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(54) STEEL MATERIAL FOR LINE PIPES AND PRODUCTION METHOD THEREFOR, AND STEEL TUBE FOR LINE PIPES AND PRODUCTION METHOD THEREFOR

(57) It is an object of the present invention to provide a steel material for a line pipe with high strength and high hydrogen embrittlement resistance in a high-pressure hydrogen gas environment, which is suitable for a steel structure used in a high-pressure hydrogen gas environment, such as a line pipe for 100% hydrogen gas or a natural gas containing hydrogen at a hydrogen partial pressure of 1 MPa or more (natural gas is a gas containing hydrocarbons, such as methane and ethane, as main components), a method for producing the steel material, a steel pipe for a line pipe, and a method for producing the steel pipe.

A steel material for a line pipe has a specific chemical composition,
wherein retained austenite constitutes 0% to 3% by area fraction, a hydrogen diffusion coefficient is 1.5×10^{-10} m^2/s or more at room temperature, and a hydrogen solubility is 0.05 mass ppm/√P or less.

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Description

Technical Field

[0001] The present invention relates to a steel material for a line pipe, a method for producing the steel material, a steel pipe for a line pipe, and a method for producing the steel pipe, suitable for applications, such as a line pipe for transporting hydrogen gas.

Background Art

[0002] There is a line pipe for transporting natural gas as an existing energy infrastructure. Such a steel material has been required to suppress the occurrence of hydrogen-induced cracking in a sour environment. At the same time, in recent years, hydrogen has attracted a great deal of attention worldwide as a clean energy source for the construction of a decarbonizing society. Thus, for the purpose of transporting a large amount of hydrogen gas, construction of a hydrogen gas transportation network that pressure-feeds natural gas partially mixed with hydrogen or hydrogen gas as an alternative through a natural gas line pipe has been studied. The transport pressure in such a pipeline operation is assumed to be a high pressure of 1 to 40 MPa, and line pipes are placed in a high-pressure hydrogen gas exposure environment. For a steel material used in such an environment, the occurrence of "hydrogen embrittlement" in which hydrogen enters the steel and degrades its characteristics is concerned. Thus, it is necessary to have not only high toughness and sour resistance required for conventional line pipes but also hydrogen embrittlement resistance required in a hydrogen gas environment.

[0003] An austenitic stainless steel, such as SUS 316L, which is more resistant to hydrogen embrittlement than low-alloy steels, has been used for a steel structure used in a high-pressure hydrogen gas environment. However, an austenitic stainless steel, such as SUS 316L, is high in steel material cost and has low strength, and when designed to withstand a high hydrogen pressure, has a large wall thickness and results in an increased price of a structure for hydrogen itself. Thus, there has been a strong demand for a low-alloy steel material that can withstand a high-pressure hydrogen gas environment at a lower cost for a steel structure for hydrogen.

[0004] In response to such a demand, for example, a steel for a high-pressure hydrogen environment described in Patent Literature 1 is a steel used in a high-pressure hydrogen environment, in which Ca/S is less than 1.5 or 11 or more to reduce the diffusible hydrogen concentration ratio and suppress embrittlement due to diffusible hydrogen.

[0005] Patent Literature 2 discloses a technique of finding that a low-alloy high-strength steel adjusted to have a specific chemical composition is used in the tensile strength range of 900 to 950 MPa in the atmosphere to increase the reduction in area and elongation as compared with JIS G 3128 SHY685NS in a 45-MPa hydrogen atmosphere and improve hydrogen embrittlement resistance in high pressure hydrogen environment.

[0006] A Cr-Mo high-strength low-alloy steel described in Patent Literature 3 is a low-alloy high-strength steel with good elongation and reduction-in-area characteristics even in a 45-MPa hydrogen atmosphere and with excellent high-pressure hydrogen environment embrittlement resistance provided by tempering at a relatively high temperature of 560°C to 580°C to adjust the grain size number after thermal refining to 8.4 or more and the tensile strength in a very narrow range of 900 to 950 MPa.

[0007] In a low-alloy steel for a high-pressure hydrogen gas environment proposed in Patent Literature 4, adding V, increasing the Mo content as compared with existing steels, increasing the tempering temperature, and utilizing a V-Mo carbide improve the carbide form at a grain boundary and greatly improve hydrogen environment embrittlement resistance.

[0008] Patent Literature 5 proposes a steel for a high-pressure hydrogen gas storage container with high hydrogen resistance. According to the technique described in Patent Literature 5, stress relief annealing for an extended period after normalizing treatment in the production of a steel plate finely and densely disperses and precipitates an MC carbide (Mo, V) C and improves the hydrogen resistance, such as hydrogen embrittlement resistance, of the steel.

[0009] Patent Literature 6 proposes a steel material with a metallic microstructure composed of 90% or more by area fraction of a bainite-based microstructure in which cementite with an average grain size of 50 nm or less and an average aspect ratio of 3 or less is dispersedly precipitated in the bainite.

[0010] Non Patent Literature 1 describes the fatigue strength of low-alloy steel.

Citation List

Patent Literature

[0011]

PTL 1: Japanese Unexamined Patent Application Publication No. 2005-2386

PTL 2: Japanese Unexamined Patent Application Publication No. 2009-46737

PTL 3: Japanese Unexamined Patent Application Publication No. 2009-275249

PTL 4: Japanese Unexamined Patent Application Publication No. 2009-74122

PTL 5: Japanese Unexamined Patent Application Publication No. 2010-37655

PTL 6: Japanese Unexamined Patent Application Publication No. 2012-107332

Non Patent Literature

[0012]

NPL 1: Matsunaga et al., Int J Hydrogen Energy, Vol. 40 (2015), pp. 5739-5748
NPL 2: Omura, Hydrogen Charging Methods for Simulating Hydrogen Entry from Actual Environments, The Japan Institute of Metals, Vol. 84, No. 9, (2020) pp. 285-294
NPL 3: (written by) The Japan Society for Heat Treatment, Introduction: Microstructure and Properties of Metallic Materials - Heat Treatment and Microstructure Controlling for Materials, 2004
NPL 4: Michiya Okada et al., Hydrogen Permeation in Iron by Electrochemical Measurement, Journal of the Japan Institute of Metals and Materials, Vol. 50, No. 2 (1986) pp. 201-207

Summary of Invention

Technical Problem

[0013] With respect to the pressure in a line pipe, due to fluctuations during operation or periodical shutdown, stress is repeatedly applied to the structure. Thus, when designing a steel structure, such as a line pipe, it is essential to consider fatigue fracture. However, as described in Non Patent Literature 1, it is known that the fatigue life of a material decreases in a high-pressure hydrogen environment. This means that the service life of a line pipe material decreases when the line pipe material is designed on the basis of a conventional natural gas line pipe. The related art described above can suppress the occurrence of hydrogen-induced cracking in a sour environment but cannot sufficiently increase the fatigue life in hydrogen gas, that is, there is a problem in that it is difficult to achieve both the suppression of the occurrence of hydrogen-induced cracking in a sour environment and high fatigue strength in hydrogen gas.

[0014] In view of the problems of the related art, it is an object of the present invention to provide a steel material for a line pipe with high strength and high hydrogen embrittlement resistance in a high-pressure hydrogen gas environment, which is suitable for a steel structure used in a high-pressure hydrogen gas environment, such as a line pipe for 100% hydrogen gas or a natural gas containing hydrogen at a hydrogen partial pressure of 1 MPa or more (natural gas is a gas containing hydrocarbons, such as methane and ethane, as main components), a method for producing the steel material, a steel pipe for a line pipe, and a method for producing the steel pipe. The hydrogen environment is assumed to be a high-pressure hydrogen gas environment with a pressure of 1 MPa or more or a natural gas (the main components are hydrocarbons, such as methane and ethane) environment containing hydrogen at a hydrogen partial pressure of 1 MPa or more.

[0015] The phrase "high hydrogen embrittlement resistance in a high-pressure hydrogen gas environment", as used herein, means that the fatigue crack growth rate da/dN mm/cycle is 2.0×10^{-3} mm/cycle or less at $\Delta K = 25$ MPa, as determined by a fatigue test in accordance with ASTM E647, Fatigue Testing, at a frequency of 1 Hz, a repetitive waveform of a sine wave, a control method of load control, a load condition of uniaxial tension, and a stress ratio of $R = 0.1$, in both environments of hydrogen gas at room temperature (20°C ± 10°C) and at a pressure of 1 MPa or more and a natural gas (the main components are hydrocarbons, such as methane and ethane) mixed atmosphere containing hydrogen at a hydrogen partial pressure of 1 MPa or more.

[0016] When the fatigue crack growth rate da/dN mm/cycle is 2.0×10^{-3} mm/cycle or less in the above environment, it is possible to design a long-life steel structure for hydrogen, such as a line pipe, within a thickness range that is available by a process of producing a steel pipe, such as a seamless steel pipe or UOE.

[0017] The term "steel material", as used herein, includes a steel sheet, a steel plate, a seamless steel pipe, an electric-resistance-welded steel pipe, a shaped steel, a steel bar, and the like.

Solution to Problem

[0018] The present inventors have conducted extensive studies on conditions to be satisfied by a steel material for obtaining a steel material for a line pipe and a steel pipe for a line pipe with high hydrogen embrittlement resistance. As a result, it was found that the fatigue crack growth rate is greatly affected by hydrogen accumulation at a crack tip and stress (stress intensity factor) at the crack tip, and the fatigue crack growth rate in hydrogen is greatly reduced by reducing the hydrogen solubility in steel to 0.05 ppm/√P or less. Furthermore, the fatigue crack growth rate in hydrogen increases with hydrogen accumulation at the crack tip. As the hydrogen diffusion coefficient decreases, the hydrogen accumulation at the crack tip increases, and the fatigue crack growth rate increases. As a result of detailed analysis of the relationship between the fatigue crack growth rate and the hydrogen diffusion coefficient, the present inventors have found that the fatigue crack growth rate in hydrogen greatly increases when the roomtemperature hydrogen diffusion coefficient is lower than 1.5 x 10^{-10} m^2/s. Based on these findings, a novel high-strength steel material for a line pipe and a novel steel pipe for a line pipe have been invented. A steel material and a steel pipe according to the present invention have high strength, and the term "high strength", as used herein, refers to a tensile strength of 520 MPa or more.

[0019] The gist of the present invention is as follows:

[1] A steel material for a line pipe, the steel material having a chemical composition containing:

on a mass percent basis,
C: 0.02% to 0.15%,
Si: 0.01% to 2.0%,
Mn: 0.5% to 1.8%,
P: 0.0001% to 0.015%,
S: 0.0002% to 0.0015%,
Al: 0.005% to 0.15%,
O: 0.01% or less,
N: 0.010% or less, and
H: 0.02 ppm or less, and
optionally at least one selected from
Nb: 0% to 0.10%,
Ca: 0% to 0.005%,
Ni: 0% to 2.0%,
Ti: 0% to 0.1%,
Cu: 0% to 1.0%,
Cr: 0% to 1.0%,
Mo: 0% to 0.60%,
W: 0% to 1.0%,
V: 0% to 0.10%,
Zr: 0% to 0.050%,
REM: 0% to 0.01%,
Mg: 0% to 0.01%,
B: 0% to 0.0020%,
Hf: 0% to 0.2%,
Ta: 0% to 0.2%,
Re: 0% to 0.005%,
Sn: 0% to 0.3%, and
Sb: 0% to 0.3%,
the remainder being Fe and an incidental impurity element,
wherein retained austenite constitutes 0% to 3% by area fraction, a hydrogen diffusion coefficient is 1.5 x 10^{-10} m^2/s or more at room temperature, and a hydrogen solubility is 0.05 mass ppm/√P or less.

[2] The steel material for a line pipe according to [1], wherein the chemical composition is, on a mass percent basis,

Nb: 0.001% to 0.10%,
Ca: 0.0001% to 0.005%,
Ni: 0.01% to 2.0%,
Ti: 0.005% to 0.1%,
Cu: 0.01% to 1.0%,

Cr: 0.01% to 1.0%,
Mo: 0.01% to 0.60%,
W: 0.01% to 1.0%,
V: 0.01% to 0.10%,
Zr: 0.0001% to 0.050%,
REM: 0.0001% to 0.01%,
Mg: 0.0001% to 0.01%,
B: 0.0001% to 0.0020%,
Hf: 0.0001% to 0.2%,
Ta: 0.0001% to 0.2%,
Re: 0.0001% to 0.005%,
Sn: 0.0001% to 0.3%, and
Sb: 0.0001% to 0.3%.

