | 6 | 4 | <5 | 2 | 6 | 619 | 95 |
| | 18 | 8 | 6 | <5 | 4 | 4 | 548 | 96 |
| 35 | 19 | 9 | 7 | <5 | 5 | 3 | 633 | 98 |
| | 20 | 6 | 4 | <5 | 2 | 4 | 560 | 91 |
| | 21 | 6 | 4 | <5 | 2 | 3 | 541 | 100 |
| 40 | 22 | 8 | 6 | <5 | 4 | 4 | 568 | 100 |
| | 23 | 5 | 3 | 0 | 0.1 | 3 | 516 | 100 |
| | 24 | 9 | 7 | <5 | 2 | 4 | 598 | 88 |
| | 25 | 11 | 4 | <5 | 3 | 3 | 508 | 85 |
| 45 | 26 | 16 | 4 | <5 | 3 | 3 | 530 | 90 |
| | 27 | 21 | 4 | <5 | 3 | 3 | 600 | 100 |
| | 28 | 23 | 4 | <5 | 3 | 3 | 524 | 85 |

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Table 4-2

| Steel | Composition of layer parts (% | | Composition of part in plate the | | Effective | Steel plate | DWTT ductile |
|-------------|-------------------------------|----|----------------------------------|----|----------------------------|---------------------------|--------------|
| pipe No. | Deformed ferrite fraction | MA | Deformed ferrite fraction | MA | crystal grain size (μm) | tensile strength (MPa) | fracture (%) |
| 29 | 9 | 6 | <5 | 3 | 5 | 375 | 100 |
| 30 | 7 | 13 | <5 | 10 | 4 | 998 | 30 |
| 31 | 9 | 6 | <5 | 3 | 7 | 837 | 50 |
| 32 | 10 | 7 | <5 | 4 | 6 | 730 | 75 |
| 33 | 7 | 4 | <5 | 1 | 3 | 568 | 20 |
| 34 | 6 | 3 | <5 | 0 | 4 | 560 | 29 |
| 35 | 8 | 5 | <5 | 2 | 9 | 522 | 65 |
| 36 | 5 | 3 | <5 | 0 | 7 | 585 | 57 |
| 37 | 7 | 4 | <5 | 1 | 3 | 557 | 80 |
| 38 | 9 | 6 | <5 | 3 | 5 | 577 | 75 |
| 39 | 7 | 4 | <5 | 1 | 8 | 509 | 69 |
| 40 | 6 | 3 | <5 | 0 | 9 | 518 | 67 |
| 41 | 9 | 5 | <5 | 2 | 23 | 505 | 57 |
| 42 | 9 | 5 | <5 | 2 | 35 | 551 | 67 |
| 43 | 0 | 0 | 0 | 0 | 6 | 640 | 50 |
| 44 | 6 | 3 | 6 | 9 | 4 | 461 | 85 |
| 45 | 40 | 14 | 15 | 11 | 5 | 580 | 45 |
| 46 | 35 | 13 | 10 | 10 | 6 | 585 | 56 |

Table 5-1

| Steel pipe No. | Plate thickness (mm) | Outside diameter (inch) | Steel pipe yield strength (MPa) | Steel pipe tensile strength (MPa) | Heat input (kJ/mm) | Compression test after 200°C aging (0.2% flow stress) (MPa) | HIC test (CLR (%)) |
|----------------------|----------------------------|-------------------------------|--|--|--------------------------|---|-----------------------------|
| 1 | 34 | 32 | 464 | 545 | 5 | 514 | 0 |
| 2 | 30 | 32 | 476 | 595 | 5.5 | 561 | 0 |
| 3 | 35 | 32 | 453 | 566 | 6 | 534 | 0 |
| 4 | 35 | 32 | 444 | 531 | 7.5 | 501 | 0 |
| 5 | 39 | 32 | 457 | 572 | 6 | 539 | 0 |
| 6 | 38 | 32 | 449 | 502 | 9.5 | 473 | 0 |
| 7 | 35 | 32 | 466 | 509 | 5 | 480 | 0 |
| 8 | 36 | 32 | 462 | 578 | 8.5 | 545 | 0 |
| 9 | 38 | 32 | 453 | 566 | 5 | 534 | 0 |
| 10 | 38 | 32 | 460 | 541 | 7.5 | 510 | 0 |
| 11 | 35 | 32 | 476 | 596 | 8.5 | 562 | 0 |

