



(11) **EP 4 520 845 A1**

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

(43) Date of publication:
12.03.2025 Bulletin 2025/11

(21) Application number: **23839276.5**

(22) Date of filing: **11.05.2023**

(51) International Patent Classification (IPC):
C22C 38/00 ^(2006.01) **C21D 8/02** ^(2006.01)
C22C 38/38 ^(2006.01) **C22C 38/58** ^(2006.01)

(52) Cooperative Patent Classification (CPC):
C21D 8/02; C22C 38/00; C22C 38/38; C22C 38/58

(86) International application number:
PCT/JP2023/017743

(87) International publication number:
WO 2024/014098 (18.01.2024 Gazette 2024/03)

(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 ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **14.07.2022 JP 2022112910**

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(54) **HIGH-STRENGTH STEEL SHEET FOR HYDROGEN TRANSPORT STEEL PIPE, MANUFACTURING METHOD THEREFOR, AND HYDROGEN TRANSPORT STEEL PIPE**

(57) There is provided a high strength steel plate for a hydrogen transport steel pipe, the high strength steel plate having excellent HISC resistance and fatigue crack growth resistance in a high-pressure hydrogen environment.

A high strength steel plate of the present invention for a hydrogen transport steel pipe has a chemical composition containing, by mass%: C: 0.030% to 0.060%, Si: 0.01% to 0.50%, Mn: 0.80% to 1.80%, P: 0.015% or less, S: 0.0015% or less, Al: 0.010% to 0.080%, Cr: 0.05% to

0.50%, Nb: 0.005% to 0.080%, Ti: 0.005% to 0.020%, N: 0.0020% to 0.0080%, and Ca: 0.0005% to 0.0050%, in which the average value of the Vickers hardness at 0.25 mm below the surface of the steel plate + 3σ is 225 HV or less, the top 20% grain size in the microstructure at the center of the thickness of the plate is 30 μm or less, the fatigue crack growth rate is less than 2.0 × 10⁻² (mm/cycle) when the stress intensity factor range ΔK is 45 (MPa·m^{1/2}), and the tensile strength is 535 MPa or more.

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Description

Technical Field

[0001] The present invention relates to high strength steel plates for hydrogen transport steel pipes, and more particularly to a high strength steel plate for a hydrogen transport steel pipe suitable for use in a line pipe for transporting high-pressure hydrogen gas, and a method for manufacturing the high strength steel plate. The present invention also relates to a steel pipe for transporting hydrogen, the steel pipe using the above-mentioned high strength steel plate for transporting hydrogen.

Background Art

[0002] Line pipes are typically produced by forming steel plates, which are produced by plate mills or hot rolling mills, into steel pipes using, for example, UOE forming, press bend forming, or roll forming.

[0003] Line pipes used for transporting high-pressure hydrogen gas are required to have hydrogen embrittlement resistance in addition to strength, toughness, weldability, and so forth. In particular, since line pipes are subjected to repeated stress due to pressure fluctuations during operation, fatigue crack growth resistance in a high-pressure hydrogen gas environment is required to extend their service life. In addition, hydrogen-induced stress cracking resistance (HISC resistance) in a high-pressure hydrogen gas environment is required. When the hydrogen pressure is about 15 MPa, low-alloy steel having a sufficient wall thickness is used. However, at a pressure higher than or equal to this, the risk of hydrogen embrittlement fracture during use increases. Thus, low-alloy steel is not used. Instead, austenitic stainless steel such as SUS316L, which is less susceptible to hydrogen embrittlement than low-alloy steel, is used.

[0004] Austenitic stainless steel has low strength in addition to the high cost of the steel material. Therefore, if austenitic stainless steel is designed to withstand high hydrogen pressure, the wall thickness of the austenitic stainless steel will be increased, and the hydrogen transport line pipe itself will also be more expensive. For this reason, there has been a demand for a steel material for hydrogen transport line pipes that is lower in cost and can withstand a high-pressure hydrogen gas environment.

[0005] To solve the above problems, for example, Patent Literature 1 discloses an austenitic steel material having a high Mn content.

Citation List

Patent Literature

[0006] PTL 1: Japanese Patent No. 6703608

Summary of Invention

Technical Problem

[0007] According to the technique described in Patent Literature 1, it is possible to provide a steel material that is lower in cost than austenitic stainless steel such as SUS316L. However, the steel material described in Patent Literature 1 is an austenitic alloy and thus is more expensive than a typical low-alloy steel. Furthermore, in the steel material described in Patent Literature 1, HISC resistance and fatigue crack growth resistance in a high-pressure hydrogen gas environment are not taken into consideration.

[0008] In view of the above problems, it is an object of the present invention to provide a high strength steel plate for a hydrogen transport steel pipe, the high strength steel plate having excellent HISC resistance and fatigue crack growth resistance in a high-pressure hydrogen environment, together with an advantageous method for manufacturing the high strength steel plate.

[0009] It is another object of the present invention to provide a steel pipe for transporting hydrogen using the above-mentioned high strength steel plate for hydrogen transport steel pipe.

Solution to Problem

[0010] The inventors have repeatedly conducted numerous experiments and studies on the chemical compositions, microstructures, and production conditions of steel materials in order to ensure HISC resistance and fatigue crack growth resistance in a high-pressure hydrogen gas environment, and have found the following. That is, letting the standard deviation of a Vickers hardness at 0.25 mm below a surface of a steel plate be denoted as σ , the average value of the

Vickers hardness at 0.25 mm below the surface of the steel plate + 3σ is controlled to 225 HV or less, and the top 20% grain size in the microstructure at the center of the plate thickness is 30 μm or less. This improves HISC resistance and fatigue crack growth resistance. To achieve such a steel microstructure, it is necessary to strictly control the rolling and cooling conditions. The inventors have succeeded in finding those conditions. The present invention has been made based on these findings.

[0011] The gist and configuration of the present invention are as described below.

[1] A high strength steel plate for a hydrogen transport steel pipe, including:
a chemical composition containing, by mass%:

C: 0.030% to 0.060%,

Si: 0.01% to 0.50%,

Mn: 0.80% to 1.80%,

P: 0.015% or less,

S: 0.0015% or less,

Al: 0.010% to 0.080%,

Cr: 0.05% to 0.50%,

Nb: 0.005% to 0.080%,

Ti: 0.005% to 0.020%,

N: 0.0020% to 0.0080%, and

Ca: 0.0005% to 0.0050%, the balance being Fe and incidental impurities; and

a microstructure in which letting the standard deviation of a Vickers hardness at 0.25 mm below a surface of the steel plate be denoted as σ , the average value of the Vickers hardness at 0.25 mm below the surface of the steel plate + 3σ is 225 HV or less, and the top 20% grain size at the center of the thickness of the plate is 30 μm or less, in which a fatigue crack growth rate is less than 2.0×10^{-2} (mm/cycle) when a stress intensity factor range ΔK is 45 (MPa $\cdot\text{m}^{1/2}$), and a tensile strength is 535 MPa or more.

[2] In the high strength steel plate for a hydrogen transport steel pipe described in [1], the chemical composition further contains, by mass%, one or more selected from:

Cu: 0.50% or less,

Ni: 0.50% or less,

Mo: 0.50% or less,

V: 0.1% or less,

Zr: 0.02% or less,

Mg: 0.02% or less, and

REM: 0.02% or less.

[3] A method for manufacturing a high strength steel plate for a hydrogen transport steel pipe, the method including:

heating a steel slab having the chemical composition described in [1] or [2] to a temperature of 1,000°C to 1,250°C;

then subjecting the steel slab to hot rolling at:

a total rolling reduction in a recrystallization temperature range: 35% or more and 55% or less,

a rolling reduction in a final rolling pass in the recrystallization temperature range: 10% or more, and

a rolling reduction in the final rolling pass in a temperature range of (the lower limit temperature in the recrystallization temperature range - 80°C) or higher and lower than the lower limit temperature in the recrystallization temperature range: 15% or more, to form a steel plate; and

thereafter subjecting the steel plate to cooling at:

the temperature of a surface of the steel plate at the start of cooling: an Ar_3 transformation point (°C) or higher,

a difference in cooling start time for the entirety of the steel plate: within 50 seconds,

an average cooling rate from 750°C to 550°C in terms of a steel plate temperature at 0.25 mm below the surface of the steel plate: 15 to 50 °C/s,

an average cooling rate from 750°C to 550°C in terms of the steel plate temperature at the center of the thickness of the plate: 15 to 50 °C/s, and

a cooling stop temperature in terms of the steel plate temperature at 0.25 mm below the surface of the steel plate and at the center of the thickness of the plate: 250°C to 550°C.