[3] The steel material for a line pipe according to [1] or [2], comprising bainite or martensite at a quarter thickness position, wherein the bainite constitutes 90% or more by area fraction, or the martensite constitutes 90% or more by area fraction.
[4] A method for producing a steel material for a line pipe, the method including:

a heating step of heating a steel raw material with the chemical composition according to [1] or [2] at 1000°C to 1250°C;
a hot rolling step of rolling the steel raw material heated in the heating step at a finish rolling temperature of an Ar_3 transformation point or higher;
a controlled cooling step of cooling a hot-rolled steel sheet (including steel plate) produced in the hot rolling step under conditions in which a cooling start temperature is the Ar_3 transformation point or higher in terms of a steel sheet surface temperature, a cooling start time difference between a front end and a rear end of the hot-rolled steel sheet is 50 seconds or less, and in terms of a temperature at 0.25 mm below a surface of the steel sheet and at a center of a sheet thickness, an average cooling rate from 750°C to 550°C ranges from 15°C/s to 50°C/s and a cooling stop temperature ranges from 250°C to 650°C; and
any one of a stabilization treatment step of subjecting the steel sheet produced in the controlled cooling step to stabilization treatment and a dehydrogenation treatment (for removing hydrogen from steel materials) step of subjecting the steel sheet produced in the controlled cooling step to dehydrogenation treatment.

[5] A steel pipe for a line pipe, the steel pipe having a chemical composition containing:

on a mass percent basis,
C: 0.02% to 0.15%,
Si: 0.01% to 2.0%,
Mn: 0.5% to 1.8%,
P: 0.0001% to 0.015%,
S: 0.0002% to 0.0015%,
Al: 0.005% to 0.15%,
O: 0.01% or less,
N: 0.010% or less, and
H: 0.02 ppm or less, and
optionally at least one selected from Nb: 0% to 0.10%,
Ca: 0% to 0.005%,
Ni: 0% to 2.0%,
Ti: 0% to 0.1%,
Cu: 0% to 1.0%,
Cr: 0% to 1.0%,
Mo: 0% to 0.60%,
W: 0% to 1.0%,
V: 0% to 0.10%,
Zr: 0% to 0.050%,
REM: 0% to 0.01%,
Mg: 0% to 0.01%,
B: 0% to 0.0020%,

Hf: 0% to 0.2%,
Ta: 0% to 0.2%,
Re: 0% to 0.005%,
Sn: 0% to 0.3%, and
Sb: 0% to 0.3%,
the remainder being Fe and an incidental impurity element,
wherein retained austenite constitutes 0% to 3% by area fraction, a hydrogen diffusion coefficient is 1.5 x 10^{-10} m^2/s or more at room temperature, and a hydrogen solubility is 0.05 mass ppm/√P or less.

[6] The steel pipe for a line pipe according to [5], wherein the chemical composition is, on a mass percent basis,

Nb: 0.001% to 0.10%,
Ca: 0.0001% to 0.005%,
Ni: 0.01% to 2.0%,
Ti: 0.005% to 0.1%,
Cu: 0.01% to 1.0%,
Cr: 0.01% to 1.0%,
Mo: 0.01% to 0.60%,
W: 0.01% to 1.0%,
V: 0.01% to 0.10%,
Zr: 0.0001% to 0.050%,
REM: 0.0001% to 0.01%,
Mg: 0.0001% to 0.01%,
B: 0.0001% to 0.0020%,
Hf: 0.0001% to 0.2%,
Ta: 0.0001% to 0.2%,
Re: 0.0001% to 0.005%,
Sn: 0.0001% to 0.3%, and
Sb: 0.0001% to 0.3%.

[7] The steel pipe for a line pipe according to [5] or [6], wherein the steel pipe has bainite or martensite at a quarter thickness position from an inner surface of the steel pipe, and the bainite constitutes 90% or more by area fraction, or the martensite constitutes 90% or more by area fraction.
[8] A method for producing a steel pipe for a line pipe, the method including:

a heating step of heating a steel raw material with the chemical composition according to [5] or [6] at 1000°C to 1250°C;
a hot rolling step of rolling the steel raw material heated in the heating step at a finish rolling temperature of an Ar_3 transformation point or higher;
a controlled cooling step of cooling a hot-rolled steel sheet produced in the hot rolling step under conditions in which a cooling start temperature is the Ar_3 transformation point or higher in terms of a steel sheet surface temperature, a cooling start time difference between a front end and a rear end of the hot-rolled steel sheet is 50 seconds or less, and in terms of a temperature at 0.25 mm below a surface of the steel sheet and at a center of a sheet thickness, an average cooling rate from 750°C to 550°C ranges from 15°C/s to 50°C/s and a cooling stop temperature ranges from 250°C to 650°C;
any one of a pipe production step of bending the hot-rolled steel sheet and butt-welding both end portions thereof after the controlled cooling step, and a pipe production step of forming the hot-rolled steel sheet into a cylindrical shape by cold roll forming and subjecting both circumferential end portions of the cylindrical shape to butt electric resistance welding after the controlled cooling step; and
any one of a stabilization treatment step of subjecting the steel pipe produced in the pipe production step to stabilization treatment and a dehydrogenation treatment step of subjecting the steel pipe produced in the pipe production step to dehydrogenation treatment.

Advantageous Effects of Invention

[0020] The present invention can easily and simply produce a steel material with considerably improved hydrogen embrittlement resistance in a high-pressure hydrogen gas environment and exhibits industrially significant effects. The present invention can considerably improve the hydrogen embrittlement resistance of a steel structure, such as a high-pressure hydrogen gas line pipe, improve the fatigue resistance, and greatly contributes to the extension of the life of the steel structure.

Description of Embodiments

[0021] Next, a method for implementing the present invention is more specifically described. The following description shows preferred embodiments of the present invention, and the present invention is not limited by the following description. A steel material is more specifically described as a first embodiment, a UOE steel pipe as an example of a steel pipe according to the present invention is more specifically described as a second embodiment, and an electric-resistance-welded steel pipe as an example of a steel pipe according to the present invention is more specifically described as a third embodiment.

First Embodiment

[Chemical Composition]

[0022] The reasons for limiting the chemical composition of a steel material according to the present invention are described below. Unless otherwise specified, "%" in the following description refers to "% by mass".

C: 0.02% to 0.15%

[0023] C effectively contributes to the improvement of strength, but the strength cannot be sufficient at a C content of less than 0.02%. Thus, the C content is 0.02% or more. The C content is preferably 0.03% or more. On the other hand, more than 0.15% results in low weldability. Thus, the C content is limited to 0.15% or less. The C content is preferably 0.13% or less. More than 0.08% may result in a decrease in SSCC resistance and HIC resistance due to an increase in the hardness of a surface layer portion or a center segregation zone at the time of accelerated cooling. Furthermore, toughness may also decrease. Thus, the C content is more preferably 0.08% or less. The C content is still more preferably 0.05% or less.

Si: 0.01% to 2.0%

[0024] Si is added for deoxidization, but the deoxidization effect is not sufficient at a Si content of less than 0.01%. Thus, the Si content is 0.01% or more. The Si content is preferably 0.08% or more, more preferably 0.10% or more. On the other hand, the effect becomes saturated at a Si content of more than 2.0%, and the Si content is therefore 2.0% or less. The Si content is preferably 1.8% or less, more preferably 1.0% or less. Furthermore, more than 0.50% results in a decrease in toughness and weldability and an increase in the hydrogen solubility, so that the Si content is still more preferably 0.50% or less.

Mn: 0.5% to 1.8%

[0025] Mn effectively contributes to the improvement of strength and toughness, but the effect of addition is insufficient at a Mn content of less than 0.5%. Thus, the Mn content is 0.5% or more. The Mn content is preferably 0.6% or more, more preferably 0.7% or more, still more preferably 0.8% or more. On the other hand, more than 1.8% results in a decrease in the SSCC (sulfide stress corrosion cracking) resistance, the HIC (hydrogen-induced cracking) resistance, and hydrogen embrittlement resistance due to an increase in the hardness of a surface layer portion or a center segregation zone at the time of controlled cooling. Furthermore, weldability deteriorates, and the hydrogen solubility increases. Thus, the Mn content is limited to 1.8% or less. The Mn content is preferably 1.5% or less, more preferably 1.4% or less, still more preferably 1.3% or less.

P: 0.0001% to 0.015%

[0026] P is an incidental impurity element, reduces weldability, and also reduces the HIC resistance due to an increase in the hardness of a center segregation zone and reduces the hydrogen embrittlement resistance due to an increase in hydrogen solubility. This tendency becomes remarkable at more than 0.015%, so that the upper limit of the P content is 0.015%. The P content is preferably 0.010% or less, more preferably 0.008% or less. Although a lower P content is better, the P content is 0.0001% or more from the perspective of refining costs.

S: 0.0002% to 0.0015%

[0027] S is an incidental impurity element, forms a MnS inclusion in steel and reduces the HIC resistance, and increases the hydrogen solubility and reduces the hydrogen embrittlement resistance, so that a lower S content is preferred, but 0.0015% or less is allowable. Thus, the S content is 0.0015% or less. The S content is preferably 0.0010% or less, more preferably 0.0008% or less. Although a lower S content is preferred, the S content is 0.0002% or more from the perspective of refining costs.

Al: 0.005% to 0.15%

[0028] Al is added as a deoxidizing agent, and the effect of addition is insufficient at less than 0.005%, so that the Al content is 0.005% or more. The Al content is preferably 0.010% or more, more preferably 0.030% or more. On the other hand, more than 0.15% results in steel with lower cleanliness and toughness, so that the Al content is limited to 0.15% or less. The Al content is preferably 0.10% or less, more preferably 0.08% or less, still more preferably 0.05% or less.

O: 0.01% or less

[0029] O can form an oxide inclusion, and a lower O content is more preferred, but an O content of 0.01% or less causes no problem. Thus, the O content is 0.01% or less. The O content is preferably 0.005% or less. The O content is more preferably less than 0.003%. The lower limit is not limited, but preferably 0.001% or more because reducing the oxygen content to 0% increases the cost.

N: 0.010% or less

[0030] N has a small influence on the fatigue property of a steel material, and the advantages of the present invention are not impaired at a N content of 0.010% or less from the perspective of toughness. Thus, the N content is 0.010% or less. The N content is preferably 0.008% or less, more preferably 0.006% or less. The N content is still more preferably 0.004% or less. On the other hand, while a lower N content is desirable from the perspective of improving the toughness, excessive reduction increases the steelmaking cost, so that the N content is preferably 0.001% or more.

H: 0.02 ppm or less

[0031] H may be introduced into a steel material in various steps during production, and a large amount of H introduced may increase the risk of cracking after solidification and accelerate fatigue crack growth. Since these effects are not problematic at a H content of 0.02 ppm or less, the H content is 0.02 ppm or less. The H content is preferably 0.01 ppm or less. The H content is more preferably 0.005 ppm or less. The H content is still more preferably 0.003 ppm or less. Although the lower limit is not particularly limited, less than 0.001 ppm causes an increase in cost, so that the H content is preferably 0.001 ppm or more. The amount of hydrogen is the amount of residual hydrogen after forming of a steel material, a steel pipe, UOE, or the like.

[0032] To further improve the strength and toughness of a steel sheet, the chemical composition in the present disclosure may optionally contain at least one selected from Nb, Ca, Ni, Ti, Cu, Cr, Mo, W, V, Zr, REM, Mg, B, Hf, Ta, Re, Sn, and Sb in the following ranges.

Nb: 0% to 0.10%

[0033] Nb is an element that contributes to an increase in the strength of a steel material, but a Nb content of more than 0.10% results in saturation of the effect and causes an increase in cost, so that when Nb is contained the Nb content is 0.10% or less. The Nb content is preferably 0.08% or less. The Nb content is more preferably 0.06% or less. To reduce the cost, the Nb content is still more preferably 0.05% or less. When Nb is contained, the Nb content may be 0% or more and is preferably 0.001% or more to achieve the above effect. The Nb content is more preferably 0.01% or more.