(continued)

| 5 | Steel pipe No. | Plate thickness (mm) | Outside diameter (inch) | Steel pipe yield strength (MPa) | Steel pipe tensile strength (MPa) | Heat input (kJ/mm) | Compression test after 200°C aging (0.2% flow stress) (MPa) | HIC test (CLR (%)) |
|----|----------------------|----------------------------|-------------------------------|--|--|--------------------------|---|-----------------------------|
| | 12 | 32 | 32 | 477 | 597 | 7 | 563 | 0 |
| | 13 | 37 | 32 | 528 | 660 | 4.5 | 623 | 0 |
| 10 | 14 | 32 | 32 | 470 | 587 | 6 | 554 | 0 |
| | 15 | 30 | 32 | 460 | 575 | 7 | 639 | 0 |
| | 16 | 36 | 32 | 448 | 513 | 6.5 | 483 | 0 |
| 15 | 17 | 39 | 32 | 504 | 631 | 7 | 595 | 0 |
| - | 18 | 39 | 32 | 443 | 554 | 8.5 | 522 | 0 |
| | 19 | 36 | 32 | 514 | 642 | 6 | 606 | 0 |
| 20 | 20 | 30 | 30 | 455 | 568 | 8.5 | 580 | 0 |
| | 21 | 33 | 32 | 465 | 547 | 7 | 516 | 0 |
| | 22 | 37 | 32 | 476 | 596 | 8 | 562 | 0 |
| 25 | 23 | 25 | 30 | 440 | 525 | 3.5 | 495 | 0 |
| | 24 | 45 | 36 | 487 | 608 | 10.5 | 574 | 0 |
| | 25 | 25 | 32 | 451 | 511 | 3.6 | 490 | 0 |
| | 26 | 37 | 32 | 478 | 544 | 5 | 525 | 0 |
| | 27 | 45 | 36 | 475 | 612 | 9.5 | 550 | 0 |
| 30 | 28 | 45 | 36 | 470 | 533 | 10 | 520 | 0 |

Table 5-2

| _ | | | | | rable 5-2 | | | |
|---|----------------------|----------------------------|-------------------------------|--|--|--------------------------|---|-----------------------------|
| | Steel pipe No. | Plate thickness (mm) | Outside diameter (inch) | Steel pipe yield strength (MPa) | Steel pipe tensile strength (MPa) | Heat input (kJ/mm) | Compression test after 200°C aging (0.2% flow stress) (MPa) | HIC test (CLR (%)) |
| Ī | 29 | 35 | 32 | 309 | 387 | 7 | 365 | 0 |
| Ī | 30 | 32 | 32 | 819 | 1024 | 6 | 965 | 40 |
| • | 31 | 34 | 32 | 672 | 841 | 15 | 793 | 35 |
| • | 32 | 39 | 32 | 589 | 736 | 8.5 | 628 | 25 |
| | 33 | 38 | 32 | 462 | 577 | 9 | 544 | 45 |
| • | 34 | 35 | 32 | 458 | 573 | 7.5 | 540 | 35 |
| • | 35 | 33 | 32 | 428 | 536 | 20 | 505 | 34 |
| Ī | 36 | 37 | 32 | 475 | 594 | 6.5 | 560 | 45 |
| • | 37 | 39 | 32 | 454 | 567 | 6.5 | 535 | 45 |
| • | 38 | 32 | 32 | 466 | 583 | 7 | 428 | 56 |
| • | 39 | 32 | 32 | 415 | 519 | 8 | 456 | 67 |
| • | 40 | 35 | 32 | 417 | 522 | 9.5 | 492 | 56 |
| • | 41 | 38 | 32 | 405 | 506 | 7 | 477 | 0 |

