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(54) **LINE PIPE STEEL MATERIAL HAVING EXCELLENT HYDROGEN EMBRITTLEMENT RESISTANCE, MANUFACTURING METHOD THEREFOR, LINE PIPE STEEL TUBE HAVING EXCELLENT HYDROGEN EMBRITTLEMENT RESISTANCE, AND MANUFACTURING METHOD THEREFOR**

(57) To provide a steel material for a line pipe with high strength and high hydrogen embrittlement resistance in a high-pressure hydrogen gas environment, a method for producing the steel material, a steel pipe for a line pipe, and a method for producing the steel pipe, 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 steel material for a line pipe with high hydrogen embrittlement resistance, wherein the steel material has a specific chemical composition and a specific microstructure, the fatigue limit stress in hydrogen at 1 MPa or more is 200 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is 0.90 or more.

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Description

Technical Field

[0001] The present invention relates to a steel material for a line pipe with high hydrogen embrittlement resistance, 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. On the other hand, 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. A steel material used in such an environment has a concern about the occurrence of "hydrogen embrittlement" in which hydrogen enters the steel and degrades its characteristics. 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 austenite 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 austenite 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 a relative concentration of diffusible hydrogen 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 has, within the tensile strength range of 900 to 950 MPa in the atmosphere, increased drawing and elongation as compared with JIS G 3128 SHY685NS in a 45-MPa hydrogen atmosphere and improved high-pressure hydrogen environment embrittlement resistance.

[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 drawing characteristics even in a 45-MPa hydrogen atmosphere and with high 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 tempering 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 sheet 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 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: (written by) The Japan Society for Heat Treatment, Introduction: Microstructure and Properties of Metallic Materials - Heat Treatment and Microstructure Controlling for Materials, 2004

Summary of Invention

Technical Problem

[0013] Because the pressure in a line pipe fluctuates during operation or periodical shutdowns, a repeated stress is 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 strength in hydrogen gas. Therefore, 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, a method for producing the steel material, a steel pipe for a line pipe, and a method for producing the steel pipe, 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).

[0015] The phrase "high hydrogen embrittlement resistance in a high-pressure hydrogen gas environment", as used herein, means that the fatigue limit stress in hydrogen at which no fracture occurs at a number of repetitions of 2,000,000 is 200 MPa or more and the fatigue limit stress in hydrogen/fatigue limit stress in an inert gas environment is 0.90 or more, as determined by a fatigue test in accordance with ASTM E466, 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 compression, and a stress ratio of $R = -1.0$, at room temperature ($20^{\circ}\text{C} \pm 10^{\circ}\text{C}$) in both environments of hydrogen gas with 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 limit stress in hydrogen in the above environment is 200 MPa or more and the fatigue limit stress in hydrogen of a steel material in the above environment/fatigue limit stress in an inert gas environment is 0.90 or more, it is possible to design a steel structure for hydrogen, such as a long-life 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 extensively studied conditions to be satisfied by a steel material for producing a steel sheet for a line pipe and a steel pipe for a line pipe with high hydrogen embrittlement resistance and have invented a new steel sheet for a high-strength line pipe and a new steel pipe for a line pipe. A steel material and a steel pipe according to the present invention have high strength. 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 with high hydrogen embrittlement resistance, the steel material having a chemical composition comprising:

on a mass percent basis,

C: 0.02% to 0.15%,

Si: 0.01% to 2.0%,

Mn: 0.5% to 1.5%,

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: 0.0010% or less, and

optionally at least one selected from

Nb: 0% to 0.10%,

Ca: 0% to 0.005%,

Ti: 0% to 0.1%,

Ni: 0% to 2.0%,

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 0.050%,

Mg: 0% to 0.050%,

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 an area fraction of retained austenite in the steel material is 0% to 3%, an area fraction of bainite at a quarter thickness position of the steel material, is 90% or more, fatigue limit stress of the steel material in hydrogen at 1 MPa or more is 200 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is 0.90 or more.