[4] A steel pipe for transporting hydrogen using the high strength steel plate for a hydrogen transport steel pipe described in [1] or [2].

Advantageous Effects of Invention

[0012] The high strength steel plate of the present invention for the hydrogen transport steel pipe and the steel pipe for transporting hydrogen using the high strength steel plate for the hydrogen transport steel pipe have excellent HISC resistance and fatigue crack growth resistance in a high-pressure hydrogen environment. The steel pipe has excellent HISC resistance in a high-pressure hydrogen environment, even in a region including the weld of the steel pipe. According to the method of the present invention for manufacturing a high strength steel plate for a hydrogen transport steel pipe, it is possible to manufacture a high strength steel plate for a hydrogen transport steel pipe, the high strength steel plate having excellent HISC resistance and fatigue crack growth resistance in a high-pressure hydrogen environment.

Brief Description of Drawings

[0013] [Fig. 1] Fig. 1 is a schematic view illustrating a method for collecting a test specimen for evaluating HISC resistance in examples.

Description of Embodiments

[0014] A high strength steel plate of the present invention for a hydrogen transport steel pipe will be specifically described below. Hereinafter, the high strength steel plate of the present invention for a hydrogen transport steel pipe is also referred to simply as a "high strength steel plate".

[Chemical Composition]

[0015] The chemical composition of the high strength steel plate of the present invention and the reasons for limitation thereof will be described. In the following description, units indicated by % are all % by mass unless otherwise specified.

C: 0.030% to 0.060%

[0016] C effectively contributes to improving strength. However, when the C content is less than 0.030%, sufficient strength cannot be ensured. Thus, the C content is 0.030% or more. The C content is preferably 0.035% or more. When the C content is more than 0.060%, the hardness increases during accelerated cooling, thereby deteriorating the HISC resistance. For this reason, the C content is 0.060% or less. The C content is preferably 0.050% or less.

Si: 0.01% to 0.50%

[0017] Si is added for deoxidation. A Si content of less than 0.01% results in an insufficient deoxidation effect. For this reason, the Si content is 0.01% or more. The Si content is preferably 0.05% or more. A Si content of more than 0.50% results in a deterioration in weldability. For this reason, the Si content is 0.50% or less. The Si content is preferably 0.45% or less.

Mn: 0.80% to 1.80%

[0018] Mn effectively contributes to improving strength. However, when the Mn content is less than 0.80%, this effect is not sufficiently provided. For this reason, the Mn content is 0.80% or more. The Mn content is preferably 1.00% or more. The Mn content is more preferably 1.20% or more. A Mn content of more than 1.80% results in an increase in hardness during accelerated cooling, thereby deteriorating the HISC resistance. For this reason, the Mn content is 1.80% or less. The Mn content is preferably 1.70% or less. The Mn content is more preferably 1.60% or less.

P: 0.015% or Less

[0019] P is an incidental impurity element that increases the hardness and thereby deteriorates the HISC resistance. When the P content is more than 0.015%, this tendency is marked. For this reason, the upper limit of the P content is

0.015%. The P content is preferably 0.008% or less. A lower P content is more preferred. However, excessive dephosphorization leads to an increase in refining cost. From the viewpoint of the refining cost, the P content is preferably 0.001% or more.

5 S: 0.0015% or Less

[0020] S is an incidental impurity element that forms MnS inclusions in steel to deteriorate low-temperature toughness. For this reason, a lower S content is more preferred. However, a S content of up to 0.0015% is acceptable. For this reason, the S content is 0.015% or less. The S content is preferably 0.0010% or less. A lower S content is more preferred. However, excessive desulfurization leads to an increase in refining cost. From the viewpoint of the refining cost, the S content is preferably 0.0002% or more.

Al: 0.010% to 0.080%

15 **[0021]** Al is added as a deoxidizing agent. When the Al content is less than 0.010%, the effect is not sufficiently provided. For this reason, the Al content is 0.010% or more. The Al content is preferably 0.015% or more. The Al content is more preferably 0.025% or more. An Al content of more than 0.080% results in clogging of a submerged nozzle with alumina during continuous casting. For this reason, the Al content is 0.080% or less. The Al content is preferably 0.070% or less. The Al content is more preferably 0.040% or less.

20 Cr: 0.05% to 0.50%

[0022] Like Mn, Cr is an effective element for achieving sufficient strength even in steel having a low C content. When the Cr content is less than 0.05%, this effect is not sufficiently provided. For this reason, the Cr content is 0.05% or more. The Cr content is preferably 0.10% or more. The Cr content is more preferably 0.15% or more. A Cr content of more than 0.50% results in excessive hardenability to increase the hardness during accelerated cooling, thereby deteriorating the HISC resistance. For this reason, the Cr content is 0.50% or less. The Cr content is preferably 0.45% or less. The Cr content is more preferably 0.35% or less.

30 Nb: 0.005% to 0.080%

[0023] When Nb is present as solute Nb, Nb extends the non-recrystallization temperature range during hot rolling and contributes to refinement of crystal grain size. When the Nb content is less than 0.005%, this effect is not sufficiently provided. For this reason, the Nb content is 0.005% or more. The Nb content is preferably 0.010% or more. The Nb content is more preferably 0.025% or more. A Nb content of more than 0.080% results in crystallization of coarse carbides during solidification, deteriorating hydrogen induced cracking resistance. For this reason, the Nb content is 0.080% or less. The Nb content is preferably 0.060% or less. The Nb content is more preferably 0.055% or less.

40 Ti: 0.005% to 0.020%

[0024] Ti has the effect of pinning austenite grains in the form of TiN during heating, thereby inhibiting the growth of the grains. When the Ti content is less than 0.005%, TiN is not sufficiently formed. Thus, the Ti content is 0.005% or more. The Ti content is preferably 0.008% or more. When the Ti content is more than 0.020%, the formed TiN coarsens, resulting in a failure to obtain sufficient toughness of the weld heat affected zone. For this reason, the Ti content is 0.020% or less. The Ti content is preferably 0.017% or less. The Ti content is more preferably 0.015% or less.

N: 0.0020% to 0.0080%

50 **[0025]** N effectively contributes to improving strength. However, when the N content is less than 0.0020%, sufficient strength cannot be ensured. For this reason, the N content is 0.0020% or more. The N content is preferably 0.0025% or more. The N content is more preferably 0.0030% or more. A N content of more than 0.0080% results in an increase in hardness during accelerated cooling, thereby deteriorating the HISC resistance. For this reason, the N content is 0.0080% or less. The N content is preferably 0.0070% or less. The N content is more preferably 0.0050% or less.

55 Ca: 0.0005% to 0.0050%

[0026] Ca is an element effective in improving hydrogen induced cracking resistance by shape control of sulfide-based inclusions. However, when the Ca content is less than 0.0005%, this addition effect is insufficient. For this reason, the Ca

content is 0.0005% or more. The Ca content is preferably 0.0008% or more. The Ca content is more preferably 0.0015% or more. A Ca content of more than 0.0050% results in saturation of the above-mentioned effect and a decrease in the cleanliness of the steel, deteriorating the hydrogen induced cracking resistance. For this reason, the Ca content is 0.0050% or less. The Ca content is preferably 0.0045% or less. The Ca content is more preferably 0.0035% or less.

[0027] The basic components (essential components) of the high strength steel plate of the present invention have been described above. In the chemical composition of the high strength steel plate of the present invention, components other than those mentioned above (the balance) can be Fe and incidental impurities.

[0028] The chemical composition of the high strength steel plate of the present invention can further contain, in addition to the above-mentioned components, one or more selected from Cu, Ni, Mo, V, Zr, Mg, and REM within the following ranges.

Cu: 0.50% or Less

[0029] Cu is an element effective in improving low-temperature toughness and increasing strength. To provide these effects, the Cu content is preferably 0.05% or more. The Cu content is more preferably 0.10% or more. When the Cu content is more than 0.50%, defects on the steel plate surface are likely to occur. For this reason, when Cu is contained, the Cu content is 0.50% or less. The Cu content is preferably 0.45% or less.