(continued)

| Steel pipe No. | Plate thickness (mm) | Outside diameter (inch) | Steel pipe yield strength (MPa) | Steel pipe tensile strength (MPa) | Heat input (kJ/mm) | Compression test after 200°C aging (0.2% flow stress) (MPa) | HIC test (CLR (%)) |
|----------------------|----------------------------|-------------------------------|--|--|--------------------------|---|-----------------------------|
| 42 | 39 | 32 | 447 | 559 | 7 | 593 | 0 |
| 43 | 36 | 32 | 515 | 644 | 8 | 607 | 0 |
| 44 | 34 | 32 | 374 | 468 | 6.5 | 508 | 25 |
| 45 | 37 | 32 | 482 | 602 | 7 | 568 | 45 |
| 46 | 36 | 32 | 478 | 598 | 8 | 564 | 56 |

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Claims

1. Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness, comprising:

steel plate with a plate thickness of 25 mm to 45 mm containing, by mass%,

C: 0.04 to 0.08%, Mn: 1.2 to 2.0%, Nb: 0.005 to 0.05%, Ti: 0.005 to 0.03%,

Ca: 0.0005 to 0.0050%, and

N: 0.001 to 0.008%, limited to Si: 0.5% or less,

Al: 0.05% or less, P: 0.03% or less, S: 0.005% or less, O: 0.005% or less, and

having a balance of Fe and unavoidable impurities, wherein

a microstructure of surface layer portion which is portion from surface of the steel plate down toward a plate thickness direction by 0.9 mm to 1.1 mm is restricted to, by area percentage,

deformed ferrite: 5% or more and $S_{\text{fe}1}\%$ found by the following formula 1a or less and

martensite-austenite mixture: 8% or less and

has a balance of one or both of polygonal ferrite and bainite, and

a microstructure of a part from the center of plate thickness toward both the front and back sides of the steel plate by within 1 mm, constituting a mid-thickness portion, is restricted to, by area percentage,

deformed ferrite: 5% or less,

martensite-austenite mixture: 5% or less and

has a balance of one or both of acicular ferrite and bainite, and

the surface layer portion and mid-thickness portion have average value of effective grain size measured by electron backscatter diffraction of 20 μm or less.

 S_{fe1} =0. 6552× T_{H} -4.7826 ··· formula 1a

where, T_{H} : plate thickness of steel plate for thick-gauge high-strength linepipe

2. Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to claim 1, further containing, by mass%, one or more of

50 Cu: 0.50% or less,

Ni: 0.50% or less,

Cr: 0.50% or less,

Mo: 0.50% or less,

W: 0.50% or less,

V: 0.10% or less,

Zr: 0.050% or less,

Ta: 0.050% or less,

B: 0.0020% or less, Mg: 0.010% or less, REM: 0.0050% or less, Y: 0.0050% or less, Hf: 0.0050% or less, and Re: 0.0050% or less