[2] The steel material for a line pipe with high hydrogen embrittlement resistance according to [1], wherein the chemical composition contains, on a mass percent basis,

Nb: 0.001% to 0.10%,

Ca: 0.0001% to 0.005%,

Ti: 0.005% to 0.1%,

Ni: 0.01% to 2.0%,

Cu: 0.01% to 1.0%,

Cr: 0.01% to 1.0%,

Mo: 0.01% to 0.60%,

W: 0.01% to 1.0%,

V: 0.01% to 0.10%,

Zr: 0.0001% to 0.050%,

REM: 0.0001% to 0.050%,

Mg: 0.0001% to 0.050%,

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] A method for producing a steel material for a line pipe, the method including:

a heating step of heating a steel raw material having 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 with a finish rolling temperature of an Ar_3 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 point or higher in terms of a temperature at a surface of the steel sheet, a cooling start time difference between a front end and a rear end of the hot-rolled steel sheet is 50 seconds or less, an average cooling rate from 750°C to 550°C ranges from 15°C/s to 50°C/s in terms of a temperature at a middle of a thickness of the steel sheet, and a cooling stop temperature ranges from 250°C to 650°C; and

a dehydrogenation treatment step of holding the steel sheet produced in the controlled cooling step in the range of room temperature to 550°C.

[4] A steel pipe for a line pipe with high hydrogen embrittlement resistance, 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 1.5%,

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: 0.0010% or less, and

optionally at least one selected from

Nb: 0% to 0.10%,

Ca: 0% to 0.005%,

Ti: 0% to 0.1%,

Ni: 0% to 2.0%,

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 0.050%,

Mg: 0% to 0.050%,

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 an area fraction of retained austenite in the steel pipe is 0% to 3%, an area fraction of bainite at a quarter thickness position from an inner surface of the steel pipe is 90% or more, fatigue limit stress of the steel pipe in hydrogen at 1 MPa or more is 200 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is 0.90 or more.

[5] The steel pipe for a line pipe with high hydrogen embrittlement resistance according to [4], wherein the chemical composition contains, on a mass percent basis,

Nb: 0.001% to 0.10%,

Ca: 0.0001% to 0.005%,

Ti: 0.005% to 0.1%,

Ni: 0.01% to 2.0%,

Cu: 0.01% to 1.0%,

Cr: 0.01% to 1.0%,
 Mo: 0.01% to 0.60%,
 W: 0.01% to 1.0%,
 V: 0.01% to 0.10%,
 Zr: 0.0001% to 0.050%,
 REM: 0.0001% to 0.050%,
 Mg: 0.0001% to 0.050%,
 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%.

[6] A method for producing a steel pipe for a line pipe, the method including:

a heating step of heating a steel raw material having the chemical composition according to [4] or [5] at 1000°C to 1250°C;
 a hot rolling step of rolling the steel raw material heated in the heating step with a finish rolling temperature of an Ar_3 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 point or higher in terms of a temperature at a surface of the steel sheet, a cooling start time difference between a front end and a rear end of the hot-rolled steel sheet is 50 seconds or less, an average cooling rate from 750°C to 550°C ranges from 15°C/s to 50°C/s in terms of a temperature at a middle of a thickness of the steel sheet, 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
 a dehydrogenation treatment step of holding a steel pipe produced in the pipe production step in the range of room temperature to 550°C.

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 component composition (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 or fatigue limit stress cannot be sufficient at a C content of less than 0.02%. Thus, the C content is 0.02% or more. Preferably, the C content is 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. Preferably, the C content is 0.13% or less. Furthermore, more than 0.08% results in a decrease in SSCC resistance (resistance to sulfide stress corrosion cracking) and HIC (hydrogen-induced cracking) resistance due to an increase in the hardness of a surface layer portion or a center segregation zone during controlled cooling. Furthermore, toughness also deteriorates. 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 0.1% 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 0.5% results in lower toughness or weldability, and the Si content is still more preferably 0.5% or less.

Mn: 0.5% to 1.5%

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

P: 0.0001% to 0.015%

[0026] P is an incidental impurity element, reduces weldability, and reduces the HIC resistance due to an increase in the hardness of a center segregation zone. 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, from the perspective of refining costs, the P content is 0.0001% or more.

S: 0.0002% to 0.0015%

[0027] S is an incidental impurity element, forms a MnS inclusion in steel, and reduces the HIC 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 better, from the perspective of refining costs, the S content is 0.0002% or more.

Al: 0.005% to 0.15%

[0028] Al is added as a deoxidizing agent, but there is no effect of addition at less than 0.005%. Thus, the Al content is 0.005% or more. The Al content is preferably 0.01% or more, more preferably 0.03% 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. More preferably, the O content is less than 0.003%. Although the lower limit is not particularly limited, the O content is 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, from the perspective of improving the toughness, a lower N content is desirable, but excessive reduction increases the steelmaking cost, so that the N content is preferably 0.00001% or more. The N content is preferably 0.001% or more.