Ca: 0% to 0.005%

[0034] Although Ca is an element effective in improving the HIC resistance by the shape control of a sulfide inclusion, more than 0.005% not only results in saturation of the effect but also a decrease in the HIC resistance due to a decrease in the cleanliness of steel, so that when Ca is contained the Ca content is 0.005% or less. The Ca content is preferably 0.003% or less. The Ca content is more preferably 0.002% or less. When Ca is contained, the Ca content may be 0% or more, but the effect of containing Ca is not sufficient at a Ca content of less than 0.0001%, so that the Ca content is preferably

0.0001% or more. The Ca content is more preferably 0.001% or more.

Ni: 0% to 2.0%

[0035] Ni is an element effective in improving the toughness and increasing the strength, but at a Ni content of more than 2.0% a fine crack called a fissure is likely to be formed in an environment with a low hydrogen sulfide partial pressure of less than 1 bar. Thus, when Ni is contained, the Ni content is 2.0% or less. The Ni content is preferably 1.5% or less, more preferably 1.2% or less, still more preferably 1.0% or less. The Ni content is preferably 0.1% or less. The Ni content is most preferably 0.02% or less. When Ni is contained, the Ni content may be 0% or more and is preferably 0.01% or more to achieve the above effect.

Ti: 0% to 0.1%

[0036] Ti contributes to an increase in the strength of a steel material, but a Ti content of more than 0.1% results in saturation of the effect and causes an increase in cost, so that when Ti is contained the Ti content is 0.1% or less. To reduce the cost, the Ti content is preferably 0.05% or less. When Ti is contained, the Ti content may be 0% or more and is preferably 0.005% or more to achieve the above effect. The Ti content is more preferably 0.008% or more.

Cu: 0% to 1.0%

[0037] Cu is an element effective in improving the toughness and the strength, but an excessively high Cu content results in a decrease in weldability and a decrease in hydrogen embrittlement resistance due to an increase in hydrogen solubility, so that when Cu is contained the Cu content is 1.0% or less. The Cu content is preferably 0.5% or less. The Cu content is more preferably 0.3% or less, still more preferably 0.2% or less. When Cu is contained, the Cu content may be 0% or more and is preferably 0.01% or more to achieve the above effect.

Cr: 0% to 1.0%

[0038] Like Mn, Cr is an element effective in obtaining sufficient strength even at a low C content, but an excessively high Cr content results in excessive hardenability, a decrease in the SSCC resistance, and a decrease in the hydrogen embrittlement resistance due to an increase in the hydrogen solubility. Furthermore, weldability also deteriorates. Thus, when Cr is contained, the Cr content is 1.0% or less. The Cr content is preferably 0.8% or less, more preferably 0.5% or less. The Cr content is still more preferably 0.1% or less. When Cr is contained, the Cr content may be 0% or more and is preferably 0.01% or more to achieve the above effect. The Cr content is more preferably 0.05% or more.

Mo: 0% to 0.60%

[0039] Mo is an element effective in improving the toughness and the strength and effective in improving the SSCC resistance regardless of the hydrogen sulfide partial pressure, but an excessively high Mo content results in excessive hardenability, a decrease in the SSCC resistance, and a decrease in the hydrogen embrittlement resistance due to an increase in the hydrogen solubility. Furthermore, weldability also deteriorates. Thus, the Mo content is 0.60% or less. The Mo content is preferably 0.50% or less, more preferably 0.40% or less. The Mo content may be 0% or more and is preferably 0.01% or more to achieve the above effect. The Mo content is more preferably 0.10% or more.

W: 0% to 1.0%

[0040] W contributes to an increase in the strength of a steel material, but a W content of more than 1.0% results in saturation of the effect and causes an increase in cost, so that when W is contained the W content is 1.0% or less. The W content is preferably 0.8% or less. To reduce the cost, 0.5% or less is preferred. The W content may be 0% or more, and when W is contained the W content is preferably 0.01% or more to achieve the above effect.

V: 0% to 0.10%

[0041] V is an element that can be optionally contained to increase the strength and toughness of a steel material. More than 0.10% results in a weld with lower toughness and a decrease in hydrogen embrittlement resistance due to an increase in the hydrogen solubility, so that when contained the content is 0.10% or less. The V content is preferably 0.08% or less. The V content is more preferably 0.06% or less, still more preferably 0.03% or less. The V content may be 0% or more, and the effect of containing V is not sufficient at a V content of less than 0.01%, so that when V is contained 0.01% or more is preferred.

Zr: 0% to 0.050%, REM: 0% to 0.01%, Mg: 0% to 0.01%

[0042] Zr, REM, and Mg are elements that can be optionally contained to increase the toughness through grain refinement or to increase cracking resistance through the control of inclusion properties. The effects of these elements are saturated when the Zr content exceeds 0.050% and the REM or Mg content exceeds 0.01%, so that when these elements are contained the Zr content is 0.050% or less, and the REM or Mg content is 0.01% or less. Thus, when Zr is contained, the Zr content is 0.050% or less. The Zr content is preferably 0.0040% or less. The Zr content is more preferably 0.0030% or less. When REM is contained, the REM content is 0.01% or less. The REM content is preferably 0.0040% or less. The REM content is more preferably 0.0030% or less. When Mg is contained, the Mg content is 0.01% or less. The Mg content is preferably 0.0040% or less. The Mg content is more preferably 0.0030% or less. Each element content may be 0% or more, and the effect of containing these elements is not sufficient at a content of less than 0.0001%, so that each content is preferably 0.0001% or more. Thus, the Zr content is preferably 0.0001% or more. The Zr content is more preferably 0.0005% or more. The REM content is preferably 0.0001% or more. The REM content is more preferably 0.0005% or more. The Mg content is preferably 0.0001% or more. The Mg content is more preferably 0.0005% or more.

B: 0% to 0.0020%

[0043] B is an element that improves hardenability, and contributes to an increase in the strength of a steel pipe, suppresses coarsening of prior-austenite grains, and improves various characteristics of the material. On the other hand, a B content of more than 0.0020% results in saturation of the effect and causes an increase in cost, so that when B is contained the B content is 0.0020% or less. The B content is preferably 0.0015% or less. The B content is more preferably 0.0012% or less. To reduce the cost, the B content is more preferably 0.0010% or less. The B content may be 0% or more, and when B is contained, the B content is preferably 0.0001% or more to achieve the above effect. The B content is more preferably 0.0005% or more.

Hf: 0% to 0.2%, Ta: 0% to 0.2%

[0044] These elements contribute to an increase in the strength of a steel material. A content of more than 0.2% results in saturation of the effect and causes an increase in cost, so that when these elements are contained each content is 0.2% or less. Thus, when Hf is contained, the Hf content is 0.2% or less. The Hf content is preferably 0.1% or less. The Hf content is more preferably 0.05% or less. When Ta is contained, the Ta content is 0.2% or less. The Ta content is preferably 0.1% or less. The Ta content is more preferably 0.05% or less. To reduce the cost, the content is preferably 0.01% or less. Each element content may be 0% or more, and when these elements are contained the Hf content is preferably 0.0001% or more to achieve the above effect. The Hf content is more preferably 0.001% or more. The Ta content is preferably 0.0001% or more. The Ta content is more preferably 0.001% or more.

Re: 0% to 0.005%

[0045] Re contributes to an increase in the strength of a steel material, but a Re content of more than 0.005% results in saturation of the effect and causes an increase in cost, so that when Re is contained the Re content is 0.005% or less. The Re content is preferably 0.003% or less. The Re content is more preferably 0.002% or less. The Re content may be 0% or more, and when Re is contained the Re content is 0.0001% or more to achieve the above effect. The Re content is preferably 0.001% or more.

Sn: 0% to 0.3%, Sb: 0% to 0.3%

[0046] These elements contribute to an increase in the strength of a steel material and an improvement in the hardenability, but a content of more than 0.3% results in saturation of the effect and causes an increase in cost, so that when contained each content is 0.3% or less. Thus, the Sn content is 0.3% or less. The Sn content is preferably 0.2% or less. The Sn content is more preferably 0.1% or less. To reduce the cost, the Sn content is still more preferably 0.01% or less. The Sb content is 0.3% or less. The Sb content is preferably 0.2% or less. The Sb content is more preferably 0.1% or less. To reduce the cost, the Sb content is still more preferably 0.01% or less. The Sn or Sb content may be 0% or more, and when Sn is contained the Sn content is preferably 0.0001% or more to achieve the above effect. The Sn content is more preferably 0.001% or more. The Sb content is preferably 0.0001% or more. The Sb content is more preferably 0.0010% or more.

[0047] In the chemical composition of a steel sheet and a steel pipe, the remainder other than above-mentioned components (elements) is composed of Fe and an incidental impurity element.

[0048] The metallic microstructure of a steel material according to the present invention is described below.

Metallic Microstructure

[0049] Retained austenite: 0% to 3% by area fraction

[0050] Retained austenite remaining in a steel material may increase the amount of hydrogen in the steel and increase hydrogen embrittlement sensitivity. Furthermore, when retained austenite is transformed into martensite by stress loading during use, hydrogen cracking is likely to occur because martensite is very hard, and cracking may occur from the martensite portion. In the present invention, retained austenite, which constitutes 3% or less by area fraction, can reduce the fatigue crack growth rate and improve the hydrogen embrittlement resistance. Thus, retained austenite constitutes 3% or less. The retained austenite preferably constitutes 2% or less. The retained austenite more preferably constitutes 1% or less. The retained austenite may constitute 0%.

[0051] Bainite or martensite is present at a quarter thickness position of sheet thickness of a steel material (in the case of a steel pipe, a quarter thickness position of wall thickness from the inner surface of the steel pipe), and the bainite constitutes 90% or more by area fraction, or the martensite constitutes 90% or more by area fraction (preferably)

[0052] To increase the tensile strength to 520 MPa or more, the steel microstructure preferably contains a bainite or martensite microstructure. On the other hand, when a steel material has a soft phase and a hard phase, fatigue damage is preferentially accumulated in the soft phase and is likely to cause cracking, thus reducing fatigue limit stress. A hydrogen environment promotes local deformation, further accelerates fatigue damage to the soft phase, and reduces the hydrogen embrittlement resistance in hydrogen. This makes it difficult to achieve a fatigue crack growth rate da/dN mm/cycle in hydrogen of 2.0×10^{-3} mm/cycle or less at $\Delta K = 25$ MPa. To address this, it is necessary to reduce the relative proportion of the soft phase. Thus, the metallic microstructure is preferably a single microstructure of bainite or martensite and preferably contains bainite or martensite, and the microstructure of bainite or martensite preferably constitutes 90% or more by area fraction. The microstructure more preferably constitutes 92% or more by area fraction, still more preferably 95% or more by area fraction. The upper limit is preferably, but not limited to, 98% or less. The upper limit is not particularly limited, and bainite may constitute 100% by area fraction. Furthermore, because a fatigue crack is generated from the inner surface of a steel pipe, the uniformity of the microstructure of the inner surface of the steel pipe is important. Thus, in a steel pipe, the metallic microstructure at a quarter thickness position from the inner surface of the steel pipe is defined. The bainite microstructure includes bainitic ferrite or granular bainite that transforms during or after controlled cooling contributing to transformation strengthening, and also includes tempered bainite. A different microstructure, such as ferrite, martensite, pearlite, a martensite-austenite constituent (MA), or retained austenite, in the bainite microstructure reduces the strength and/or toughness. Thus, a lower volume fraction of the microstructure other than the bainite phase is better. The martensite microstructure includes tempered martensite.

Hydrogen diffusion coefficient at room temperature: 1.5×10^{-10} m^2/s or more

[0053] The fatigue crack growth rate in hydrogen increases with hydrogen accumulation at a crack tip. As the hydrogen diffusion coefficient decreases, the hydrogen accumulation at the crack tip increases, and the fatigue crack growth rate increases. When the hydrogen diffusion coefficient is less than 1.5×10^{-10} m^2/s, the fatigue crack growth rate in hydrogen increases greatly, so that the hydrogen diffusion coefficient is 1.5×10^{-10} m^2/s or more. The hydrogen diffusion coefficient is preferably 2.0×10^{-10} m^2/s or more, more preferably 3.0×10^{-10} m^2/s or more. The hydrogen diffusion coefficient is still more preferably 5.0×10^{-10} m^2/s or more. The hydrogen diffusion coefficient is most preferably 6.0×10^{-10} m^2/s or more. The upper limit is preferably, but not limited to, 5.0×10^{-9} m^2/s or less in consideration of the material strength because a decrease in the hydrogen diffusion coefficient is accompanied by strength reduction. The retained austenite, having a low hydrogen diffusion coefficient at room temperature, needs to have the fraction described above to achieve the hydrogen diffusion coefficient at room temperature described above. Hydrogen enters a steel material from the surface of the steel material (in the case of a steel pipe, the inner surface of the steel pipe). Thus, the hydrogen diffusion coefficient is critical for the thickness through which a fatigue crack propagates and leads to rapid fracture. The thickness leading to rapid fracture can be determined by the fracture toughness of the material and the stress generated in the steel pipe. In practice, however, most of the fatigue crack growth life of a steel material (in the case of a steel pipe, the steel pipe) is taken for growth through 1/4t of the thickness, and the hydrogen diffusion coefficient may therefore be measured at 1/4t from the inner surface of the steel pipe. Furthermore, due to its large temperature dependency, the hydrogen diffusion coefficient is defined at room temperature (20°C ± 10°C) in the present invention.