Ni: 0.50% or Less

[0030] Ni is an element effective in improving low-temperature toughness and increasing strength. To provide these effects, the Ni content is preferably 0.05% or more. The Ni content is more preferably 0.10% or more. Ni is an expensive element. For this reason, when Ni is contained, the Ni content is 0.50% or less. The Ni content is preferably 0.45% or less.

Mo: 0.50% or Less

[0031] Mo is an element in improving low-temperature toughness and increasing strength. To provide these effects, the Mo content is preferably 0.05% or more. Mo is an expensive element. For this reason, when Mo is contained, the Mo content is 0.50% or less. The Mo content is preferably 0.45% or less.

V: 0.1% or Less

[0032] V is an element that can be added to the steel plate to enhance its strength and low-temperature toughness. When the V content is less than 0.005%, the effect is not sufficiently provided. For this reason, when V is contained, the V content is preferably 0.005% or more. A V content of more than 0.1% results in a deterioration in the toughness of the weld. For this reason, when V is contained, the V content is preferably 0.1% or less. The V content is more preferably 0.050% or less, still more preferably 0.010% or less.

Zr: 0.02% or Less, Mg: 0.02% or Less, and REM: 0.02% or Less

[0033] Zr, Mg, and a rare earth metal (REM) are elements that can be optionally added to enhance fatigue crack growth resistance through the refinement of crystal grains and to enhance crack resistance through control of inclusion properties. When the amount of each element contained is less than 0.0005%, the effects are not sufficiently provided. For this reason, when these elements are contained, the amount of each element contained is preferably 0.0005% or more. When the amount of each element contained is more than 0.02%, the effects are saturated. For this reason, when Zr, Mg, and REM are contained, the amount of each element contained is preferably 0.02% or less. The amount of each of the above elements contained is more preferably 0.0050% or less, still more preferably 0.0030% or less. REM is a general term for Sc, Y, and 15 elements from lanthanum (La) of atomic number 57 to lutetium (Lu) of atomic number 71. The amount of REM contained refers to the total amount of these elements.

[0034] The balance other than the above elements is Fe and incidental impurities. However, other trace elements may be contained as long as they do not impair the effects of the present invention. For example, O is an element that is incidentally contained in steel, and is acceptable in the present invention as long as the O content is 0.0050% or less, preferably 0.0040% or less.

[Hardness at 0.25 mm below Surface of Steel Plate]

[0035] In the high strength steel plate of the present invention, letting the standard deviation of a Vickers hardness (HV 0.5) at 0.25 mm below a surface of the steel plate be denoted as σ , it is important that the average value of the Vickers

hardness (HV 0.5) at 0.25 mm below the surface of the steel plate + 3σ be 225 HV or less. Meeting this condition can provide excellent HISC resistance in a high-pressure hydrogen environment. When the average value of the Vickers hardness (HV 0.5) at 0.25 mm below the surface of the steel plate + 3σ is more than 225 HV, the hardness varies greatly within the steel plate, causing hydrogen to accumulate locally. The HISC resistance deteriorates in a region where hydrogen has accumulated locally. Here, the "Vickers hardness (HV 0.5) at 0.25 mm below the surface of the steel plate" refers to the Vickers hardness (HV 0.5) measured at 100 equally spaced points in the plate width direction from each of the leading end and the trailing end in the rolling direction of the steel plate, the 100 equally spaced points being located at 0.25 mm below the surface of the steel plate (at a depth of 0.25 mm from the surface of the steel plate toward the center of the plate thickness). The leading end of the steel plate in the rolling direction is a position 1 m downstream of the leading edge of the steel plate in the rolling direction. The trailing end of the steel plate in the rolling direction is a position 1 m upstream of the trailing edge of the steel plate in the rolling direction. The measurement was performed in a region excluding non-steady portions near the ends in the plate width direction. Here, the reason for measuring the hardness of the steel plate at 0.5 kgf instead of the commonly used 10 kgf is that measurement at 0.5 kgf results in a smaller indentation, making it possible to obtain hardness information at a position closer to the surface and hardness information that is more sensitive to the microstructure. Measuring the Vickers hardness with a test load of less than 0.5 kgf results in a too small indentation size and thus an increase in measurement variability, which is not preferred. The average value of the Vickers hardness at 0.25 mm below the surface of the steel plate + 3σ is preferably 220 HV or less. As an example, the average value of the Vickers hardness at 0.25 mm below the surface of the steel plate + 3σ is 200 HV or more.

[Top 20% Grain Size at Center of Plate Thickness]

[0036] Refinement of the average crystal grain size improves fatigue crack growth resistance. However, when cooling is started at a temperature equal to or higher than the Ar_3 transformation point, there is a limit to the refinement of the average crystal grain size. In the present invention, it is important to inhibit the formation of coarse crystal grains. That is, when the top 20% grain size is large, the fatigue crack growth resistance deteriorates. In particular, in a microstructure in which the top 20% of a crystal grain size distribution at the center of the plate thickness is more than $30\ \mu\text{m}$, cracks propagate easily, thus significantly deteriorating the fatigue crack growth resistance. Therefore, it is necessary to have a microstructure in which the top 20% grain size at the center of the plate thickness (1/2 position of the plate thickness) is $30\ \mu\text{m}$ or less. The top 20% grain size is preferably $25\ \mu\text{m}$ or less. As an example, the top 20% grain size is $15\ \mu\text{m}$ or more. The top 20% grain size is a grain size corresponding to the 20% position from the largest crystal grain size when the crystal grain sizes are arranged in descending order in the crystal grain size distribution.

[0037] The measurement range of the crystal grain size was $1\ \text{mm} \times 1\ \text{mm}$ at the center position of the plate thickness. More specifically, the crystal grain size was determined as follows: The microstructure at the center of the plate thickness was analyzed by an electron backscatter diffraction (EBSD) method. A boundary having an orientation difference of 15° or more was determined to be a crystal grain boundary. The equivalent circular diameter was calculated as the crystal grain size from the area of each crystal grain. In the present invention, a frequency distribution table is prepared for all crystal grains to be measured, and the crystal grain size corresponding to 20% of the cumulative relative frequency from the largest crystal grain size calculated is referred to as the "top 20% grain size".

[Fatigue Crack Growth Rate]

[0038] In a fatigue crack growth test of the high strength steel plate of the present invention in a high-pressure hydrogen gas of 21 MPa, the fatigue crack growth rate is less than 2.0×10^{-2} (mm/cycle) when the stress intensity factor range ΔK is 45 (MPa $\cdot\text{m}^{1/2}$). The fatigue crack growth rate is preferably 1.5×10^{-2} (mm/cycle) or less. A lower fatigue crack growth rate is more preferred. As an example, the fatigue crack growth rate is 1.0×10^{-2} (mm/cycle) or more.

[Tensile Strength]

[0039] The high strength steel plate of the present invention is intended mainly for steel plates for steel pipes having a strength of API 5L grade X65 or higher, and thus has a tensile strength of 535 MPa or higher. The upper limit of the tensile strength of the high strength steel plate of the present invention is not particularly limited, but as an example, the tensile strength of the high strength steel plate of the present invention is 760 MPa or less. The high strength steel plate of the present invention may have a tensile strength of 600 MPa or less.

[Thickness of High Strength Steel Plate]

[0040] The plate thickness of the high strength steel plate of the present invention is not particularly limited, but is preferably 12 mm or more. The plate thickness of the high strength steel plate of the present invention is not particularly

limited, but is preferably 39 mm or less.

[Manufacturing Method]

[0041] A manufacturing method and manufacturing conditions for manufacturing the above-mentioned high strength steel plate are specifically described below.

[0042] The method for manufacturing the high strength steel plate of the present invention includes heating a steel slab (slab) having the above-mentioned chemical composition, then subjecting the steel slab to hot rolling to form a steel plate (hot rolling step), and thereafter cooling the steel plate under predetermined conditions (cooling step).

[Heating Temperature of Steel Slab]

Heating Temperature of steel Slab: 1,000°C to 1,250°C

[0043] A heating temperature of the steel slab (slab) of lower than 1,000°C results in insufficient dissolution of carbides to reduce the amount of steel that is subjected to solid solution strengthening by solute C and so forth, resulting in a failure to achieve the required strength. A heating temperature of the steel slab of higher than 1,250°C results in excessively coarse crystal grains to deteriorate the fatigue crack growth resistance. Thus, the heating temperature of the steel slab is 1,000°C to 1,250°C. The heating temperature of the steel slab is preferably 1,030°C or higher. The heating temperature of the steel slab is preferably 1,200°C or lower. The steel slab (slab) is heated to the heating temperature all the way to the center.