H: 0.0010% or less

[0031] H may be introduced into a steel material in various steps during production, and a large amount of H introduced increases the risk of cracking after solidification and accelerates fatigue crack growth. A large amount of H introduced also reduces the fatigue limit stress, and it is therefore important to decrease the amount of hydrogen in the steel material. Since these effects are not problematic at a H content of 0.0010% or less, the H content is 0.0010% or less. The H content is preferably 0.0005% or less, more preferably 0.0003% or less, still more preferably 0.0001% or less. On the other hand, a H content of less than 0.00001% causes an increase in cost, and the H content is therefore preferably 0.00001% 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, Ti, Ni, 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 effective in increasing the strength and toughness of a steel material, but more than 0.10% results in a weld with lower toughness, 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. Although the Nb content may be 0% or more, the effects of containing Nb are difficult to obtain at a Nb content of less than 0.001%, so that when Nb is contained the Nb content is preferably 0.001% or more. 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, not only the effect is saturated but also the HIC resistance decreases due to a decrease in the cleanliness of steel, so that when Ca is contained the Ca content is limited to 0.005% or less. The Ca content is preferably 0.003% or less. The Ca content is more preferably 0.002% or less. Although the Ca content may be 0% or more, the effect of addition is difficult to obtain at less than 0.0001%, so that when Ca is contained the Ca content is preferably 0.0001% or more. The Ca content is more preferably 0.001% or more.

Ti: 0% to 0.1%

[0035] Ti is an element effective in increasing the strength and toughness of a steel material, but more than 0.1% results in a weld with lower toughness, so that when Ti is contained the Ti content is 0.1% or less. The Ti content is preferably 0.05% or less. The Ti content is more preferably 0.03% or less, still more preferably 0.02% or less. Although the Ti content may be 0% or more, the effects of containing Ti are difficult to obtain at a Ti content of less than 0.005%, so that when Ti is contained the Ti content is preferably 0.005% or more. The Ti content is more preferably 0.008% or more.

Ni: 0% to 2.0%

[0036] Ni is an element effective in improving the toughness and increasing the strength, but, for cost reduction, when Ni is contained the Ni content is 2.0% or less. The Ni content is preferably 1.5% or less. The Ni content is more preferably 1.2% or less, still more preferably 1.0% or less. The Ni content may be 0% or more and is preferably 0.01% or more to achieve the above effects.

Cu: 0% to 1.0%

[0037] Cu is an element effective in improving the toughness and increasing the strength, but an excessively high Cu content results in a decrease in weldability, 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. The Cu content may be 0% or more and is preferably 0.01% or more to achieve the above effects.

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 and a decrease in the SSCC resistance. 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. The Cr content is more preferably 0.5% or less, still more preferably 0.1% or less. The Cr content may be 0% or more and is preferably 0.01% or more to achieve the effect. The Cr content is more preferably 0.02% or more.

Mo: 0% to 0.60%

[0039] Mo is an element effective in improving the toughness and increasing 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 and a decrease in the SSCC resistance. Furthermore, weldability also deteriorates. Thus, when Mo is contained, the Mo content is 0.60% or less, preferably 0.50% or less, more preferably 0.40% or less. Most preferably, the Mo content is 0.03% or less. The Mo content may be 0% or more and is preferably 0.005% or more to achieve the above effects. The Mo content is more preferably 0.01% or more.

W: 0% to 1.0%

[0040] W contributes to an increase in the strength of a steel pipe, 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 further reduce the cost, the W content is more preferably 0.5% or less. The W content is still more preferably 0.03% or less. The W content may be 0% or more and is preferably 0.01% or more to achieve the 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, but a V content of more than 0.10% results in a weld with lower toughness, so that when V is contained the V 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, but the effects of containing V are difficult to obtain at a content of less than 0.01%, so that the V content is preferably 0.01% or more.