Hydrogen solubility: 0.05 mass ppm/$\sqrt{P}$ or less

[0054] In the present invention, the hydrogen solubility is the most important factor. The fatigue crack growth rate is greatly affected by hydrogen accumulation at a crack tip and stress (stress intensity factor) at the crack tip. In other words, it is important to reduce the hydrogen accumulation at the crack tip to achieve a desired fatigue crack growth rate. A lower hydrogen solubility results in a greater decrease in the fatigue crack growth rate in hydrogen, and to achieve a desired fatigue crack growth rate, the hydrogen solubility in a steel material is 0.05 mass ppm/√P or less. 0.03 mass ppm/√P or less is preferred, and 0.02 mass ppm/√P or less is more preferred. Stabilization treatment or dehydrogenation treatment (for removing hydrogen from steel materials) is performed to reduce the hydrogen solubility. On the other hand, heat treatment to reduce the hydrogen solubility to less than 0.005 mass ppm/√P reduces the strength of the material and significantly increases the production cost, and 0.005 mass ppm/√P or more is therefore preferred.

[0055] The hydrogen solubility s is the slope [mass ppm/√P] between the amount of entering hydrogen H [mass ppm] in an environment of a hydrogen pressure P [MPa] and the square root of the hydrogen pressure P [MPa]. P in a gas mixture environment can be read as P' corresponding to the hydrogen partial pressure. More specifically, in a gas environment containing 20% of hydrogen in 25 MPa, the hydrogen partial pressure P' is 25 MPa x 0.2 = 5 MPa.

[0056] One example of several methods for calculating the hydrogen solubility is described below. For example, a test specimen is exposed to an arbitrary pressure environment among high-pressure hydrogen gas environments of 0 to 40 MPa and is held for a predetermined time. The amount of hydrogen in steel is measured with a hydrogen analyzer to determine the relationship between H and √P and calculate s from the slope thereof. Alternatively, for example, it can also be calculated by a cathodic hydrogen charge test simulating a high-pressure gas environment as in Non Patent Literature 2.

[0057] The tensile strength is preferably 520 MPa or more, more preferably 580 MPa or more. Although the upper limit is not particularly limited, the tensile strength is preferably 950 MPa or less, more preferably 800 MPa or less.

[0058] The sheet thickness is preferably, but not limited to, 5 mm or more. The sheet thickness is preferably 30 mm or less.

[0059] Next, a method for producing a steel sheet according to the present invention is described below. A steel material according to the present invention can be produced by sequentially performing a heating step of a steel raw material (slab), a hot rolling step, a controlled cooling step, and any one of a stabilization treatment step and a dehydrogenation treatment step.

[0060] Unless otherwise specified, the temperature in the following description is the temperature at the center of the thickness of a steel raw material or a steel pipe. The average cooling rate means the temperature at a quarter thickness position from the inner surface of a steel pipe. The temperature at the center of the sheet thickness and the temperature at the quarter thickness position from the inner surface of a steel pipe are estimated from the surface temperature of the steel pipe measured with a radiation thermometer using heat-transfer calculation or the like in consideration of the heat transfer coefficient of the steel material.

Heating temperature of steel raw material: 1000°C to 1250°C

[0061] When the heating temperature of a steel raw material, such as a billet or a slab, is less than 1000°C, the diffusion of a microsegregated impurity element, such as C, P, or S, is insufficient, and a homogeneous material cannot be produced. Thus, the heating temperature of the steel raw material is 1000°C or more. The heating temperature of the steel raw material is preferably 1180°C or more, more preferably 1200°C or more. On the other hand, more than 1250°C results in excessively coarse crystal grains and lower toughness. Thus, the heating temperature of the steel raw material is 1250°C or less. The heating temperature of the steel raw material is preferably 1230°C or less, more preferably 1210°C or less.

Hot-rolling finish temperature: Ar_3 transformation point or higher

[0062] After being reheated, the steel raw material is hot-rolled to a desired wall thickness or sheet thickness, and the finish temperature of the hot rolling is equal to or higher than the Ar_3 transformation point, which is the ferrite formation temperature. This is because, in a process including cooling immediately after hot rolling, a temperature lower than the Ar_3 transformation point results in strength reduction due to the formation of a soft ferrite phase. The finish temperature of the hot rolling is preferably 770°C or more, and when the Ar_3 transformation point is higher than 770°C the finish rolling delivery temperature is preferably the Ar_3 transformation point + 30°C or more, more preferably the Ar_3 transformation point + 50°C or more. Furthermore, more than 1250°C results in excessively coarse crystal grains and lower toughness, so that the upper limit is preferably 1250°C or less.

[0063] The Ar_3 transformation point varies depending on an alloy component of the steel and may therefore be determined by measuring the transformation temperature by experiment for each steel or can also be determined from the chemical composition using the following formula.

$$Ar_3\ (^\circ C) = 910 - 310C\ (\%) - 80Mn\ (\%) - 20Cu\ (\%) - 15Cr\ (\%) - 55Ni\ (\%) - 80Mo\ (\%)$$

[0064] Each alloying element indicates its content (% by mass).

Controlled Cooling Step

Cooling start temperature: Ar_3 transformation point or higher in terms of steel sheet surface temperature

[0065] When the steel sheet surface temperature at the start of cooling is lower than the Ar_3 transformation point, ferrite is formed before controlled cooling and greatly decreases the strength. Thus, the steel sheet surface temperature at the start of cooling is the Ar_3 transformation point or higher. The steel sheet surface temperature at the start of cooling is preferably 770°C or more. When the Ar_3 transformation point is higher than 770°C, the finish rolling delivery temperature is preferably the Ar_3 transformation point + 30°C or more, more preferably the Ar_3 transformation point + 50°C or more. The upper limit is preferably, but not limited to, 1250°C or less. The steel sheet surface temperature at the start of cooling is the temperature of the rear end of the steel sheet (including steel plate) at which the cooling start temperature is lowest.

Cooling start time difference between front end and rear end of steel sheet: 50 seconds or less

[0066] A time difference of more than 50 seconds between the front end and the rear end in the steel sheet rolling direction at the start of cooling results in a large difference in temperature between the front end and the rear end at the start of cooling, a large temperature variation at the cooling stop, a large variation in Vickers hardness at 0.25 mm below the steel sheet surface, and lower HISC resistance. Thus, the cooling start time difference between the front end and the rear end of the steel sheet is 50 seconds or less, preferably 45 seconds or less. It is more preferably 40 seconds or less. Although the steel sheet length can be shortened to shorten the cooling start time difference, it reduces the productivity, and the cooling start time difference is therefore preferably shortened by increasing the steel sheet line speed. Although the lower limit is not particularly limited, the cooling start time difference may be more than 0 seconds.

Cooling rate in controlled cooling step

[0067] To achieve high HISC resistance (HISC: Hydrogen Induced Stress Cracking) and reinforcement, it is necessary to control the cooling rate at 0.25 mm below the steel sheet surface and at the center of the sheet thickness. The cooling rate in the thickness direction is determined by simulation using heat-transfer calculation or the like from the surface temperature measured with a radiation thermometer.

Average cooling rate from 750°C to 550°C at 0.25 mm below steel sheet surface: 15°C/s to 50°C/s

[0068] It is important to minimize the average cooling rate from 750°C to 550°C in terms of the steel sheet temperature at 0.25 mm below the steel sheet surface and to form granular bainite. The temperature range of 750°C to 550°C is important for bainite transformation, and it is therefore important to control the cooling rate in this temperature range. A cooling rate of more than 50°C/s may cause variations in hardness and results in lower HISC resistance after pipe production. Thus, the average cooling rate is 50°C/s or less, preferably 45°C/s or less, more preferably 40°C/s or less. On the other hand, an excessively low cooling rate results in insufficient strength due to the formation of ferrite or pearlite and, from the perspective of preventing this, the cooling rate is 15°C/s or more, preferably 17°C/s or more, more preferably 20°C/s or more, still more preferably 25°C/s or more. Cooling at 550°C or less in terms of the steel sheet temperature at 0.25 mm below the steel sheet surface is not in a stable nucleate boiling state at a low cooling rate and may cause variations in hardness in an extreme surface layer portion of the steel sheet, so that the average cooling rate from 550°C to the cooling stop temperature in terms of the steel sheet temperature at 0.25 mm below the steel sheet surface is preferably 150°C/s or more. Since the hardness may vary, the average cooling rate is preferably 250°C/s or less.

Average cooling rate from 750°C to 550°C at center of sheet thickness: 15°C/s to 50°C/s

[0069] When the average cooling rate from 750°C to 550°C at the center of the sheet thickness is less than 15°C/s, a granular bainite microstructure is not formed, and the strength decreases. Furthermore, retained austenite is excessively formed, and the hydrogen diffusion coefficient at room temperature decreases. Thus, the average cooling rate at the center of the sheet thickness is 15°C/s or more. From the perspective of reducing variations in microstructure, the average cooling rate at the center of the sheet thickness is preferably 17°C/s or more. The average cooling rate at the center of the sheet thickness is more preferably 20°C/s or more, still more preferably 25°C/s or more. On the other hand, to reduce variations in grain size, the average cooling rate is 50°C/s or less, preferably 45°C/s or less. The average cooling rate at the center of the sheet thickness is more preferably 40°C/s or less. Cooling at a steel sheet temperature of 550°C or less at the center of the sheet thickness is not particularly limited but, from the perspective of reducing variations in the microstructure and grain size, the average cooling rate at the center of the sheet thickness is preferably 15°C/s or more. The average cooling rate at the center of the sheet thickness is preferably 50°C/s or less. Furthermore, at a high C content, the form of transformation changes from bainite transformation to martensite transformation. However, when the average cooling rate from 750°C to 550°C at the center of a cooled sheet thickness is less than 15°C/s, a mixed microstructure of martensite and bainite is formed. Thus, the average cooling rate is 15°C/ or more. From the perspective of reducing variations in microstructure, the average cooling rate at the center of the sheet thickness is preferably 17°C/s or more. The average cooling rate at the center of the sheet thickness is more preferably 20°C/s or more, still more preferably 25°C/s or more. On the other hand, to reduce variations in grain size, the average cooling rate is 50°C/s or less, preferably 45°C/s or less. The average cooling rate at the center of the sheet thickness is more preferably 40°C/s or less. Cooling at a steel sheet temperature of 550°C or less at the center of the sheet thickness is not particularly limited but, from the perspective of reducing variations in the microstructure and grain size, the average cooling rate at the center of the sheet thickness is preferably 15°C/s or more. The average cooling rate at the center of the sheet thickness is preferably 50°C/s or less.

[0070] The steel sheet temperature at 0.25 mm below the steel sheet surface and at the center of the sheet thickness cannot be physically measured directly but can be determined in real time from the result of calculating the temperature distribution in a thickness cross section by difference calculation using, for example, a process computer based on the surface temperature at the start of cooling measured with a radiation thermometer and the target surface temperature at the cooling stop. The temperature at 0.25 mm below the steel sheet surface in the temperature distribution is defined herein as "the steel sheet temperature at 0.25 mm below the steel sheet surface", and the temperature at the center of the sheet thickness in the temperature distribution is defined herein as "the steel sheet temperature at the center of the sheet thickness".

Cooling Stop Temperature

Cooling stop temperature: 250°C to 650°C in terms of steel sheet temperature at 0.25 mm below steel sheet surface and at center of sheet thickness

[0071] A cooling stop temperature of more than 650°C results in incomplete bainite transformation and insufficient strength. Thus, the cooling stop temperature is 650°C or less. The cooling stop temperature is preferably 625°C or less, more preferably 600°C or less, still more preferably 500°C or less. A cooling stop temperature of less than 250°C results in lower HISC resistance due to an increase in hardness. Thus, the cooling stop temperature is 250°C or more. The cooling stop temperature is preferably 270°C or more. The cooling stop temperature is more preferably 300°C or more.