[Total Rolling Reduction in Recrystallization Temperature Range: 35% or More and 55% or Less]

[0044] To refine the top 20% grain size in the microstructure at the center of the plate thickness, the recrystallization of crystal grains is required to be promoted during hot rolling in the recrystallization temperature range to inhibit the formation of coarse grains. When the total rolling reduction in the recrystallization temperature range is less than 35%, recrystallization is insufficient, resulting in coarse grains remaining. Thus, the total rolling reduction in the recrystallization temperature range is 35% or more, preferably 38% or more. When the total rolling reduction in the recrystallization temperature range is more than 55%, coarsening of the crystal grains can be inhibited. However, the rolling reduction in the non-recrystallization range is insufficient, resulting in a failure to refine the crystal grains. Thus, the total rolling reduction in the recrystallization temperature range is 55% or less, preferably 52% or less. Here, the lower limit temperature T_{nr} (°C) of the recrystallization temperature range can be calculated, for example, from the components of the steel using the following formula. The temperature in the hot rolling is the surface temperature of the material being rolled (steel slab or steel plate), and the surface temperature can be measured with a radiation thermometer or the like.

$$T_{nr} \text{ (}^{\circ}\text{C)} = 174 \times \log[\%Nb] [\%C + (12/14)\%N] + 1444$$

where in the above formula, each [%X] is the element X content (mass%) of the steel.

[Rolling Reduction in Final Rolling Pass in

Recrystallization Temperature Range: 10% or More]

[0045] Rolling in the partial recrystallization range needs to be started in a uniform grain state free of coarse grains by ensuring a sufficient rolling reduction in the final rolling pass in the recrystallization temperature range to sufficiently promote recrystallization, in addition to the total rolling reduction in the recrystallization temperature range of 35% or more and 55% or less. When the rolling reduction in the final rolling pass in the recrystallization temperature range is less than 10%, recrystallization is insufficient, and the grains grow into coarse grains during the holding time between rough rolling and the start of finish rolling. Thus, the rolling reduction of the final rolling pass in the recrystallization temperature range is 10% or more, preferably 11% or more. The upper limit of the rolling reduction in the final rolling pass in the recrystallization temperature range is not limited, and a higher rolling reduction is more preferred. As an example, the rolling reduction in the final rolling pass in the recrystallization temperature range is 20% or less.

[Rolling Reduction in Final Rolling Pass in Temperature Range of (Lower Limit Temperature in Recrystallization Temperature Range - 80°C) or Higher and Lower Than Lower Limit Temperature in Recrystallization Temperature Range: 15% or More]

5 **[0046]** Even after the rolling in the recrystallization temperature range is completed, recrystallization occurs partially. Thus, recrystallization can be promoted by further increasing the rolling reduction in the temperature range of (the lower limit temperature in the recrystallization temperature range - 80°C) or higher and lower than the lower limit temperature in the recrystallization temperature range. This makes it possible to effectively refine the top 20% grain size in the microstructure at the center of the plate thickness. Thus, the rolling reduction in the final rolling pass in the temperature
10 range of (the lower limit temperature in the recrystallization temperature range - 80°C) or higher and lower than the lower limit temperature in the recrystallization temperature range is 15% or more, preferably 16% or more. The upper limit of the rolling reduction in the final rolling pass in the above temperature range is not particularly limited, and a higher rolling reduction is more preferred. As an example, the rolling reduction in the final rolling pass in the above temperature range is 25% or less.

15 **[0047]** Rolling at a temperature lower than (the lower limit temperature in the recrystallization temperature range - 80°C) is effective in refining grains because more strain is introduced when the rolling is performed at a lower temperature. For this reason, rolling is preferably performed at a low temperature lower than (the lower limit temperature of the recrystallization temperature range - 80°C) within a range in which the cooling start temperature can be observed.

20 [Finish Rolling Temperature]

[0048] In the hot rolling step, a lower finish rolling temperature is more preferred in order to refine the crystal grains. From the viewpoint of ensuring the HISC resistance in a high-pressure hydrogen environment, the cooling start temperature in the cooling step after the hot rolling step needs to be higher than or equal to the Ar_3 transformation point in terms of a
25 surface temperature of the steel plate. In consideration of this, the finish rolling temperature needs to be set. The term " Ar_3 transformation point" refers to the ferrite transformation start temperature during cooling, and can be calculated, for example, from the components of the steel using the following formula. The surface temperature of the steel plate can be measured using a radiation thermometer or the like.

30 Ar_3 transformation point (°C) = $910 - 310[\%C] - 80[\%Mn] - 20[\%Cu] - 15[\%Cr] - 55[\%Ni] - 80[\%Mo]$

where in the above formula, each [%X] is the element X content (mass%) of the steel, and an element that is not contained is defined as 0.

35 [Cooling Start Temperature in Cooling]

Cooling Start Temperature: Temperature Higher than or Equal to Ar_3 Transformation Point (°C) in Terms of Surface Temperature of Steel Plate

40 **[0049]** After the hot rolling step, the steel plate is cooled (controlled cooling). When the surface temperature of the steel plate at the start of cooling is lower than the Ar_3 transformation point (°C), ferrite forms before cooling, resulting in a significant decrease in strength. For this reason, the surface temperature of the steel plate at the start of cooling is higher than or equal to the Ar_3 transformation point (°C). The surface temperature of the steel plate at the start of cooling is the temperature of the surface region of the steel plate where the cooling start temperature is the lowest. Specifically, the
45 surface temperature of the steel plate at the start of cooling is the surface temperature of the steel plate at its trailing end portion when, for example, the steel plate is cooled while traveling in one direction with respect to a cooling device. For example, in the case where cooling is performed individually for each specific region of the entire steel plate and where different cooling start times are set for different regions, the surface temperature of the steel plate is the surface temperature of the region that is cooled last. As an example, the upper limit of the surface temperature of the steel plate
50 at the start of cooling is the above-mentioned finish rolling temperature.

[Cooling Start Time in Cooling]

Difference in Cooling Start Time for Entirety of Steel Plate: Within 50 seconds

55 **[0050]** When the difference in cooling start time for the entirety of the steel plate is more than 50 seconds, the difference in the temperature of the steel plate is large, resulting in a large variation in the temperature of the steel plate when cooling is stopped. This increases the variation in Vickers hardness at 0.25 mm below the surface of the steel plate and

deteriorates the HISC resistance. Therefore, the difference in cooling start time for the entirety of the steel plate is within 50 seconds, preferably within 45 seconds. Specifically, for example, when the steel plate is cooled while traveling in one direction with respect to the cooling device, the difference in cooling start time between the leading end of the steel plate and the trailing end of the steel plate is within 50 seconds. For example, in the case where cooling is performed individually for each specific region of the entire steel plate and where different cooling start times are set for different regions, the difference in cooling start time between the first region and the last region is within 50 seconds. When the entire steel plate can be cooled at once, the difference in cooling start time for the entire steel plate may be 0 seconds.

[Cooling Rate of Cooling]

[0051] To achieve high strength while obtaining excellent HISC resistance, it is necessary to control the cooling rates at 0.25 mm below the surface of the steel plate and at the center of the plate thickness.

Average Cooling Rate from 750°C to 550°C at 0.25 mm below Surface of Steel Plate: 15 to 50 °C/s

[0052] It is important to minimize the average cooling rate from 750°C to 550°C in terms of a steel plate temperature at 0.25 mm below the surface of the steel plate to thereby form granular bainite. The temperature range of 750°C to 550°C is an important temperature range for bainite transformation. It is thus important to control the cooling rate in this temperature range. When the average cooling rate in the temperature range is more than 50 °C/s, the hardness may vary, and the HISC resistance after pipe production deteriorates. Therefore, the average cooling rate is 50 °C/s or less, preferably 45 °C/s or less. When the cooling rate is too low, ferrite and pearlite are formed, resulting in insufficient strength. From the viewpoint of inhibiting this, the average cooling rate in the above-mentioned temperature range is 15 °C/s or more, preferably 17 °C/s or more. With regard to cooling in a temperature range of 550°C or lower in terms of the steel plate temperature at 0.25 mm below the surface of the steel plate, when the cooling rate is low, cooling in a stable nucleate boiling state may fail to be achieved, resulting in a variation in hardness in the extreme surface layer portion of the steel plate. Therefore, the average cooling rate in the temperature range of 550°C to the cooling stop temperature in terms of the steel plate temperature at 0.25 mm below the surface of the steel plate is preferably 150 °C/s or more. The average cooling rate is preferably 250 °C/s or less from the viewpoint of more easily inhibiting the variation in hardness.