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

[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. On the other hand, the effects are saturated at more than 0.050%, so that when they are contained each content is 0.050% or less. More specifically, when Zr is contained, the Zr content is 0.050% or less. The Zr content is preferably 0.040% or less. The Zr content is more preferably 0.030% or less. The Zr content is still more preferably 0.010% or less, most preferably 0.005% or less. When REM is contained, the REM content is 0.050% or less. The REM content is preferably 0.040% or less. The REM content is more preferably 0.030% or less. When Mg is contained, the Mg content is 0.050% or less. The Mg content is preferably 0.040% or less. The Mg content is more preferably 0.030% or less. Each element content may be 0% or more, but the effects of containing these elements are difficult to obtain at a content of less than 0.0001%, so that each content is preferably 0.0001% or more. More specifically, 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, 0.0010% or less is still more preferred. The B content may be 0% or more and is preferably 0.0001% or more to achieve the effects. More preferably, the B content is 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, but 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. More specifically, 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. The Hf or Ta content may be 0% or more and is preferably 0.0001% or more to achieve the effects. More specifically, the Hf content is preferably 0.0001% or more. More preferably, the Hf content is 0.0010% or more. The Ta content is preferably 0.0001% or more. More preferably, the Ta content is 0.0010% or more.

Re: 0% to 0.005%

[0045] Re contributes to an increase in the strength of a steel material, but a 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 is preferably 0.0001% or more to achieve the effects. More preferably, the Re content is 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. More specifically, 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 is preferably 0.0001% or more to achieve the effects. More specifically, the Sn content is preferably 0.0001% or more. More preferably, the Sn content is 0.0010% or more. The Sb content is preferably 0.0001% or more. More preferably, the Sb content is 0.0010% or more.

[0047] In the chemical composition of a steel sheet and a steel pipe, the remainder other than these 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

Retained austenite: 0% to 3%

[0049] Austenite remaining in a steel material may increase the amount of hydrogen in the steel and increase hydrogen embrittlement sensitivity. Furthermore, when 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 is 3% or less to reduce the fatigue crack growth rate. A decrease in residual γ can reduce the occurrence of a fatigue crack in a hydrogen environment and reduce the decrease in the fatigue limit stress in hydrogen. Thus, a content of retained austenite is 3% or less. The content of retained austenite preferably constitutes 2% or less. The content of retained austenite is more preferably 1% or less. The content of retained austenite may be 0%.

Area fraction of Bainite at quarter thickness position: 90% or more

[0050] To increase the tensile strength to 520 MPa or more, the steel microstructure needs to be a bainite microstructure. 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. Different microstructures, such as ferrite, martensite, pearlite, a martensite-austenite constituent (MA), or retained austenite, in the bainite microstructure reduces the strength or toughness. Therefore, the volume fraction of microstructures other than the bainite phase is therefore preferably as small as possible.

[0051] Regarding the occurrence of a fatigue crack, 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 fatigue limit stress in hydrogen. Consequently, the fatigue limit stress/fatigue limit stress in an inert gas environment becomes less than 0.90. To address this, it is necessary to reduce the relative proportion of the soft phase. Therefore, an

area fraction of bainite is 90% or more. The area fraction of bainite is preferably 92% or more. The area fraction of bainite is more preferably 95% or more, still more preferably 98% or more. The upper limit is not particularly limited, and the area fraction of bainite may be 100%. 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, the metallic microstructure at the quarter thickness position from the inner surface of a steel pipe is defined, and for a steel material, the metallic microstructures at the quarter thickness positions are defined to achieve the above effects regardless of which surface is the inner surface side of a steel pipe.

[0052] Fatigue limit stress in hydrogen at 1 MPa or more is 200 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is 0.90 or more

[0053] When the fatigue limit stress in hydrogen at 1 MPa or more is less than 200 MPa, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is less than 0.90, it is necessary to increase the thickness of a steel material (for a steel pipe, the thickness of the steel pipe) because of a large difference from known pipeline design conditions. Thus, the fatigue limit stress in hydrogen at 1 MPa or more is 200 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is 0.90 or more. The fatigue limit stress in hydrogen at 1 MPa or more is preferably 220 MPa or more. The fatigue limit stress in hydrogen at 1 MPa or more is more preferably 250 MPa or more, still more preferably 270 MPa or more. Although the upper limit is not particularly limited, the fatigue limit stress in hydrogen at 1 MPa or more is preferably 500 MPa or less. The fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is preferably 0.92 or more. The fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is more preferably 0.94 or more, still more preferably 0.96 or more. Although the upper limit is not particularly limited, the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment may be 1.1 or less. The term "inert gas", as used herein, includes six elements of Group 0 of the periodic table, helium, neon, argon, krypton, xenon, and radon, as well as air, and the term "inert gas environment" refers to an environment containing any one of these.

[0054] In the present invention, the chemical composition and metallic microstructure described above can improve the fatigue limit stress in a high-pressure hydrogen atmosphere and reduce the decrease in the fatigue limit stress in hydrogen/fatigue limit stress in an inert gas and can achieve a tensile strength of 520 MPa or more. Thus, the present invention can be applied to a hydrogen line pipe. The upper limit of the tensile strength is preferably, but not limited to, 950 MPa or less.