Tempering Step

[0072] For the purpose of improving toughness and adjusting material strength, tempering treatment may be performed. The effects of tempering cannot be obtained at a tempering temperature of 200°C or less and therefore, when tempering is performed, the tempering temperature is preferably 200°C or more. On the other hand, tempering also causes strength reduction, and the microstructure is transformed again at an excessively high temperature, so that the temperature is preferably the Ar_3 transformation point or lower. The holding time can be arbitrarily determined but is preferably 10 minutes or more at a predetermined temperature at the center of the sheet thickness. 180 minutes or less is preferred.

Stabilization Treatment Step

[0073] Hydrogen that has entered a steel material is trapped mainly by various defects, such as dislocation. When hydrogen is trapped by these various defects, the hydrogen diffusion coefficient decreases, and the hydrogen solubility increases. This reduces the hydrogen embrittlement resistance. Thus, it is important to reduce these defects or to reduce bonding between these defects and hydrogen. Thus, to weaken the bonding between hydrogen and dislocation after production, stabilization treatment of the dislocation is performed. Holding a product at a predetermined temperature for a certain period before use can fix solute carbon to dislocation, and stabilizing the dislocation can reduce the bonding between hydrogen and the dislocation. This can increase the hydrogen diffusion coefficient and decrease the hydrogen solubility, and a steel material with high hydrogen embrittlement resistance in a high-pressure hydrogen gas environment can be produced. The stabilization treatment step is performed before pipe production and welding for connecting steel pipes. The diffusion of carbon is extremely low at a temperature lower than room temperature (25°C ± 10°C), and the temperature is therefore room temperature or higher. Furthermore, since the carbon diffusion coefficient Dc is smaller and carbon diffuses in a shorter time at a higher temperature, the temperature is preferably 100°C or more, more preferably 200°C or more. On the other hand, an excessively high temperature in the stabilization treatment step results in a significant decrease in the material strength, and the stabilization treatment temperature is the Ar_3 transformation point

(°C) or lower or 700°C or less. For the stabilization treatment of a tempered material, the upper limit is preferably a temperature lower by 50°C or more than the tempering temperature. The holding time is 72 hours or more at a stabilization treatment temperature of less than 100°C and is 10 minutes or more at a stabilization treatment temperature of 100°C or more. The holding time is preferably 400 hours or less at a stabilization treatment temperature of less than 100°C and is preferably 100 hours or less at a stabilization treatment temperature of 100°C or more. The temperature is a temperature at the center of the sheet thickness. When heating is performed in a pipe production step of an electric-resistance-welded pipe, a UOE steel pipe, or the like, the time and temperature in the stabilization treatment step may also be the same in the step. "The step" refers to a step of performing heat treatment after pipe production, such as tempering or stress relief annealing.

Dehydrogenation Treatment Step

[0074] Hydrogen originally present in a steel material increases the acceleration of fatigue crack growth and decreases the fatigue life and the fatigue limit stress in hydrogen. Thus, dehydrogenation treatment may be performed to release hydrogen remaining after production. In the dehydrogenation treatment, holding a product at a high temperature for a certain period before use can decrease the amount of hydrogen in the steel, and a steel material with high hydrogen embrittlement resistance in a high-pressure hydrogen gas environment can be produced. The holding time R (s) is preferably determined from the sheet thickness or wall thickness t (mm) of a steel material or a steel pipe and the hydrogen diffusion coefficient D ($mm^2 \cdot s^{-1}$) in the steel at room temperature using the following formula (A).

$$R \geq t^2/D \quad (A)$$

[0075] The hydrogen diffusion coefficient can be that described above. The dehydrogenation treatment step is performed before pipe production and welding for connecting steel pipes. The dehydrogenation treatment is preferably performed at a high temperature because the hydrogen diffusion coefficient D at a high temperature is small and hydrogen is released quickly. At a high temperature, the calculation may be performed using a diffusion coefficient D' (diffusion coefficient at corresponding temperature) at the holding temperature for the value of D in the formula (A). Furthermore, an excessively high temperature T in the dehydrogenation step results in a significant decrease in the material strength, and the dehydrogenation treatment temperature is preferably 550°C or less. The dehydrogenation treatment temperature T is more preferably 500°C or less. The dehydrogenation treatment temperature T is still more preferably 400°C or less, most preferably 300°C or less. Furthermore, the dehydrogenation treatment temperature T is preferably room temperature or higher for the reason that the dehydrogenation treatment at a temperature lower than room temperature increases the treatment time and cost. The dehydrogenation treatment temperature T is more preferably 50°C or more. The dehydrogenation treatment temperature T is still more preferably 100°C or more, most preferably 150°C or more. The dehydrogenation treatment temperature T is the temperature of the atmosphere in the dehydrogenation treatment step. The room temperature refers to 20°C ± 10°C. For the dehydrogenation treatment of a tempered material, a temperature lower by 50°C or more than the tempering temperature is the upper limit.

[0076] In particular, heating, if conducted, takes time for the temperature Tc at the center of the sheet thickness of a steel material or a steel pipe to reach the temperature of the atmosphere in the dehydrogenation treatment step (dehydrogenation treatment temperature T), so even if the holding time R (s) is satisfied at the ambient temperature, the dehydrogenation treatment may be insufficient if the dehydrogenation treatment temperature T (ambient temperature) has not been reached at the center of the sheet thickness. Thus, it is preferable to hold for R (s) or more after the temperature Tc at the center of the sheet thickness reaches the target temperature T. Furthermore, to achieve a predetermined crack growth rate in hydrogen gas, it is necessary to appropriately adjust the amount of hydrogen in a steel material in a surface layer portion and at the center of the sheet thickness, and for this purpose, it is preferable to hold the steel material at the ambient temperature T for R (s) or more defined by the formula (A), and it is further preferable to hold the steel material for R (s) or more after the temperature Tc at the center of the sheet thickness reaches the target temperature T. In other words, at least the former can appropriately control the amount of hydrogen in the steel material in the surface layer portion of the steel material or the steel pipe, and when the latter is also performed, the amount of hydrogen in the steel material from the surface layer portion to the center of the sheet thickness of the steel material or the steel pipe can be appropriately controlled. The temperature Tc at the center of the sheet thickness may be actually measured with a thermocouple or the like or may be predicted using a finite element method or the like.

[0077] The time and temperature in the dehydrogenation treatment step may include the temperature and time applied at the time of heating in the pipe production step of an electric-resistance-welded pipe, UOE, or the like, as described later. Furthermore, the scale on the steel surface inhibits dehydrogenation and is therefore preferably removed before dehydrogenation treatment. The removal method may be, for example, but is not limited to, physical cleaning by high-pressure cleaning or a chemical method using a scale remover. If the scale is removed by approximately 100 μm in thickness, the effects of scale removal can be obtained.

Second Embodiment

[0078] Furthermore, a UOE steel pipe, which is an example of a high-strength steel pipe for a line pipe, can be produced by limiting the following production conditions, and the production method and conditions are more specifically described below. The chemical composition, the metallic microstructure, the hydrogen solubility, and the hydrogen diffusion coefficient of a UOE steel pipe are the same as those described for the steel material of the first embodiment, and the heating step, the hot rolling step, the controlled cooling step after hot rolling, the stabilization treatment step, and the dehydrogenation treatment step in the production method are performed in the same manner as described for the steel material. The pipe production step after rolling is more specifically described below.

Pipe Production Step

[0079] A UOE steel pipe is produced by bending a hot-rolled steel plate, more specifically, conducting weld preparation to an end portion of the hot-rolled steel plate, forming the steel sheet into a steel pipe shape by C-press, U-press, or O-press, seam-welding a butt joint by inner surface welding and outer surface welding, and if necessary, performing an expansion step. The welding method may be any method that can achieve sufficient joint strength and joint toughness and, from the perspective of good weld quality and production efficiency, submerged arc welding is preferably used. Furthermore, a steel pipe produced by press bending into a pipe shape and then seam-welding a butt joint can also be subjected to expansion.

Third Embodiment

[0080] Furthermore, an electric-resistance-welded steel pipe, which is an example of a high-strength steel pipe for a line pipe according to the present invention, can be produced by limiting the following production conditions, and the production method and conditions are more specifically described below. The chemical composition, the metallic microstructure, the hydrogen solubility, and the hydrogen diffusion coefficient of the steel material are the same as those described for the steel material of the first embodiment, and the steps (the heating step, the hot rolling step, the stabilization treatment step, and the dehydrogenation treatment step) other than the controlled cooling step after rolling and the pipe production step in the production method are performed in the same manner as described for the steel material.

Cooling Step after Rolling (Controlled Cooling Step)

[0081] The cooling start temperature of the controlled cooling and the average cooling rate of the controlled cooling are the same as those described in the first embodiment.

Cooling stop temperature: 250°C to 650°C

[0082] A cooling stop temperature of more than 650°C after hot rolling results in incomplete bainite transformation and a greatly decrease in the material strength. Thus, the cooling stop temperature is 650°C or less. The cooling stop temperature is preferably 620°C or less. The cooling stop temperature is more preferably 600°C or less, still more preferably 580°C or less. On the other hand, when the cooling stop temperature is less than 250°C, a quenching crack is likely to occur during cooling. Furthermore, to form a uniform bainite microstructure, the cooling stop temperature is 250°C or more. Also from the perspective of reducing the amount of hydrogen in the steel, the cooling stop temperature should be a predetermined temperature or higher. More specifically, hydrogen in the steel is gradually released during cooling, and this effect increases with the temperature, but an excessively low cooling stop temperature results in supercooling and hydrogen remaining in the steel. Furthermore, an excessively low cooling stop temperature tends to result in the formation of retained austenite, which stores a larger amount of hydrogen than other phases. Thus, it is necessary for the cooling stop temperature to be 250°C or more to decrease the amount of hydrogen in the steel. The cooling stop temperature is preferably 300°C or more, more preferably 390°C or more. The cooling stop temperature is still more preferably 450°C or more. After the cooling is stopped, the steel may be allowed to cool and, to promote the formation of bainite, is preferably gradually cooled until the temperature is lowered by approximately 50°C from the cooling stop temperature. The cooling stop temperature referred to herein is the temperature at the center of the sheet thickness.

[0083] A hot-rolled steel sheet thus produced is then coiled. The coiling temperature is preferably 550°C or less.

Pipe Production Step

[0084] An electric-resistance-welded steel pipe as an example of the present invention is produced by forming a cylindrical shape by cold roll forming and butt-welding both circumferential end portions of the cylindrical shape. An electric-resistance-welded steel pipe may also be produced by forming an electric-resistance-welded steel pipe material (electric-resistance-welded steel pipe) using a sizing roll satisfying the following formula (1) (a sizing step) and applying an internal pressure p (MPa) satisfying the following formula (2) to the inner surface of the electric-resistance-welded steel pipe material (an internal pressure applying step). The term "cylindrical shape" means that the cross section of the pipe has a "C" shape.

$$\text{Diameter (mm) of sizing roll} \geq \text{Thickness (mm) of hot-rolled steel sheet}/0.020 \text{ (1)} \qquad (1)$$

[0085] The thickness of a hot-rolled steel sheet refers to the thickness of the hot-rolled steel sheet before the sizing step.

$$X < p \leq X \text{ x } 1.5 \qquad (2)$$

X = (wall thickness (mm) of electric-resistance-welded steel pipe material/radius (mm) of electric-resistance-welded steel pipe material) x yield strength (MPa) of electric-resistance-welded steel pipe material

[0086] The internal pressure can be applied, for example, by sealing a pipe end with a packing made of a rubber material and applying water pressure to the inside of the pipe. To stabilize the shape, if necessary, a die with a desired diameter may be used as an outer frame.

[0087] An electric-resistance-welded steel pipe material as an example of a steel pipe according to the present invention preferably has a wall thickness of 5 mm or more and 30 mm or less. Although the radius of the electric-resistance-welded steel pipe material does not necessarily have any upper limit, the load on the facilities increases with the radius, and the electric-resistance-welded pipe material therefore preferably has a radius of 400 mm or less. The electric-resistance-welded pipe material preferably has a radius of 200 mm or more. The electric-resistance-welded steel pipe material preferably has a yield strength of 480 MPa or more to withstand pipeline operation gas pressures. The yield strength is more preferably 500 MPa or more. On the other hand, to avoid an increase in hydrogen embrittlement sensitivity, the yield strength is preferably 600 MPa or less. The yield strength is more preferably 560 MPa or less.