Average Cooling Rate from 750°C to 550°C at Center of Plate Thickness: 15 to 50 °C/s

[0053] When the average cooling rate from 750°C to 550°C at the center of the plate thickness is less than 15 °C/s, a granular bainite structure is not formed, resulting in a reduction in strength. Therefore, the average cooling rate from 750°C to 550°C at the center of the plate thickness is 15 °C/s or more. The average cooling rate is preferably 17 °C/s or more from the viewpoint of inhibiting the variation of the microstructure. The average cooling rate is 50 °C/s or less, preferably 45 °C/s or less, in order to inhibit a variation in grain size. The cooling in the temperature range of 550°C or lower in terms of the steel plate temperature at the center of the plate thickness is not particularly limited, but the average cooling rate in the above-mentioned temperature range is preferably 15 °C/s or more from the viewpoint of inhibiting the variations of the microstructure and grain size. From the above viewpoint, the average cooling rate in the above temperature range is preferably 50 °C/s or less.

[0054] The steel plate temperature at 0.25 mm below the surface of the steel plate and at the center of the plate thickness cannot be measured directly and physically. However, based on the surface temperature at the start of cooling measured by a radiation thermometer and a target surface temperature at the stop of cooling, the temperature distribution in the thickness section is calculated by difference calculation using, for example, a process computer, and the temperature distribution can be obtained in real time from the results. The temperature at 0.25 mm below the surface of the steel plate in the temperature distribution is defined as the "temperature of the steel plate at 0.25 mm below the surface of the steel plate" in the present specification. The temperature at the center of the plate thickness in the temperature distribution is defined as the "steel plate temperature at the center of the plate thickness" in the present specification.

[Cooling Stop Temperature]

Cooling Stop Temperature: 250°C to 550°C in Terms of Steel Plate Temperature at 0.25 mm below Surface of Steel Plate and at Center of Plate Thickness

[0055] When the cooling stop temperature is higher than 550°C in terms of the steel plate temperature at 0.25 mm below the surface of the steel plate and at the center of the plate thickness, bainite transformation is incomplete, resulting in a failure to obtain sufficient strength. Thus, the cooling stop temperature is 550°C or lower, preferably 500°C or lower. When the cooling stop temperature is lower than 250°C, the hardness increases to thereby deteriorate the HISC resistance.

Thus, the cooling stop temperature is 250°C or higher, preferably 300°C or higher.

[Steel Pipe for Transporting Hydrogen]

[0056] A steel pipe for transporting hydrogen (UOE steel pipe, electric resistance welded steel pipe, spiral steel pipe, or the like) suitable for transporting high-pressure hydrogen gas can be manufactured by forming the high strength steel plate of the present invention into a tubular shape using press bend forming, roll forming, UOE forming, or the like, and then welding the butting portions. In addition, by producing a steel pipe using the high strength steel plate of the present invention, it is possible to produce a steel pipe having excellent HISC resistance even if a high hardness region is present in the weld. In the present invention, the high-pressure hydrogen refers to, for example, a hydrogen gas environment with a pressure of 15 MPa or more.

[0057] For example, a UOE steel pipe is manufactured by groove cutting the ends of a steel plate, forming the steel plate into a steel pipe shape by C press, U press, and O press, then seam welding the butting portions by inner surface welding and outer surface welding, and optionally subjecting it to an expansion process. Any welding method may be used as long as sufficient joint strength and joint toughness can be obtained, but it is preferable to use submerged arc welding from the viewpoint of excellent welding quality and production efficiency. A steel pipe produced by forming a steel plate into a pipe shape using press bend forming and then seam welding the butting portions may also be subjected to pipe expansion.

EXAMPLES

[0058] Steels having the chemical compositions given in Table 1 (steel types A to W) were formed into steel slabs (slabs) by a continuous casting method. The steel slabs were heated to the heating temperature given in Table 2 and then subjected to hot rolling and cooling under the conditions given in Table 2 to form steel plates having the final thickness given in Table 2. In the cooling step, each steel plate was subjected to controlled cooling using a water cooling-type controlled cooling device while the steel plate was traveling in one direction. Thereafter, the edges of the steel plate were subjected to groove cutting, and the steel plate was formed into a steel pipe shape by C press, U press, and O press. Subsequently, the butting portions of the inner surface and the outer surface were seam welded by submerged arc welding, and a pipe expansion process was performed to obtain a steel pipe. The A_{r3} transformation point and the lower limit temperature T_{nr} of the recrystallization temperature range in Table 1 were determined from the above formulae.

[Measurement of Vickers hardness]

[0059] With respect to a section perpendicular to the rolling direction, the Vickers hardness (HV 0.5) was measured at 100 equally spaced points in the plate width direction from each of the leading end and the trailing end in the rolling direction of the steel plate in accordance with JIS Z 2244 (2009), the 100 equally spaced points being located at 0.25 mm below the surface of the steel plate. The average value and the standard deviation σ of the Vickers hardness values (HV 0.5) at 200 points in total were determined. The leading end of the steel plate in the rolling direction is a position 1 m downstream of the leading edge of the steel plate in the rolling direction. The trailing end of the steel plate in the rolling direction is a position 1 m upstream of the trailing edge of the steel plate in the rolling direction. The measurement was performed in a region excluding non-steady portions near the ends in the plate width direction. Table 3 presents the average value of the Vickers hardness at 0.25 mm below the surface of the steel plate $+ 3\sigma$.

[Calculation of Top 20% Grain Size]

[0060] A sample for observing the metallic microstructure was taken from the central portion of the width of the steel plate obtained as described above. A section of this sample perpendicular to the plate width direction was mirror-polished and then etched with colloidal silica. Thereafter, crystal data was collected by an electron backscatter diffraction (EBSD) method in a field of view of 1 mm $\times$ 1 mm at the center of the plate thickness (measurement step: 0.8 μ m). After the data collection, a boundary having an orientation difference of 15° or more was determined as a crystal grain boundary using OIM-Analysis (OIM Analysis software, manufactured by EDAX). The equivalent circular diameter was calculated as the crystal grain size from the area of each crystal grain. A frequency distribution table was prepared for all crystal grains measured, and the crystal grain size corresponding to 20% of the cumulative relative frequency from the largest crystal grain size calculated was defined as the "top 20% grain size". The measurement results are presented in Table 3.

[Derivation of Fatigue Crack Growth Rate]

[0061] A CT test specimen conforming to ASTM E 647 was taken from the steel plate obtained as described above in such a manner that the direction of load application was parallel to the rolling direction. The CT test specimen was a 10-

mm-thick test specimen taken from the 1/2 thickness position. The length of the fatigue crack was measured by the compliance method using a clip gage, and the fatigue crack growth rate in a high-pressure hydrogen gas of 21 MPa was determined. The fatigue crack growth rate (mm/cycle) when the stress intensity factor range ΔK was 45 (MPa·m^{1/2}) was evaluated. Table 3 presents the results.

[Measurement of tensile strength]

[0062] A full-thickness test piece in the direction perpendicular to the rolling direction was used as a test piece for a tensile test, and the tensile test was performed in accordance with the provisions of JIS Z2241 (2011) to measure tensile strength and yield strength. Table 3 presents the results.

[Evaluation of HISC resistance]

[0063] With regard to the HISC resistance, as illustrated in Fig. 1, a test piece (coupon) cut out from the obtained steel pipe was flattened, and then a test specimen of 3 mm × 10 mm × 50 mm was taken from the inner surface of the steel pipe. At this time, a test specimen containing both the weld and the base material was collected in addition to a test specimen containing only the base material without the weld. The inner surface to be tested was left intact without removing the scale in order to leave the state of the outermost layer. That is, the position 0.25 mm below the surface of the steel plate is included in the test specimen. A stress of 90% of the actual yield strength (0.5% YS) of each steel pipe was applied to the test specimen thus collected, and a four-point bending test was performed in a high-pressure hydrogen gas of 21 MPa. When no cracking was observed in both the test specimen of the base material alone without the weld and the test specimen including both the weld and the base material after the exposure for 720 hours, the HISC resistance was determined to be excellent (good) and marked with ◯. In addition, when a crack occurred in at least one of the test specimens, the test specimen was determined to be defective, and was marked with ×. Table 3 presents the results.