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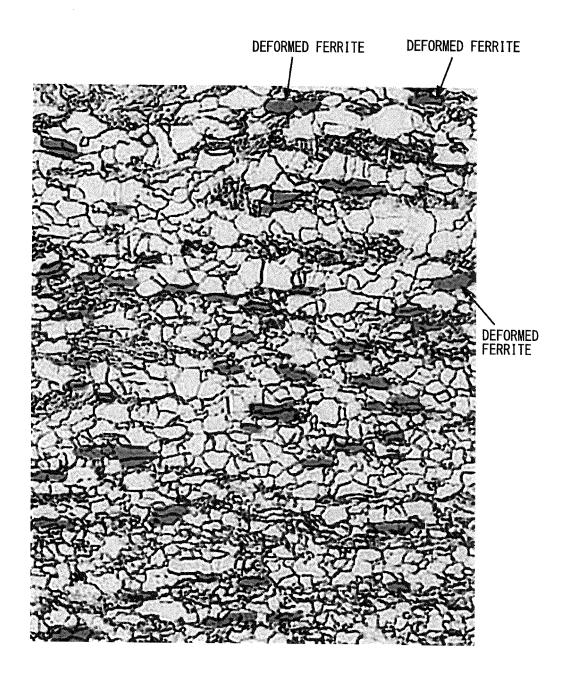
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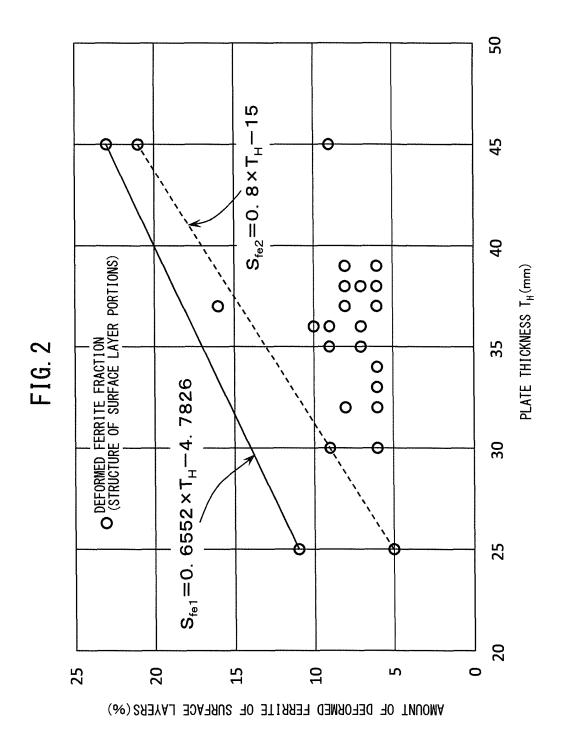
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- 3. Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to claim 1 or 2, wherein a content of Al is 0.005% or less.
- **4.** Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to any one of claims 1 to 3, wherein a tensile strength is 500 to 700 MPa.
- 5. Steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to any one of claims 1 to 3, wherein a yield stress after pipe formation is 440 MPa or more, a tensile strength is 500 to 700 MPa, and a 0.2% flow stress of compression in the circumferential direction after aging at 200°C is 450 MPa or more.
- 6. Thick-gauge high-strength linepipe produced by shaping steel plate for thick-gauge high-strength linepipe excellent in sour resistance, collapse resistance, and low-temperature toughness according to any one of claims 1 to 4 into a pipe shape, then arc welding abutting ends and having a yield stress of 440 MPa or more, a tensile strength of 500 to 700 MPa, and a 0.2% flow stress of compression in the circumferential direction after aging at 200°C of 450 MPa or more.

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FIG. 1





International application No. INTERNATIONAL SEARCH REPORT PCT/JP2014/072833 A. CLASSIFICATION OF SUBJECT MATTER 5 C22C38/00(2006.01)i, C21D8/02(2006.01)i, C22C38/14(2006.01)i, C22C38/58 (2006.01)iAccording to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) 10 C22C38/00, 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 15 1971-2014 Toroku Jitsuyo Shinan Koho Kokai Jitsuyo Shinan Koho 1994-2014 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category* Citation of document, with indication, where appropriate, of the relevant passages Α JP 2009-127069 A (JFE Steel Corp.), 1-6 11 June 2009 (11.06.2009), claims; 0053 to 0073; tables 1 to 4 25 (Family: none) Α JP 8-41536 A (Kawasaki Steel Corp.), 1-6 13 February 1996 (13.02.1996), entire text; all drawings (Family: none) 30 Α JP 2010-235993 A (JFE Steel Corp.), 1-6 21 October 2010 (21.10.2010), claims; 0001, 0042 to 0050, 0063; tables 1, 2 (Family: none) 35 Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: later document published after the international filing date or priority document defining the general state of the art which is not considered — to be of particular relevance date and not in conflict with the application but cited to understand the principle or theory underlying the invention "A" "E" earlier application or patent but published on or after the international filing 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 "L" document which may throw doubts on priority claim(s) or which is 45 cited to establish the publication date of another citation or other document of particular relevance; the claimed invention cannot be special reason (as specified) considered to involve an inventive step when the document is combined with one or more other such documents, such combination "O" document referring to an oral disclosure, use, exhibition or other means being obvious to a person skilled in the art document published prior to the international filing date but later than the document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 50 06 November, 2014 (06.11.14) 18 November, 2014 (18.11.14) Name and mailing address of the ISA/ Authorized officer Japanese Patent Office 55 Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2014/072833

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