[0088] In the sizing step, passage through rolls causes bending deformation along the roll shape in the pipe axis direction and generates residual stress in the pipe axis direction. The absolute value of the residual stress in the pipe axis direction increases with the bending strain in the bending deformation. The bending strain increases as the diameter of the sizing roll decreases and as the thickness of the hot-rolled steel sheet increases. Thus, in the present invention, from the perspective of reducing the shear residual stress, the diameter of the sizing roll satisfies the formula (1) to reduce the absolute value of the residual stress in the pipe axis direction. When the sizing roll has a diameter smaller than the right side of the formula (1), the shear residual stress intended in the present invention cannot be obtained. Although the diameter of the sizing roll does not necessarily have any upper limit, the load on the facilities increases with the sizing roll, and the sizing roll therefore preferably has a diameter of 2000 mm or less.

[0089] In the internal pressure applying step, the electric-resistance-welded steel pipe material is expanded to generate tensile stress in the circumferential direction of the pipe and reduce the absolute value of residual stress in the circumferential direction of the pipe. As the internal pressure p (MPa) in the internal pressure applying step increases, the absolute value of the residual stress in the circumferential direction of the pipe decreases. The tensile stress generated in the circumferential direction of the pipe increases as the radius of the steel pipe increases and as the wall thickness of the steel pipe decreases.

[0090] The left side (X) of the formula (2) corresponds to the internal pressure p when the tensile stress generated in the circumferential direction of the pipe is equal to the yield stress of the electric-resistance-welded steel pipe material.

[0091] In the present invention, from the perspective of reducing the shear residual stress, to reduce the absolute value of the residual stress in the pipe axis direction, the internal pressure p is larger than the left side (X) of the formula (2) to expand the electric-resistance-welded steel pipe material to the plastic region. On the other hand, when the internal pressure p exceeds the right side (X x 1.5) of the formula (2), the absolute value of the residual stress in the circumferential direction of the pipe decreases, but the amount of work hardening due to expansion increases excessively, the dislocation density on the pipe surface increases, and the hydrogen embrittlement resistance decreases.

[0092] As partially described above, regarding a steel pipe according to the present invention, a high-strength steel pipe for a line pipe for sour gas service (a UOE steel pipe, an electric-resistance-welded steel pipe, a spiral steel pipe, or the like) with high material uniformity in the steel sheet suitable for transportation of crude oil or natural gas can be produced by forming a steel material disclosed in the present invention into a tubular shape by press bending, roll forming, UOE forming, or the like and then welding a butt joint. Furthermore, a steel material according to the present disclosure can be used for a steel pipe to produce a steel pipe with high HISC resistance even when a high hardness region of a weld is present.

EXAMPLE 1

[0093] The present invention is more specifically described in the following examples. The examples are preferred examples of the present invention, and the present invention is not limited to these examples.

[0094] Steel pipes made of steel materials with the chemical compositions shown in Table 1 were produced. The production procedure is described below. First, billets with the chemical compositions shown in Table 1 were produced. The casting speed ranged from 0.05 to 0.2 m/min. The billets were heated to 1000°C to 1100°C and were subjected to hot rolling at 950°C ± 50°C. Controlled cooling was started when surface temperature reached 900°C as the cooling start temperature. The hot rolling was performed such that the cooling start time difference between the front and rear ends ranged from 30 to 45 seconds and the cooling stop temperature ranged from 300°C ± 50°C, and the target thickness of the steel sheet was 20 mm. The average cooling rate in the controlled cooling step is shown in Table 2. For some steel materials (steel materials Nos. 1 to 11), the hot-rolled steel sheet was subjected to the pipe production step of bending the hot-rolled steel sheet and butt-welding both end portions thereof after the controlled cooling step, and for some steel materials (steel materials Nos. 12 to 22), the hot-rolled steel sheet was subjected to the pipe production step of forming the hot-rolled steel sheet into a cylindrical shape by cold roll forming and subjecting both circumferential end portions of the cylindrical shape to butt electric resistance welding after the controlled cooling step, thereby producing the steel pipes Nos. 1 to 22. Those subjected to the stabilization treatment (or the dehydrogenation treatment) were indicated by a circle. All the treatments were performed at 200°C for 30 minutes. The steel materials and steel pipes thus produced were evaluated as described below.

[0095] Furthermore, billets with the chemical compositions shown in Steel No. 8 and Steel No. 22 in Table 1 were produced at various casting speeds shown in Table 3. The billets were heated to 1000°C to 1100°C and were subjected to hot rolling at 950°C ± 50°C. Controlled cooling was started when surface temperature reached 900°C as the cooling start temperature. The hot rolling was performed such that the cooling start time difference between the front and rear ends ranged from 30 to 45 seconds and the cooling stop temperature ranged from 300°C ± 50°C, and the target thickness of the steel sheet was 20 mm. The average cooling rate in the controlled cooling step was shown in Table 3, and steel materials and steel pipes were produced. The steel materials Nos. 8-1, 8-2, 8-3, 22-1, 22-2, and 22-3 were steel materials themselves, the steel pipes Nos. 8-11, 8-12, and 8-13 were produced by the pipe production step of bending the hot-rolled steel sheet and butt-welding both end portions thereof, and the steel pipes Nos. 22-11, 22-12, and 22-13 were produced by the pipe production step of forming the hot-rolled steel sheet into a cylindrical shape by cold roll forming and subjecting both circumferential end portions of the cylindrical shape to butt electric resistance welding after the controlled cooling step. Those subjected to the stabilization treatment (or the dehydrogenation treatment) were indicated by a circle, and all the treatments were performed at 200°C for 30 minutes. The steel materials and steel pipes thus produced were evaluated as described below.

Measurement of Area Fraction of Retained Austenite

[0096] A sample for metallic microstructure observation was taken from the center of the sheet width in the center in the longitudinal direction of each of the steel materials and the steel pipes thus produced, a cross section parallel to the longitudinal direction was buffed as an observation surface, the surface layer was then removed by chemical polishing using picric acid etching, and X-ray diffractometry was performed. More specifically, a Co-Kα radiation source was used for an incident X-ray, and the area fraction of retained austenite was calculated from the intensity ratios of the (200), (211), and (220) planes of ferrite to the (200), (220), and (311) planes of austenite.

Measurement of Area Fraction of Bainite and Martensite

[0097] The metallic microstructure at a quarter thickness position on the inner side of each steel pipe was evaluated as described below. A test specimen was taken from the steel pipe such that the quarter thickness position on the inner side and the center position of the wall thickness in the center in the longitudinal direction of the steel pipe were observation positions, and a cross section of the taken test specimen was etched using a 3% by volume nital solution. A scanning electron microscope photograph was taken at an appropriate magnification in the range of 1000 to 5000 times, and martensite (including tempered martensite), ferrite, bainite, and pearlite were observed. Martensite and bainite were visually identified by comparison with a microstructure photograph of Non Patent Literature 3, the microstructure fraction was determined by image analysis using an image obtained by dividing the SEM photograph into regions based on the identification (for example, to calculate the fraction of bainite, the bainite and another region were binarized to determine the fraction of bainite), and this was taken as the area fraction of each phase.

Hydrogen Temperature-Programmed Analysis

[0098] The amount of hydrogen remaining in the steel was measured by thermal desorption spectrometry using a low-temperature programmed hydrogen analyzer <gas chromatograph type> (JTF-20AL). The thermal desorption spectrometry was performed in the temperature range of room temperature to 400°C at a heating rate of 200°C/h, and the sum total thereof was taken as the amount of hydrogen. The specimen has a columnar shape with 20 mm in length, 10 mm in thickness, and 10 mm in width in the longitudinal direction of the steel pipe at the quarter thickness position of the steel sheet and at the quarter thickness position from the inner surface of the steel pipe. The amount of hydrogen was measured before a high-pressure hydrogen fatigue crack growth test and a high-pressure hydrogen exposure test described in the next section.

High-Pressure Hydrogen Exposure Test (Calculation of Hydrogen Solubility)

[0099] A method for calculating the hydrogen solubility is described below. First, the specimen had a columnar shape with 20 mm in length, 10 mm in thickness, and 10 mm in width in the longitudinal direction of the steel material and the steel pipe at the quarter thickness position of the steel material and at the quarter thickness position from the inner surface of the steel pipe. The amount of hydrogen penetration depends on the surface state of the test specimen, and the test specimen after cutting was therefore polished with emery paper from No. 160 to No. 1000 to make the surface state uniform in all the samples. Pd plating was applied to the entire surface of the test specimen for the purpose of removing an oxide film that may inhibit hydrogen penetration. The Pd plating may be replaced by another method, such as vapor deposition, or may be replaced by Ni plating or the like. The specimen was exposed to a high-pressure hydrogen environment (99.999% or more by volume fraction of hydrogen) at room temperature (20°C ± 10°C) and at a pressure of 0, 5, 25, or 40 MPa for 72 hours. After the exposure, the specimen was immediately taken out from the exposure environment and was stored in liquid nitrogen to prevent hydrogen from being released from the specimen. The hydrogen storage amount H was determined by the hydrogen temperature-programmed analysis method as described above. The square root of the exposure pressure $\sqrt{P}$ [MPa] is plotted on the horizontal axis, and the measured hydrogen storage amount H [mass ppm/$\sqrt{P}$] is plotted on the vertical axis. Taking the amount of hydrogen in the specimen at 0 MPa (before the exposure test) as the initial amount of hydrogen (intercept), the hydrogen solubility s [mass ppm/$\sqrt{P}$] was calculated from the slope of $\sqrt{P}$-H.

Hydrogen Diffusion Coefficient

[0100] The hydrogen diffusion coefficient was evaluated using a 1 x 40 x 40 mm test specimen taken from the middle of the sheet thickness at the quarter thickness position of the steel material and at the quarter thickness position from the inner surface of the steel pipe. One surface of the test specimen was plated with Ni, and using a Devanathan-type cell, the surface not plated with Ni was immersed in a 0.2% NaCl solution, cathodic hydrogen charging was performed, the surface plated with Ni was immersed in 0.1 N aqueous NaOH, and the extraction potential was 0 V. The diffusion coefficient was determined by fitting the hydrogen permeation start time (2nd build up), which is the second rise of the permeation current, to a theoretical curve of Non Patent Literature 4.

Evaluation of High-Pressure Hydrogen Fatigue Crack Growth Rate

[0101] It was determined by a fatigue test in accordance with ASTM E647, Fatigue Testing, at a frequency of 1 Hz, a repetitive waveform of a sine wave, a control method of load control, a load condition of uniaxial tension, and a stress ratio of R = 0.1, in hydrogen gas at a pressure of 25 MPa, in hydrogen gas at a pressure of 1 MPa or more, or in a natural gas (the main components are hydrocarbons, such as methane and ethane) mixed atmosphere containing hydrogen at a hydrogen partial pressure of 1 MPa or more, at room temperature (20°C ± 10°C). A steel material or a steel pipe with high hydrogen embrittlement resistance has a fatigue crack growth rate da/dN mm/cycle in hydrogen of 2.0×10^{-3} mm/cycle or less at ΔK = 25 MPa in this experiment.

Tensile Strength (TS)

[0102] JIS No. 14 proportional test pieces (parallel portion diameter: 7 mm, gauge length: 35 mm) were taken in accordance with JIS Z 2201 from the steel materials and the steel pipes thus produced, and the tensile strength was measured.

[0103] Steel materials and steel pipes satisfying the examples of the present invention had good effects on fatigue crack growth characteristics in the hydrogen environments. Furthermore, when the hydrogen solubility s was less than 0.02 mass ppm/$\sqrt{P}$, the fatigue crack growth rate was further improved by 30% or more and reduced to 1.5×10^{-3} mm/cycle or less as compared with a material with a hydrogen solubility s of approximately 0.05 mass ppm/$\sqrt{P}$, resulting in good effects.

EXAMPLE 2

[0104] Examples in which the advantages of the present invention have been verified are described below. In the following examples, steel pipes were produced under the following production conditions and were characterized. Steel Nos. 1, 8, 10, 12, and 22 shown in Tables 1-1 and 1-2 were used to produce steel pipes under the same conditions as steel materials Nos. 1, 8-2, 10, 12, and 22-2 shown in Tables 2 and 3 up to the controlled cooling step, and the characteristics were evaluated when the dehydrogenation treatment conditions were changed. The steel pipes were formed in the same manner as in Example 1. Table 4 shows the results.