[0064] The target ranges of the present invention are as described below. As a high strength steel plate for a hydrogen transport steel pipe, the average value of the Vickers hardness at 0.25 mm below the surface of the plate + 3σ is 225 HV or less. The top 20% grain size in the microstructure at the center of the plate thickness is 30 μm or less. The fatigue crack growth rate is less than 2.0×10^{-2} (mm/cycle) when the stress intensity factor range ΔK is 45 (MPa·m^{1/2}). The tensile strength is 535 MPa or more. In addition, no cracking is observed in the evaluation of the HISC resistance (four-point bending test).

[Table 1]

Steel type	Chemical composition (mass%)																			Ar ₃ transformation point (°C)	T _{nr} temperature (°C)
	C	Si	Mn	P	S	Al	Cr	Nb	Ti	N	Ca	Cu	Ni	Mo	V	Zr	Mg	REM			
A	0.045	0.19	1.55	0.006	0.0006	0.028	0.26	0.030	0.011	0.0042	0.0023								768	950	
B	0.050	0.15	1.43	0.005	0.0005	0.026	0.31	0.043	0.010	0.0039	0.0015								775	985	
C	0.038	0.17	1.37	0.007	0.0008	0.030	0.16	0.055	0.010	0.0045	0.0021	0.42							778	985	
D	0.047	0.31	1.28	0.008	0.0007	0.025	0.28	0.052	0.012	0.0029	0.0018		0.44						765	993	
E	0.035	0.08	1.25	0.005	0.0010	0.033	0.20	0.037	0.009	0.0053	0.0025			0.43					762	951	
F	0.049	0.26	1.32	0.006	0.0013	0.029	0.34	0.015	0.008	0.0044	0.0040				0.006				784	904	
G	0.046	0.44	1.30	0.009	0.0009	0.031	0.27	0.026	0.013	0.0047	0.0022					0.0010			788	942	
H	0.043	0.17	1.69	0.004	0.0004	0.036	0.10	0.040	0.011	0.0043	0.0025						0.0013		760	969	
I	0.048	0.35	1.09	0.011	0.0011	0.040	0.45	0.053	0.010	0.0040	0.0031							0.0011	801	998	
J	0.029	0.30	1.34	0.005	0.0005	0.029	0.18	0.036	0.010	0.0034	0.0019								791	932	
K	0.063	0.33	1.39	0.009	0.0006	0.027	0.27	0.039	0.009	0.0046	0.0024								775	995	
L	0.048	0.09	0.77	0.005	0.0007	0.027	0.45	0.024	0.012	0.0038	0.0026			0.10					819	938	
M	0.040	0.10	1.81	0.009	0.0005	0.030	0.15	0.037	0.010	0.0040	0.0028								751	958	
N	0.045	0.23	1.35	0.016	0.0008	0.032	0.32	0.033	0.011	0.0041	0.0030								783	958	
O	0.038	0.15	1.19	0.008	0.0009	0.034	0.03	0.025	0.010	0.0043	0.0032			0.20					787	925	
P	0.046	0.21	1.28	0.011	0.0010	0.028	0.52	0.045	0.012	0.0048	0.0033								786	983	
Q	0.041	0.13	1.47	0.005	0.0005	0.025	0.38	0.004	0.009	0.0037	0.0018		0.30						757	791	
R	0.039	0.22	1.50	0.006	0.0005	0.030	0.26	0.016	0.004	0.0038	0.0025								774	892	
S	0.037	0.11	1.26	0.007	0.0006	0.031	0.18	0.040	0.010	0.0019	0.0017								795	955	
T	0.047	0.18	1.51	0.010	0.0009	0.026	0.33	0.033	0.011	0.0082	0.0029								770	966	
U	0.060	0.04	1.55	0.006	0.0009	0.035	0.27	0.029	0.010	0.0041	0.0020		0.27	0.07					743	968	
V	0.042	0.31	1.80	0.006	0.0008	0.029	0.27	0.040	0.012	0.0039	0.0021			0.12					739	967	
W	0.044	0.20	1.45	0.005	0.0005	0.031	0.22	0.048	0.020	0.0080	0.0025								777	989	

Note 1: The balance is Fe and incidental impurities.

Note 2: Underlined shows outside the scope of the present invention.

[Table 2]

No.	Steel type	Final thickness (mm)	Steel slab heating temperature (°C)	Hot rolling step			Cooling step							Class			
				Rolling in recrystallization temperature range		Rolling reduction in final rolling pass in temperature range of (lower limit temperature in recrystallization temperature range - 80°C) or higher*1 (%)	Finish rolling temperature (°C)	Surface temperature of steel plate at start of cooling*2 (°C)	Surface temperature of steel plate at start of cooling - Ar3 transformation point (°C)	Difference in cooling start time for entirety of steel plate (seconds)	Average cooling rate from 750°C to 550°C		Average cooling rate from 550°C to cooling stop temperature		Cooling stop temperature		
				Total rolling reduction (%)	Rolling reduction in final rolling pass (%)						0.25 mm below surface of steel plate (°C/s)	Center of plate thickness (°C/s)	0.25 mm below surface of steel plate (°C/s)		Center of plate thickness (°C/s)	0.25 mm below surface of steel plate (°C)	Center of plate thickness (°C)
1	A	35	1030	37	12	17	805	780	12	41	18	16	170	16	450	450	Example
2	B	30	1060	39	11	16	817	788	13	35	21	18	190	18	410	410	Example
3	C	18	1160	49	11	17	855	785	7	19	35	31	230	33	500	500	Example
4	D	27	1090	40	10	15	813	775	10	32	24	21	200	22	430	430	Example
5	E	39	1000	35	12	17	804	781	19	50	17	15	150	15	400	400	Example
6	F	21	1130	46	13	20	842	794	10	20	30	26	220	27	250	250	Example
7	G	12	1250	55	13	20	890	790	2	10	50	44	250	47	550	550	Example
8	H	24	1100	43	12	16	816	775	15	25	26	23	210	24	300	300	Example
9	I	15	1200	52	10	18	883	802	1	15	41	36	240	38	520	520	Example
10	J	27	1080	39	13	19	833	798	7	29	25	22	210	23	470	470	Comparative Example
11	K	18	1150	48	10	17	851	783	8	18	34	30	230	32	270	510	Comparative Example
12	L	30	1050	38	13	20	850	820	1	34	20	17	180	17	470	470	Comparative Example
13	M	15	1190	51	12	18	847	765	14	14	39	35	230	37	320	530	Comparative Example
14	N	12	1240	54	12	20	884	786	3	11	49	44	250	47	350	540	Comparative Example
15	O	21	1120	45	13	20	845	795	8	21	31	27	220	28	480	480	Comparative Example

(continued)

No.	Steel type	Final thickness (mm)	Steel slab heating temperature (°C)	Hot rolling step			Cooling step							Class			
				Rolling in recrystallization temperature range		Rolling reduction in final rolling pass in temperature range of (lower limit temperature in recrystallization temperature range - 80°C) or higher*1 (%)	Finish rolling temperature (°C)	Surface temperature of steel plate at start of cooling*2 (°C)	Surface temperature of steel plate at start of cooling - Ar3 transformation point (°C)	Difference in cooling start time for entirety of steel plate (seconds)	Average cooling rate from 750°C to 550°C		Average cooling rate from 550°C to cooling stop temperature		Cooling stop temperature		
				Total rolling reduction (%)	Rolling reduction in final rolling pass (%)						0.25 mm below surface of steel plate (°C/s)	Center of plate thickness (°C/s)	0.25 mm below surface of steel plate (°C/s)		Center of plate thickness (°C/s)	0.25 mm below surface of steel plate (°C)	Center of plate thickness (°C)
16	P	18	1170	48	11	18	864	790	4	17	36	220	34	290	510	Comparative Example	
17	Q	39	1010	36	15	20	780	760	3	45	17	160	15	510	510	Comparative Example	
18	R	35	1040	37	14	20	811	787	13	40	19	170	17	530	530	Comparative Example	
19	S	24	1110	42	12	18	842	799	4	24	25	200	23	490	490	Comparative Example	
20	T	15	1210	52	12	19	861	775	5	16	40	240	37	300	510	Comparative Example	
21	C	35	990	38	10	15	806	780	2	39	20	160	17	480	480	Comparative Example	
22	F	27	1260	41	12	20	829	796	12	27	23	200	21	430	430	Comparative Example	
23	E	39	1020	33	11	16	800	777	15	47	18	150	16	480	480	Comparative Example	
24	A	35	1020	57	11	17	808	781	13	42	17	160	15	540	540	Comparative Example	
25	A	30	1070	37	9	17	814	782	14	36	22	190	19	490	490	Comparative Example	
26	B	35	1030	36	10	11	819	794	19	41	19	180	17	520	520	Comparative Example	