[0055] The sheet thickness of a steel material is preferably, but not limited to, 5 mm or more. The sheet thickness is preferably 30 mm or less.

[0056] Next, a method for producing a steel material 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 a dehydrogenation treatment step. Unless otherwise specified, the temperature in the following description is the temperature at the middle of the sheet 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 middle 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 Step

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

[0057] When the heating temperature of a steel raw material, such as a billet or a slab, is less than 1000°C, the diffusion of microsegregated impurity elements, 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. 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 is preferably 1200°C or less. The heating temperature is more preferably 1180°C or less.

Hot Rolling Step

Finish hot-rolling temperature: A_{r3} point or higher

[0058] 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 A_{r3} point, which is the ferrite formation temperature. This is because, in a process including cooling immediately after hot rolling, a temperature lower than the A_{r3} point results in strength reduction due to the formation of a soft ferrite phase. The finish temperature of the hot rolling is preferably $A_{r3} +$

30°C or more. The finish temperature of the hot rolling is more preferably $Ar_3 + 50^\circ\text{C}$ 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. The finish temperature of the hot rolling is more preferably 1200°C or less, still more preferably 1150°C or less.

[0059] The Ar_3 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.

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

[0060] Each alloying element indicates its content (% by mass).

Controlled Cooling Step

Cooling start temperature of controlled cooling: Ar_3 point or higher in terms of temperature at surface of steel sheet

[0061] When the steel sheet surface temperature at the start of cooling is lower than the Ar_3 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 point or higher. The steel sheet surface temperature at the start of cooling is preferably $Ar_3 + 30^\circ\text{C}$ or more, more preferably $Ar_3 + 50^\circ\text{C}$ or more. An excessively high cooling start temperature results in an excessively large grain size and lower toughness, so that the steel sheet surface temperature at the start of cooling is preferably less than 1250°C. The steel sheet surface temperature at the start of cooling is more preferably 1200°C or less, still more preferably 1150°C or less. The steel sheet surface temperature at the start of cooling is the temperature of the rear end of the steel sheet at which the cooling start temperature is lowest.

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

[0062] 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, more preferably 40 seconds or less. Although the steel sheet length can be shortened to reduce the cooling start time difference, it reduces the productivity, and the cooling start time difference is therefore preferably reduced by increasing the steel sheet line speed. The lower limit may be, but is not limited to, 0 seconds or more.

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

[0063] When the average cooling rate from 750°C to 550°C at the middle of the sheet thickness is less than 15°C/s, a bainite microstructure is not formed, and the strength decreases. Thus, the average cooling rate at the middle of the sheet thickness is 15°C/s or more. From the perspective of reducing variations in microstructure, the average cooling rate at the middle of the sheet thickness is preferably 17°C/s or more. The average cooling rate at the middle 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 suppress variations in bainite grain size, the average cooling rate at the middle of the sheet thickness is 50°C/s or less. The average cooling rate at the middle of the sheet thickness is preferably 45°C/s or less. The average cooling rate at the middle of the sheet thickness is more preferably 40°C/s or less. Cooling to a steel sheet temperature of 550°C or less at the middle of the sheet thickness is not particularly limited. However, from the perspective of reducing variations in the microstructure and grain size, for example, the average cooling rate from 550°C to 300°C is preferably 15°C/s or more. The average cooling rate from 550°C to 300°C is preferably 50°C/s or less.

Cooling stop temperature: 250°C to 650°C

[0064] 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 625°C or less. The cooling stop temperature is more preferably 600°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. 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, the cooling stop temperature should be 250°C or more to decrease the amount of hydrogen in the steel. The cooling stop temperature is preferably 270°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 middle of the sheet thickness.

Dehydrogenation Treatment Step

[0065] 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 reduce the amount of hydrogen in the steel, and a steel sheet 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 the wall thickness t (mm) of a steel pipe and the hydrogen diffusion coefficient D (mm $\cdot$ s $^{-1}$) in the steel at room temperature using the following formula (A).

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

[0066] The hydrogen diffusion coefficient varies depending on components contained and the metallic microstructure and may range from, for example, 1×10^{-5} to 5×10^{-3} mm 2 /s, more preferably 5×10^{-4} mm 2 /s or less.