[0105] In the present examples, for the steel pipes and steel materials Nos. 1A, 10A, 12A, 8-2A, and 22-2A, the dehydrogenation treatment temperature T (ambient temperature) was 50°C, and the holding time tc after the temperature Tc at the center of the sheet thickness reached 50°C satisfied the formula (A). For the steel pipes and steel materials Nos. 10B, 12B, 8-2B, and 22-2B, the dehydrogenation treatment temperature T (ambient temperature) was 50°C, and the holding time tc satisfied the formula (A) at a dehydrogenation treatment temperature T of 50°C, but the holding time tc after the temperature Tc at the center of the sheet thickness reached 50°C did not satisfy the formula (A).

[0106] For the steel pipes and steel materials Nos. 10C, 12C, 8-2C, and 22-2C, the dehydrogenation treatment temperature T (ambient temperature) was 50°C, but both the holding time t at the ambient temperature and the holding time tc after the temperature Tc at the center of the sheet thickness reached 50°C did not satisfy the formula (A).

[0107] In Table 4, "Dehydrogenation holding time t is Y" means that the dehydrogenation treatment temperature T (ambient temperature) is 50°C and the holding time t satisfies the formula (A), and "Dehydrogenation holding time t is N" means that the dehydrogenation treatment temperature T (ambient temperature) is 50°C, but the holding time t does not satisfy the formula (A). Furthermore, "Holding time tc at steel material center temperature Tc is Y" means that the holding time tc after the temperature Tc at the middle of the sheet thickness reaches 50°C satisfies the formula (A), and "Holding time tc at steel material center temperature Tc is N" means that the temperature Tc at the center of the sheet thickness reaches 50°C, but the holding time tc after Tc reaches 50°C does not satisfy the formula (A).

[0108] Various evaluations were performed by the methods described in Example 1.

[0109] The inventive examples of the present invention all had a good fatigue crack growth rate. Among them, the fatigue crack growth rate was lower when the dehydrogenation treatment was performed under more suitable conditions.

[Table 1]

Type of steel No.	Chemical composition (% by mass) *1																											Ar3 (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H (ppm)	Nb	Ca	Ni	Ti	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb		
1	0.09	1.35	1.2	0.0109	0.0010	0.140	0.007	0.004	0.005																			786	Conforming steel
2	0.02	0.34	1.0	0.0073	0.0015	0.087	0.010	0.005	0.006																			824	Conforming steel
3	0.15	1.88	1.2	0.0082	0.0015	0.108	0.005	0.003	0.009																			768	Conforming steel
4	0.13	0.73	1.2	0.0045	0.0010	0.130	0.010	0.004	0.030																			774	Comparative steel
5	0.28	1.35	0.8	0.0109	0.0010	0.050	0.007	0.004	0.005																			761	Comparative steel
6	0.15	1.01	1.7	0.0081	0.0004	0.110	0.009	0.002	0.009																			728	Conforming steel
7	0.09	0.10	1.5	0.0047	0.0005	0.058	0.009	0.003	0.018																			762	Conforming steel
8	0.04	2.00	1.0	0.0107	0.0012	0.092	0.010	0.001	0.006																			818	Conforming steel
9	0.07	1.01	0.9	0.0068	0.0012	0.128	0.003	0.004	0.000																			816	Conforming steel
10	0.07	1.92	1.5	0.0064	0.0004	0.030	0.003	0.004	0.010	0.100	0.0045	1.88	0.087	0.43	0.44	0.20	0.56	0.02	0.005	0.007	0.003	0.0002	0.173	0.063	0.001	0.112	0.0629	634	Conforming steel
11	0.09	1.78	1.6	0.0137	0.0014	0.104	0.008	0.004	0.040	0.051	0.0022	0.05	0.096	0.41	0.42	0.38		0.02	0.031		0.002	0.0013						706	Comparative steel
12	0.02	1.81	1.3	0.0050	0.0010	0.102	0.004	0.003	0.012	0.061	0.0026	1.55	0.085	0.71	0.52	0.35	0.53	0.03	0.001	0.008	0.003	0.0012	0.157	0.051	0.003	0.228	0.2005	665	Conforming steel
13	0.06	2.50	1.0	0.0081	0.0010	0.095	0.007	0.003	0.008																			811	Comparative steel
14	0.08	1.60	2.0	0.0077	0.0008	0.079	0.008	0.007	0.005																			725	Comparative steel
15	0.07	1.01	0.9	0.0200	0.0010	0.050	0.007	0.004	0.005																			816	Comparative steel
16	0.04	2.00	1.5	0.0064	0.0020	0.030	0.003	0.005	0.006																			778	Comparative steel
17	0.09	1.78	1.6	0.0127	0.0014	0.140	0.007	0.004	0.005	0.088	0.0022	0.43	0.085	1.10	0.84	0.44	0.44	0.08		0.010		0.0010			0.004	0.186		661	Comparative steel
18	0.10	1.50	0.9	0.0098	0.0012	0.116	0.002	0.003	0.004	0.035	0.0043	0.89	0.094	0.64	1.10	0.59	0.32			0.006			0.111			0.219		682	Comparative steel
19	0.04	1.40	1.4	0.0074	0.0008	0.094	0.004	0.001	0.007	0.044	0.0034	1.35	0.068	0.86	0.69	0.70		0.05	0.014		0.001			0.124			0.1680	628	Comparative steel
20	0.05	1.30	1.4	0.0098	0.0010	0.094	0.004	0.001	0.006	0.044	0.0034	0.10		0.30	0.69	0.44		0.15	0.014		0.001			0.124			0.1680	725	Comparative steel
21	0.10	0.83	1.3	0.0052	0.0013	0.025	0.002	0.002	0.010						0.88			_										762	Conforming steel
22	0.04	0.15	1.2	0.0068	0.0012	0.054	0.006	0.005	0.010	0.040	0.0020	0.11	0.010	0.10	0.03	0.01												792	Conforming steel

Underline: outside the scope of the present invention. Blank: no intended addition

*1 ppm % by mass for H.

[Table 2]

Steel material No.	Steel pipe No.	Type of steel No.	Production method									
			Cooling step									
			Average cooling rate at surface 0.25 mm at 750°C-5-50°C (°C/s)	Average cooling rate at center of thickness at 750°C-5-50°C (°C/s)	Stabilization treatment step (or dehydrogenation treatment step)	r ratio (%)	B-fraction (%)	M fraction (%)	Hydrogen solubility mass ppm/√P	Hydrogen diffusion coefficient 1 x $10^{\wedge-10}$ (m^2/s)	Fatigue crack growth rate (mm/cycles)	Tensile strength (MPa)	Notes
1	1	1	32	27	○	0.0	90	0	0.012	2.0	0.0017	605	Inventive example
2	2	2	50	45	○	0.1	95	0	0.021	1.9	0.0018	535	Inventive example
3	3	3	45	42	○	2.3	0	90	0.020	5.3	0.0020	690	Inventive example
4	4	4	45	42	-	0.3	92	0	0.038	4.3	0.0033	635	Comparative example
5	5	5	48	42	○	0.0	0	100	0.055	4.8	0.0040	753	Comparative example
6	6	6	20	15	○	0.7	0	90	0.039	5.9	0.0018	612	Inventive example
7	7	7	5	5	○	2.9	60	0	0.050	0.2	0.0055	540	Comparative example
8	8	8	45	40	○	2.4	96	0	0.022	1.9	0.0018	550	Inventive example
9	9	9	15	3	○	5.0	92	0	0.025	1.9	0.0050	586	Comparative example
10	10	10	38	36	○	1.4	97	0	0.036	3.9	0.0019	592	Inventive example
11	11	11	20	18	-	0.2	99	0	0.038	0.5	0.0043	580	Comparative example

(continued)

Steel material No.	Steel pipe No.	Type of steel No.	Production method			r ratio (%)	B-fraction (%)	M fraction (%)	Hydrogen solubility mass ppm/√P	Hydrogen diffusion coefficient 1 x 10^-10 (m^2/s)	Fatigue crack growth rate (mm/cycles)	Tensile strength (MPa)	Notes
			Cooling step		Stabilization treatment step (or dehydrogenation treatment step)								
			Average cooling rate at surface 0.25 mm at 750°C-5-50°C (°C/s)	Average cooling rate at center of thickness at 750°C-5-50°C (°C/s)									
12	12	12	48	45	○	0.1	95	0	0.021	6.1	0.0019	560	Inventive example
13	13	13	50	45	○	0.1	95	0	0.055	1.8	0.0042	573	Comparative example
14	14	14	50	45	○	0.1	95	0	0.062	1.0	0.0054	579	Comparative example
15	15	15	50	45	○	0.1	95	0	0.058	1.6	0.0048	589	Comparative example
16	16	16	50	45	○	0.1	96	0	0.061	2.0	0.0079	583	Comparative example
17	17	17	50	45	○	0.1	95	0	0.060	2.2	0.0069	608	Comparative example
18	18	18	50	45	○	0.1	97	0	0.058	1.8	0.0045	582	Comparative example
19	19	19	50	45	○	0.1	96	0	0.055	1.9	0.0044	579	Comparative example
20	20	20	35	30	○	0.3	95	0	0.060	1.1	0.0044	587	Comparative example
21	21	21	22	15	○	0.1	93	0	0.022	2.1	0.0018	566	Inventive example

(continued)

Steel material No.	Steel pipe No.	Type of steel No.	Production method									
			Cooling step		Stabilization treatment step (or dehydrogenation treatment step)	r ratio (%)	B-fraction (%)	M fraction (%)	Hydrogen solubility mass ppm/√P	Hydrogen diffusion coefficient 1 x 10$^{\wedge-10}$ (m^2/s)	Fatigue crack growth rate (mm/cycles)	Tensile strength (MPa)	Notes
			Average cooling rate at surface 0.25 mm at 750°C-5-50°C (°C/s)	Average cooling rate at center of thickness at 750°C-5-50°C (°C/s)									
22	22	22	45	40	○	0.6	95	0	0.001	2.3	0.0020	598	Inventive example
Underline: outside the scope of the present invention or outside the target range. B: bainite, M: martensite, γ: austenite													

[Table 3]

Type of steel No.	Steel material No.	Steel pipe No.	Casting speed (m/min)	Cooling step		Dehydrogenation treatment step	Microstructure of steel sheet and steel pipe		Hydrogen solubility mass ppm/√P	Hydrogen diffusion coefficient 1 x 10^-10 (m²/s)	Fatigue crack growth rate (mm/cycles)	Tensile strength (MPa)	Notes
				Average cooling rate at surface 0.25 mm at 750°C-5-50°C (°C/s)	Average cooling rate at center of thickness at 750°C-5-50°C (°C/s)	Dehydrogenation treatment	r ratio (%)	B fraction (%)					
8	8-1	-	0.8	45	40	○	2.4	96	0.022	2.7	0.0018	550	Inventive example
8	8-11	8-11	0.8	42	39	○	2.4	96	0.022	2.7	0.0018	550	Inventive example
8	8-2	-	1.2	44	40	○	2.4	96	0.030	1.7	0.0019	562	Inventive example
8	8-12	8-12	1.2	45	38	○	2.4	96	0.030	1.7	0.0019	562	Inventive example
8	8-3	-	1.8	43	40	○	2.4	96	0.038	1.5	0.0020	568	Inventive example
8	8-13	8-13	1.8	45	41	○	2.4	96	0.038	1.5	0.0020	568	Inventive example
22	22-1	-	0.8	43	40	○	0.1	93	0.018	2.9	0.0012	587	Inventive example
22	22-11	22-11	0.8	45	38	○	0.1	93	0.018	2.9	0.0012	590	Inventive example
22	22-2	-	1.2	43	40	○	0.1	93	0.027	1.9	0.0015	599	Inventive example
22	22-12	22-12	1.2	45	38	○	0.1	93	0.027	1.9	0.0015	601	Inventive example
22	22-3	-	1.5	43	40	○	0.1	93	0.035	1.5	0.0020	605	Inventive example

(continued)