(continued)

No.	Steel type	Final thickness (mm)	Steel slab heating temperature (°C)	Hot rolling step			Cooling step							Class			
				Rolling in recrystallization temperature range		Rolling reduction in final rolling pass in temperature range of (lower limit temperature in recrystallization temperature range - 80°C) or higher*1 (%)	Finish rolling temperature (°C)	Surface temperature of steel plate at start of cooling*2 (°C)	Surface temperature of steel plate at start of cooling - Ar ₃ transformation point (°C)	Difference in cooling start time for entirety of steel plate (seconds)	Average cooling rate from 750°C to 550°C		Average cooling rate from 550°C to cooling stop temperature		Cooling stop temperature		
				Total rolling reduction (%)	Rolling reduction in final rolling pass (%)						0.25 mm below surface of steel plate (°C/s)	Center of plate thickness of steel plate (°C/s)	0.25 mm below surface of steel plate (°C/s)		Center of plate thickness of steel plate (°C/s)	0.25 mm below surface of steel plate (°C)	Center of plate thickness of steel plate (°C)
27	I	30	1050	38	11	15	820	791	-10	35	20	17	180	17	480	480	Comparative Example
28	D	24	1090	44	11	15	817	778	13	53	27	24	210	25	280	280	Comparative Example
29	G	39	1010	35	12	18	821	799	11	34	11	12	160	12	490	490	Comparative Example
30	H	15	1200	53	11	18	848	767	7	15	57	51	240	53	330	520	Comparative Example
31	E	18	1160	50	11	19	845	770	8	19	34	30	230	32	240	240	Comparative Example
32	C	35	1020	38	10	16	820	793	15	40	20	17	170	17	560	560	Comparative Example
33	U	39	1020	36	10	16	767	745	2	48	17	15	150	15	330	330	Example
34	V	35	1030	35	10	15	765	742	3	42	18	16	170	16	340	340	Example
35	W	20	1100	44	12	18	840	790	13	21	32	28	230	32	450	450	Example

Note 1: Underlined shows outside the scope of the present invention.

*1 Rolling reduction in the final rolling pass in the temperature range of (the lower limit temperature in the recrystallization temperature range - 80°C) or higher and lower than the lower limit temperature in the recrystallization temperature range.

*2 Temperature at the trailing end of the steel plate.

Note 1: Underlined shows outside the scope of the present invention.

*1 Rolling reduction in the final rolling pass in the temperature range of (the lower limit temperature in the recrystallization temperature range - 80°C) or higher and lower than the lower limit temperature in the recrystallization temperature range.

*2 Temperature at the trailing end of the steel plate.

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[Table 3]

No.	Average value of Vickers hardness $+3\sigma^{*1}$ (HV)	Top 20% grain size ^{*2} (μm)	Fatigue crack growth rate (mm/cycle)	Yield strength (MPa)	Tensile strength (MPa)	HISC resistance	Class
1	210	26	1.6×10^{-2}	472	561	○	Example
2	211	23	1.4×10^{-2}	485	578	○	Example
3	220	19	1.3×10^{-2}	477	572	○	Example
4	215	21	1.3×10^{-2}	482	585	○	Example
5	208	30	1.9×10^{-2}	465	550	○	Example
6	218	19	1.1×10^{-2}	487	582	○	Example
7	225	17	1.0×10^{-2}	486	589	○	Example
8	217	20	1.1×10^{-2}	470	569	○	Example
9	222	18	1.3×10^{-2}	473	565	○	Example
10	213	22	1.3×10^{-2}	422	<u>508</u>	○	Comparative Example
11	<u>234</u>	19	1.4×10^{-2}	501	583	×	Comparative Example
12	212	24	1.4×10^{-2}	420	<u>510</u>	○	Comparative Example
13	<u>234</u>	17	1.1×10^{-2}	511	595	×	Comparative Example
14	<u>233</u>	18	1.4×10^{-2}	484	591	×	Comparative Example
15	219	19	1.1×10^{-2}	432	<u>518</u>	○	Comparative Example
16	<u>232</u>	18	1.3×10^{-2}	503	590	×	Comparative Example
17	206	<u>32</u>	<u>2.0×10^{-2}</u>	471	558	○	Comparative Example
18	210	<u>34</u>	<u>2.2×10^{-2}</u>	479	575	○	Comparative Example
19	217	21	1.1×10^{-2}	435	<u>513</u>	○	Comparative Example
20	<u>231</u>	18	1.3×10^{-2}	508	593	×	Comparative Example
21	207	23	1.1×10^{-2}	442	<u>511</u>	○	Comparative Example
22	214	<u>35</u>	<u>2.2×10^{-2}</u>	475	569	○	Comparative Example
23	210	<u>32</u>	<u>2.1×10^{-2}</u>	488	579	○	Comparative Example
24	209	<u>31</u>	<u>2.0×10^{-2}</u>	482	580	○	Comparative Example
25	212	<u>32</u>	<u>2.1×10^{-2}</u>	478	571	○	Comparative Example
26	208	31	<u>2.0×10^{-2}</u>	473	555	○	Comparative Example
27	204	23	1.4×10^{-2}	443	<u>524</u>	○	Comparative Example
28	<u>239</u>	22	1.6×10^{-2}	497	575	×	Comparative Example
29	211	30	1.9×10^{-2}	439	<u>522</u>	○	Comparative Example
30	<u>235</u>	18	1.4×10^{-2}	503	590	×	Comparative Example
31	<u>237</u>	19	1.4×10^{-2}	505	588	×	Comparative Example
32	213	28	1.8×10^{-2}	445	<u>523</u>	○	Comparative Example
33	224	19	1.7×10^{-2}	516	609	○	Example
34	225	18	1.8×10^{-2}	523	613	○	Example

(continued)

No.	Average value of Vickers hardness $+3\sigma^{*1}$ (HV)	Top 20% grain size ^{*2} (μm)	Fatigue crack growth rate (mm/cycle)	Yield strength (MPa)	Tensile strength (MPa)	HISC resistance	Class
35	215	25	1.5×10^{-2}	477	570	○	Example
Note 1: Underlined shows outside the scope of the present invention. *1 Position 0.25 mm below the surface of the steel plate. *2 Microstructure at the center of the plate thickness.							

[0065] As presented in Table 2, No. 1 to No. 9 and No. 33 to No. 35 are Examples in which the chemical composition and production conditions satisfy the appropriate ranges of the present invention. As presented in Table 3, in each of No. 1 to No. 9 and No. 33 to No. 35, the average value of the Vickers hardness $+3\sigma$ was 225 HV or less at 0.25 mm below the surface of the steel plate as a high strength steel plate. The top 20% grain size in the microstructure at the center of the plate thickness was less than 30 μm . The fatigue crack growth rate was less than 2.0×10^{-2} (mm/cycle) when the stress intensity factor range ΔK was 45 ($\text{MPa} \cdot \text{m}^{1/2}$). The tensile strength was 535 MPa or more. Furthermore, the HISC resistance was also good.

[0066] In contrast, the chemical composition of the steel plate of each of No. 10 to No. 20 is outside the scope of the present invention. In each of No. 10, No. 12, No. 15, and No. 19, the solid solution strengthening was insufficient, resulting in insufficient strength. In each of No. 11, No. 13, No. 14, No. 16, and No. 20, the Vickers hardness at 0.25 mm below the surface of the steel plate was increased, resulting in poor HISC resistance. In each of No. 17 and No. 18, the grain growth was not sufficiently inhibited by precipitates, resulting in poor fatigue crack growth resistance.