[0067] The dehydrogenation treatment step is performed before pipe production or 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 each temperature) at a temperature at which the value of D in the formula (A) is held. On the other hand, an excessively high temperature T in the dehydrogenation step results in a significant decrease in the material strength, and the dehydrogenation treatment temperature T is 550°C or less. The dehydrogenation treatment temperature T is preferably 500°C or less. The dehydrogenation treatment temperature T is more preferably 400°C or less, still more preferably 300°C or less. Furthermore, the dehydrogenation treatment temperature T is 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 preferably 50°C or more. The dehydrogenation treatment temperature T is more preferably 100°C or more, still more preferably 150°C or more. The room temperature refers to 20°C $\pm$ 10°C.

[0068] In particular, when heating, it takes time for the temperature T_c at the middle of the sheet thickness of a steel material or a steel pipe to reach the temperature of the ambient in the dehydrogenation treatment step (dehydrogenation treatment temperature T). Therefore, 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 middle of the sheet thickness. Thus, it is preferable to hold for R (s) or more after the temperature T_c at the middle of the sheet thickness reaches a target dehydrogenation treatment temperature T . Furthermore, to achieve a predetermined fatigue limit stress in hydrogen and a predetermined fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment, it is necessary to appropriately adjust the amount of hydrogen in a steel material in a surface layer portion and at the middle of the sheet thickness. For this purpose, it is preferable to hold the steel material at the dehydrogenation treatment 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 T_c at the middle of the sheet thickness reaches the target dehydrogenation treatment temperature T . The temperature T_c at the middle 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.

[0069] 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 the 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 μ m in thickness, the effects of scale removal can be obtained.

Second Embodiment

[0070] Furthermore, a UOE steel pipe as an example of a high-strength steel pipe for a line pipe can be produced by specifying the following production conditions, and the production method and conditions are more specifically described below. The chemical composition, the metallic microstructure, the fatigue limit stress in hydrogen at 1 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment of a UOE steel pipe are the same as those described for the steel material of the first embodiment. Further, the heating step, the hot rolling step, the controlled cooling step after hot rolling, 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

[0071] A UOE steel pipe is produced by bending a hot-rolled steel sheet, more specifically, groove-cutting an end portion of the hot-rolled steel sheet, forming the steel sheet into a steel pipe shape by C-press, U-press, and O-press, seam-welding a butt joint by inner surface welding and outer surface welding, and performing an expansion step if necessary. 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 an expansion.

Third Embodiment

[0072] Furthermore, an electric-resistance-welded steel pipe as an example of a high-strength steel pipe for a line pipe according to the present invention can be produced by specifying the following production conditions, and the production method and conditions are more specifically described below. The chemical composition, the metallic microstructure, the fatigue limit stress in hydrogen at 1 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment of the steel material are the same as those described for the steel material of the first embodiment. Further, the steps other than the cooling step after rolling and the pipe production step (the heating step, the hot rolling step, and the dehydrogenation treatment step) in the production method are performed in the same manner as described for the steel material.

Cooling Step after Rolling (Controlled Cooling Step)

[0073] 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

[0074] 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 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. 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, the cooling stop temperature should be 250°C or more to decrease the amount of hydrogen in the steel. The cooling stop temperature is preferably 390°C or more. More preferably, the cooling stop temperature is 450°C or more. The cooling stop temperature is still more preferably 480°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 middle of the sheet thickness.

[0075] A hot-rolled steel sheet thus produced is then coiled. The coiling temperature is preferably 650°C or less. The coiling temperature is preferably 250°C or more.

Pipe Production Step

[0076] 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.

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

[0077] The thickness of a hot-rolled steel sheet refers to the thickness of the hot-rolled steel sheet before the sizing step.

$$X < p \leq X \times 1.5 \quad (2)$$

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

[0078] 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.

[0079] 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 may have any upper limit, the load on the facilities increases with the radius, and the electric-resistance-welded steel 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, more preferably 500 MPa or more, to withstand pipeline operation gas pressures. On the other hand, to avoid an increase in hydrogen embrittlement sensitivity, the yield strength is preferably 560 MPa or less.

[0080] 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 may 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.

[0081] 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.

[0082] 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. In the present invention, from the perspective of reducing the shear residual stress, 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 in order to reduce the absolute value of the residual stress in the pipe axis direction. On the other hand, when the internal pressure p exceeds the right side ($X \times 1.5$) 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 fatigue resistance in hydrogen decreases.

[0083] 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 sheet 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

[0084] Next, 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.