Type of steel No.	Steel material No.	Steel pipe No.	Casting speed (m/min)	Cooling step		Dehydrogenation treatment step	Microstructure of steel sheet and steel pipe		Hydrogen solubility mass ppm/$\sqrt{P}$	Hydrogen diffusion coefficient 1 x 10$^{\wedge-10}$ (m^2/s)	Fatigue crack growth rate (mm/cycles)	Tensile strength (MPa)	Notes
				Average cooling rate at surface 0.25 mm at 750°C-5-50°C (°C/s)	Average cooling rate at center of thickness at 750°C-5-50°C (°C/s)	Dehydrogenation treatment	r ratio (%)	B fraction (%)					
22	22-13	22-13	1.5	45	38	○	0.1	93	0.035	1.5	0.0020	605	Inventive example

B: bainite, γ: austenite

[Table 4]

Type of steel No.	Steel material No.	Steel pipe No.	Dehydrogenation holding time t	Holding time tc at steel material center temperature Tc	Microstructure of steel sheet and steel pipe		Hydrogen solubility mass ppm/√P	Hydrogen diffusion coefficient 1 x $10^{\wedge-10}$ (m^2/s)	Fatigue crack growth rate (mm/cycles)	Tensile strength (MPa)	Notes
					r ratio (%)	B fraction (%)					
1	1	1A	Y	Y	0.0	90	0.010	2.2	0.0014	605	Inventive example
10	10	10A	Y	Y	1.4	97	0.031	4.5	0.0013	580	Inventive example
10	10	10B	Y	N	1.4	97	0.036	3.9	0.0019	592	Inventive example
10	10	10C	N	N	1.4	97	0.039	2.5	0.0020	592	Inventive example
12	12	12A	Y	Y	0.1	95	0.015	7.0	0.0010	548	Inventive example
12	12	12B	Y	N	0.1	95	0.021	6.1	0.0013	560	Inventive example
12	12	12C	N	N	0.1	95	0.025	4.0	0.0018	570	Inventive example
8	8-2	8-2A	Y	Y	2.4	96	0.025	2.3	0.0015	550	Inventive example
8	8-2	8-2B	Y	N	2.4	96	0.030	1.7	0.0018	562	Inventive example
8	8-2	8-2C	N	N	2.4	96	0.035	1.5	0.0020	575	Inventive example
22	22-2	22-2A	Y	Y	0.1	93	0.020	2.3	0.0015	590	Inventive example
22	22-2	22-2B	Y	N	0.1	93	0.027	1.9	0.0017	601	Inventive example
22	22-2	22-2C	N	N	0.1	93	0.035	1.5	0.0020	610	Inventive example

B: bainite, γ: austenite

Claims

1. A steel material for a line pipe, the steel material having a chemical composition containing:

    on a mass percent basis,
    C: 0.02% to 0.15%,
    Si: 0.01% to 2.0%,
    Mn: 0.5% to 1.8%,
    P: 0.0001% to 0.015%,
    S: 0.0002% to 0.0015%,
    Al: 0.005% to 0.15%,
    O: 0.01% or less,
    N: 0.010% or less, and
    H: 0.02 ppm or less, and
    optionally at least one selected from
    Nb: 0% to 0.10%,
    Ca: 0% to 0.005%,
    Ni: 0% to 2.0%,
    Ti: 0% to 0.1%,
    Cu: 0% to 1.0%,
    Cr: 0% to 1.0%,
    Mo: 0% to 0.60%,
    W: 0% to 1.0%,
    V: 0% to 0.10%,
    Zr: 0% to 0.050%,
    REM: 0% to 0.01%,
    Mg: 0% to 0.01%,
    B: 0% to 0.0020%,
    Hf: 0% to 0.2%,
    Ta: 0% to 0.2%,
    Re: 0% to 0.005%,
    Sn: 0% to 0.3%, and
    Sb: 0% to 0.3%,
    the remainder being Fe and an incidental impurity element,
    wherein retained austenite constitutes 0% to 3% by area fraction, a hydrogen diffusion coefficient is 1.5×10^{-10} m^2/s or more at room temperature, and a hydrogen solubility is 0.05 mass ppm/$\sqrt{P}$ or less.

2. The steel material for a line pipe according to Claim 1, wherein the chemical composition is, on a mass percent basis,

    Nb: 0.001% to 0.10%,
    Ca: 0.0001% to 0.005%,
    Ni: 0.01% to 2.0%,
    Ti: 0.005% to 0.1%,
    Cu: 0.01% to 1.0%,
    Cr: 0.01% to 1.0%,
    Mo: 0.01% to 0.60%,
    W: 0.01% to 1.0%,
    V: 0.01% to 0.10%,
    Zr: 0.0001% to 0.050%,
    REM: 0.0001% to 0.01%,
    Mg: 0.0001% to 0.01%,
    B: 0.0001% to 0.0020%,
    Hf: 0.0001% to 0.2%,
    Ta: 0.0001% to 0.2%,
    Re: 0.0001% to 0.005%,
    Sn: 0.0001% to 0.3%, and
    Sb: 0.0001% to 0.3%.

3. The steel material for a line pipe according to Claim 1 or 2, comprising bainite or martensite at a quarter thickness position, wherein the bainite constitutes 90% or more by area fraction, or the martensite constitutes 90% or more by area fraction.

4. A method for producing a steel material for a line pipe, the method comprising:

   a heating step of heating a steel raw material with the chemical composition according to Claim 1 or 2 at 1000°C to 1250°C;
   a hot rolling step of rolling the steel raw material heated in the heating step at a finish rolling temperature of an Ar_3 transformation point or higher;
   a controlled cooling step of cooling a hot-rolled steel sheet produced in the hot rolling step under conditions in which a cooling start temperature is the Ar_3 transformation point or higher in terms of a steel sheet surface temperature, a cooling start time difference between a front end and a rear end of the hot-rolled steel sheet is 50 seconds or less, and in terms of a temperature at 0.25 mm below a surface of the steel sheet and at a center of a sheet thickness, an average cooling rate from 750°C to 550°C ranges from 15°C/s to 50°C/s and a cooling stop temperature ranges from 250°C to 650°C; and
   any one of a stabilization treatment step of subjecting the steel sheet produced in the controlled cooling step to stabilization treatment and a dehydrogenation treatment step of subjecting the steel sheet produced in the controlled cooling step to dehydrogenation treatment.

5. A steel pipe for a line pipe, the steel pipe having a chemical composition containing:

   on a mass percent basis,
   C: 0.02% to 0.15%,
   Si: 0.01% to 2.0%,
   Mn: 0.5% to 1.8%,
   P: 0.0001% to 0.015%,
   S: 0.0002% to 0.0015%,
   Al: 0.005% to 0.15%,
   O: 0.01% or less,
   N: 0.010% or less, and
   H: 0.02 ppm or less, and
   optionally at least one selected from
   Nb: 0% to 0.10%,
   Ca: 0% to 0.005%,
   Ni: 0% to 2.0%,
   Ti: 0% to 0.1%,
   Cu: 0% to 1.0%,
   Cr: 0% to 1.0%,
   Mo: 0% to 0.60%,
   W: 0% to 1.0%,
   V: 0% to 0.10%,
   Zr: 0% to 0.050%,
   REM: 0% to 0.01%,
   Mg: 0% to 0.01%,
   B: 0% to 0.0020%,
   Hf: 0% to 0.2%,
   Ta: 0% to 0.2%,
   Re: 0% to 0.005%,
   Sn: 0% to 0.3%, and
   Sb: 0% to 0.3%,
   the remainder being Fe and an incidental impurity element,
   wherein retained austenite constitutes 0% to 3% by area fraction, a hydrogen diffusion coefficient is 1.5×10^{-10} m^2/s or more at room temperature, and a hydrogen solubility is 0.05 mass ppm/$\sqrt{P}$ or less.

6. The steel pipe for a line pipe according to Claim 5, wherein the chemical composition is, on a mass percent basis,

   Nb: 0.001% to 0.10%,

Ca: 0.0001% to 0.005%,
Ni: 0.01% to 2.0%,
Ti: 0.005% to 0.1%,
Cu: 0.01% to 1.0%,
Cr: 0.01% to 1.0%,
Mo: 0.01% to 0.60%,
W: 0.01% to 1.0%,
V: 0.01% to 0.10%,
Zr: 0.0001% to 0.050%,
REM: 0.0001% to 0.01%,
Mg: 0.0001% to 0.01%,
B: 0.0001% to 0.0020%,
Hf: 0.0001% to 0.2%,
Ta: 0.0001% to 0.2%,
Re: 0.0001% to 0.005%,
Sn: 0.0001% to 0.3%, and
Sb: 0.0001% to 0.3%.

7. The steel pipe for a line pipe according to Claim 5 or 6, wherein the steel pipe has bainite or martensite at a quarter thickness position from an inner surface of the steel pipe, and the bainite constitutes 90% or more by area fraction, or the martensite constitutes 90% or more by area fraction.

8. A method for producing a steel pipe for a line pipe, the method comprising:

a heating step of heating a steel raw material with the chemical composition according to Claim 5 or 6 at 1000°C to 1250°C;
a hot rolling step of rolling the steel raw material heated in the heating step at a finish rolling temperature of an Ar_3 transformation point or higher;
a controlled cooling step of cooling a hot-rolled steel sheet produced in the hot rolling step under conditions in which a cooling start temperature is the Ar_3 transformation point or higher in terms of a steel sheet surface temperature, a cooling start time difference between a front end and a rear end of the hot-rolled steel sheet is 50 seconds or less, and in terms of a temperature at 0.25 mm below a surface of the steel sheet and at a center of a sheet thickness, an average cooling rate from 750°C to 550°C ranges from 15°C/s to 50°C/s and a cooling stop temperature ranges from 250°C to 650°C;
any one of a pipe production step of bending the hot-rolled steel sheet and butt-welding both end portions thereof after the controlled cooling step, and a pipe production step of forming the hot-rolled steel sheet into a cylindrical shape by cold roll forming and subjecting both circumferential end portions of the cylindrical shape to butt electric resistance welding after the controlled cooling step; and
any one of a stabilization treatment step of subjecting the steel pipe produced in the pipe production step to stabilization treatment and a dehydrogenation treatment step of subjecting the steel pipe produced in the pipe production step to dehydrogenation treatment.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/035559

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; ***C21D 8/02***(2006.01)i; ***C21D 8/10***(2006.01)i; ***C22C 38/60***(2006.01)i
FI: C22C38/00 301F; C22C38/00 301Z; C22C38/60; C21D8/02 C; C21D8/10 C

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)

C22C38/00-38/06; C21D8/02; C21D8/10

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2020/137812 A1 (JFE STEEL CORPORATION) 02 July 2020 (2020-07-02) claims	1-8
A	JP 2022-68942 A (JFE STEEL CORPORATION) 11 May 2022 (2022-05-11) claims	1-8
A	WO 2014/156187 A1 (JFE STEEL CORPORATION) 02 October 2014 (2014-10-02) claims	1-8
A	WO 2019/064459 A1 (JFE STEEL CORPORATION) 04 April 2019 (2019-04-04) claims	1-8
A	JP 2012-122103 A (SUMITOMO METAL IND LTD) 28 June 2012 (2012-06-28) claims	1-8
A	WO 2022/030818 A1 (POSCO) 10 February 2022 (2022-02-10) claims	1-8

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

* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier application or patent but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family
“O” document referring to an oral disclosure, use, exhibition or other means	
“P” document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search **06 December 2023**	Date of mailing of the international search report **19 December 2023**
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

International application No.
PCT/JP2023/035559

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2018-12855 A (NIPPON STEEL & SUMITOMO METAL CORP) 25 January 2018 (2018-01-25) claims	1-8
P, A	WO 2022/209896 A1 (JFE STEEL CORPORATION) 06 October 2022 (2022-10-06) claims	1-8

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/035559

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	EP 3904541 A1 claims US 2022/0064770 A1 CN 113272452 A	
JP 2022-68942 A	11 May 2022	(Family: none)	
WO 2014/156187 A1	02 October 2014	EP 2980246 A1 claims US 2016/0053355 A1 CN 105102657 A	
WO 2019/064459 A1	04 April 2019	EP 3677698 A1 claims CN 111183238 A	
JP 2012-122103 A	28 June 2012	(Family: none)	
WO 2022/030818 A1	10 February 2022	EP 4194581 A1 claims CN 116113722 A JP 2023-536356 A	
JP 2018-12855 A	25 January 2018	(Family: none)	
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Form PCT/ISA/210 (patent family annex) (January 2015)

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