[0067] No. 21 to No. 32 are Comparative Examples in which the chemical compositions are within the scope of the present invention, but the production conditions are outside the scope of the present invention. In No. 21, since the heating temperature of the steel slab (slab) was low, carbides were not sufficiently dissolved, resulting in low strength. In No. 22, since the heating temperature of the steel slab was high, the crystal grains were coarsened, resulting in a deterioration in fatigue crack growth resistance. In No. 23, since the total rolling reduction in the recrystallization temperature range was insufficient, coarse grains remained, resulting in a deterioration in fatigue crack growth resistance. In No. 24, the top 20% grain size in the microstructure at the center of the plate thickness was large due to excessive total rolling reduction in the recrystallization temperature range, resulting in a deterioration in the fatigue crack growth resistance. In No. 25, since the rolling reduction in the final rolling pass in the recrystallization temperature range was insufficient, coarse grains remained, resulting in a deterioration in fatigue crack growth resistance. In No. 26, since the rolling reduction in the final rolling pass in the temperature range of (the lower limit temperature in the recrystallization temperature range - 80°C) or higher and lower than the lower limit temperature in the recrystallization temperature range was insufficient, the top 20% grain size in the microstructure at the center of the plate thickness was large, resulting in a deterioration in fatigue crack growth resistance. In No. 27, since the cooling start temperature was low, ferrite was partially formed, resulting in low strength. In No. 28, since the difference in cooling start time was large for the entirety of the steel plate, the variation in Vickers hardness at 0.25 mm below the surface of the steel plate was large, resulting in a deterioration in HISC resistance. In No. 29, since the average cooling rate from 750°C to 550°C was low, ferrite is partially formed, resulting in low strength. In No. 30, since the average cooling rate from 750°C to 550°C was high, the variation in Vickers hardness at 0.25 mm below the surface of the steel plate was large, resulting in a deterioration in HISC resistance. In No. 31, since the cooling stop temperature was low, the variation in Vickers hardness at 0.25 mm below the surface of the steel plate was large, resulting in a deterioration in HISC resistance. In No. 32, since the cooling stop temperature was high, ferrite was partially formed, resulting in low strength.

Industrial Applicability

[0068] According to the present invention, the high strength steel plate for a hydrogen transport steel pipe can be provided, the high strength steel plate having excellent HISC resistance and fatigue crack growth resistance in a high-pressure hydrogen environment.

Claims

1. A high strength steel plate for a hydrogen transport steel pipe, comprising:
a chemical composition containing, by mass%:

C: 0.030% to 0.060%,

Si: 0.01% to 0.50%,

Mn: 0.80% to 1.80%,

P: 0.015% or less,

S: 0.0015% or less,

Al: 0.010% to 0.080%,

Cr: 0.05% to 0.50%,

Nb: 0.005% to 0.080%,

Ti: 0.005% to 0.020%,

N: 0.0020% to 0.0080%, and

Ca: 0.0005% to 0.0050%, the balance being Fe and incidental impurities; and

a microstructure in which letting a standard deviation of a Vickers hardness at 0.25 mm below a surface of the steel plate be denoted as σ , an average value of the Vickers hardness at 0.25 mm below the surface of the steel plate + 3σ is 225 HV or less, and top 20% grain size at a center of a thickness of the plate is 30 μm or less,

wherein a fatigue crack growth rate is less than 2.0×10^{-2} (mm/cycle) when a stress intensity factor range ΔK is 45 (MPa $\cdot\text{m}^{1/2}$), and a tensile strength is 535 MPa or more.

2. The high strength steel plate for a hydrogen transport steel pipe according to Claim 1, wherein the chemical composition further contains, by mass%, one or more selected from:

Cu: 0.50% or less,

Ni: 0.50% or less,

Mo: 0.50% or less,

V: 0.1% or less,

Zr: 0.02% or less,

Mg: 0.02% or less, and

REM: 0.02% or less.

3. A method for manufacturing a high strength steel plate for a hydrogen transport steel pipe, the method comprising:

heating a steel slab having the chemical composition according to Claim 1 or 2 to a temperature of 1,000°C to 1,250°C;

then subjecting the steel slab to hot rolling at:

a total rolling reduction in a recrystallization temperature range: 35% or more and 55% or less,

a rolling reduction in a final rolling pass in the recrystallization temperature range: 10% or more, and

a rolling reduction in the final rolling pass in a temperature range of (a lower limit temperature in the recrystallization temperature range - 80°C) or higher and lower than the lower limit temperature in the recrystallization temperature range: 15% or more, to form a steel plate; and

thereafter subjecting the steel plate to cooling at:

a temperature of a surface of the steel plate at a start of cooling: an A_{r3} transformation point (°C) or higher,

a difference in cooling start time for an entirety of the steel plate: within 50 seconds,

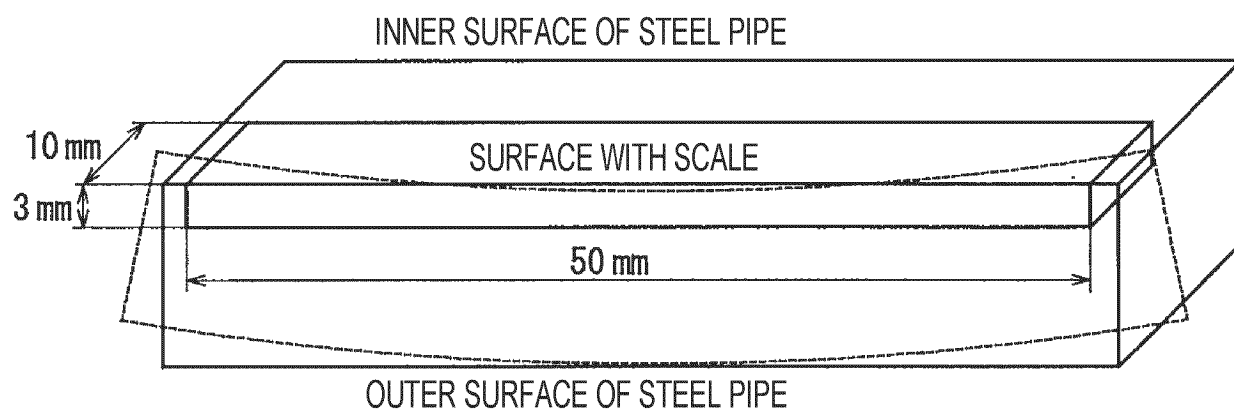
an average cooling rate from 750°C to 550°C in terms of a steel plate temperature at 0.25 mm below the surface of the steel plate: 15 to 50 °C/s,

an average cooling rate from 750°C to 550°C in terms of the steel plate temperature at a center of a thickness of the plate: 15 to 50 °C/s, and

a cooling stop temperature in terms of the steel plate temperature at 0.25 mm below the surface of the steel plate and at the center of the thickness of the plate: 250°C to 550°C.

4. A steel pipe for transporting hydrogen using the high strength steel plate for a hydrogen transport steel pipe according to Claim 1 or 2.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/017743

A. CLASSIFICATION OF SUBJECT MATTER <i>C22C 38/00</i> (2006.01)i; <i>C21D 8/02</i> (2006.01)i; <i>C22C 38/38</i> (2006.01)i; <i>C22C 38/58</i> (2006.01)i FI: C22C38/00 301F; C21D8/02 C; C22C38/38; C22C38/58 According to International Patent Classification (IPC) or to both national classification and IPC												
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C22C38/00-38/60; C21D8/02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2023 Registered utility model specifications of Japan 1996-2023 Published registered utility model applications of Japan 1994-2023 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)												
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>WO 2020/137812 A1 (JFE STEEL CORP.) 02 July 2020 (2020-07-02)</td> <td>1-4</td> </tr> <tr> <td>A</td> <td>WO 2021/020220 A1 (JFE STEEL CORP.) 04 February 2021 (2021-02-04)</td> <td>1-4</td> </tr> <tr> <td>A</td> <td>WO 2020/067209 A1 (JFE STEEL CORP.) 02 April 2020 (2020-04-02)</td> <td>1-4</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	WO 2020/137812 A1 (JFE STEEL CORP.) 02 July 2020 (2020-07-02)	1-4	A	WO 2021/020220 A1 (JFE STEEL CORP.) 04 February 2021 (2021-02-04)	1-4	A	WO 2020/067209 A1 (JFE STEEL CORP.) 02 April 2020 (2020-04-02)	1-4
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Name and mailing address of the ISA/JP Japan Patent Office (ISA/JP) 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915 Japan	Authorized officer Telephone No.											

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/017743

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2020/137812 A1	02 July 2020	US 2022/0064770 A1 EP 3904541 A1 CN 113272452 A KR 10-2021-0094029 A	
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