[0085] First, billets with the chemical compositions shown in Tables 1-1, 1-2, and 1-3 were produced. The casting speed ranged from 0.05 to 0.2 m/min. The billets were heated to 1000°C to 1100°C. Hot rolling was then performed at 1000°C $\pm$ 50°C. The time difference between the front and rear ends of the hot rolling ranged from 30 to 45 seconds, and a steel sheet was produced at a target thickness of 20 mm. Controlled cooling was started when the surface temperature reached $A_{r3} + 50^\circ\text{C}$ as a cooling start temperature. Steel materials were then produced under the conditions shown in Tables 2-1, 2-2, and 2-3. For some steel materials (steel materials Nos. 1 to 14, 16 to 30, and 92), 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. For some steel materials (steel materials Nos. 15, 31 to 55, and 93 to 98), 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 14, 16 to 30, and 92 and Nos. 15, 31 to 55, and 93 to 98. In the dehydrogenation treatment of Example 1, the dehydrogenation treatment was performed in the range of room temperature to 550°C. In the dehydrogenation treatment temperature shown in Table 2, Y indicates that the dehydrogenation treatment is performed in the range of room temperature to 550°C, and N indicates that the dehydrogenation treatment temperature is more than 550°C. After it was confirmed that the temperature T_c at the middle of the sheet thickness reached room temperature as a target temperature, held for R (s) so as to satisfy the formula (A).

[0086] Furthermore, billets with the chemical compositions shown in the steel No. 15 in Table 1-1 and the steel No. 56 in Table 1-2 were produced at various casting speeds shown in Table 3 and were heated to 1000°C to 1100°C. Hot rolling was then performed at 1000°C $\pm$ 50°C. The time difference between the front and rear ends of the hot rolling ranged from 30 to 45 seconds, and a steel sheet was produced at a target thickness of 20 mm. Controlled cooling was started when the surface temperature reached $A_{r3} + 50^\circ\text{C}$ as a cooling start temperature. Steel materials and steel pipes were then produced under the conditions shown in Table 3. The steel materials Nos. 15-1 to 15-3 and 56-1 to 56-3 were steel materials as they were. The steel pipes Nos. 15-11, 15-12, 56-11, and 56-12 were produced by a pipe production step of bending the hot-rolled steel sheet and butt-welding both end portions thereof. The steel pipes Nos. 15-13 and 56-13 were produced by 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. The metallic microstructure and mechanical properties were evaluated. The evaluation method is described below. The tempering temperature was arbitrarily adjusted so that the materials had a tensile strength in the range of 520 MPa to 700 MPa. Tables 2-1, 2-2, 2-3, and 3 show the evaluation results of the metallic microstructure and the material quality of each of the steel materials and steel pipes thus produced. The evaluation method is described below.

Retained Austenite Measurement

[0087] A sample for metallic microstructure observation was taken from a central portion of the sheet width in a central portion 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 $\text{Co-K}\alpha$ 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

[0088] Test specimens taken from a central portion in the longitudinal direction of a steel sheet at a quarter thickness position and test specimens taken from a central portion in the longitudinal direction of a steel pipe at a quarter thickness position were buffed and etched using 3% by volume nital. Three visual fields were then observed with an optical microscope at a magnification of 100 times, and scanning electron microscope photographs were taken at an appropriate magnification in the range of 1000 to 5000 times to observe bainite. The bainite was visually identified by comparison with the microstructure photograph of Non Patent Literature 2, and the microstructure fraction was determined as an area fraction of bainite from an image produce by binarizing the bainite and the other region in an optical micrograph or a SEM photograph based on the above identification by image analysis. The average value of the values obtained from the optical micrograph or the SEM photograph was defined as an area fraction of a bainite.

Tensile Strength (TS)

[0089] 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.

Hydrogen Temperature-Programmed Analysis

[0090] 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 cylindrical shape with 30 mm in length and 7Φ in diameter 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 is the amount of H shown in Tables 1-1, 1-2, and 1-3 before being subjected to a high-pressure hydrogen fatigue test as explained in the item described later.

Fatigue Test

[0091] A fatigue test was conducted at room temperature (20°C ± 10°C) in a high-pressure gas mixture atmosphere in the atmosphere in accordance with ASTM E466, Fatigue Testing, at a frequency in the range of 1 to 15 Hz, a repetitive waveform of a sine wave, a control method of load control, a load condition of uniaxial tension and compression, and a stress ratio of R = -1.0. The stress at which no fracture occurred at a number of repetitions of 10,000,000 was defined as the fatigue limit strength in the atmosphere.

High-Pressure Hydrogen Fatigue Test

[0092] A fatigue test was conducted at room temperature (20°C ± 10°C) in hydrogen gas (100% gas) with a pressure of 40 MPa, in hydrogen gas with 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 in accordance with ASTM E466, 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 compression, and a stress ratio of R = -1.0. The stress at which no fracture occurred at a number of repetitions of 2,000,000 was defined as the fatigue limit stress in hydrogen. Passing was judged when the fatigue limit stress in hydrogen in this test was 200 MPa or more, and its ratio to the fatigue limit strength in an inert gas atmosphere, that is, the fatigue limit stress in hydrogen/fatigue limit stress in an inert gas environment, was 0.90 or more.

[0093] In all of Inventive examples of the present invention, the fatigue limit stress in hydrogen was 200 MPa or more, its ratio to the fatigue limit strength in the inert gas atmosphere, that is, the fatigue limit stress in hydrogen/fatigue limit stress in the inert gas environment, was 0.90 or more, and high hydrogen embrittlement resistance was satisfied. Furthermore, the tensile strength satisfied 520 MPa or more.

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[Table 1-1]

Type of steel	Chemical composition (% by mass) *1																											Ar3 point (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H	Nb	Ca	Ti	Ni	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb		
1	0.09	0.73	1.2	0.0056	0.0010	0.121	0.008	0.004	0.00082	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	788	Conforming steel
2	0.02	1.30	0.7	0.0104	0.0006	0.065	0.006	0.005	0.00075	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	848	Conforming steel
3	0.15	0.88	1.1	0.0119	0.0011	0.044	0.008	0.002	0.00040	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	776	Conforming steel
4	0.09	0.73	1.2	0.0056	0.0010	0.121	0.008	0.004	0.00200	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	788	Comparative steel
5	0.10	1.01	0.9	0.0068	0.0012	0.128	0.003	0.004	0.00036	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	807	Conforming steel
6	0.11	0.01	1.2	0.0054	0.0012	0.027	0.003	0.003	0.00066	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	780	Conforming steel
7	0.10	2.00	1.0	0.0133	0.0015	0.019	0.005	0.002	0.00083	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	799	Conforming steel
8	0.10	1.01	0.9	0.0068	0.0012	0.128	0.003	0.004	0.00340	-	-	-	-	-	0.30	-	-	-	-	-	-	-	-	-	-	-	-	783	Comparative steel
9	0.14	0.14	1.0	0.0030	0.0012	0.027	0.008	0.002	0.00046	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	787	Conforming steel
10	0.06	1.73	0.5	0.0020	0.0011	0.045	0.008	0.006	0.00079	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	851	Conforming steel
11	0.12	0.74	1.5	0.0070	0.0010	0.066	0.001	0.003	0.00048	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	753	Conforming steel
12	0.01	0.14	1.0	0.0030	0.0012	0.027	0.009	0.002	0.00046	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	827	Comparative steel
13	0.12	0.44	1.1	0.0076	0.0010	0.031	0.004	0.003	0.00080	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	785	Conforming steel
14	0.05	0.13	0.9	0.0001	0.0012	0.115	0.001	0.004	0.00084	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	823	Conforming steel
15	0.13	0.31	0.6	0.0150	0.0003	0.021	0.003	0.004	0.00074	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	822	Conforming steel
16	0.05	1.19	1.3	0.0124	0.0009	0.018	0.008	0.002	0.00099	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	791	Conforming steel
17	0.07	1.36	1.1	0.0114	0.0002	0.078	0.003	0.004	0.00014	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	800	Conforming steel
18	0.15	0.25	1.2	0.0146	0.0015	0.026	0.008	0.004	0.00028	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	768	Conforming steel
19	0.07	0.34	1.5	0.0131	0.0011	0.078	0.008	0.006	0.00064	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	768	Conforming steel
20	0.03	0.55	1.3	0.0138	0.0010	0.005	0.008	0.004	0.00026	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	797	Conforming steel
21	0.09	1.48	0.7	0.0006	0.0013	0.150	0.005	0.002	0.00032	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	826	Conforming steel
22	0.12	1.89	1.0	0.0005	0.0003	0.083	0.006	0.002	0.00005	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	793	Conforming steel
23	0.14	1.69	1.0	0.0085	0.0009	0.134	0.001	0.005	0.00042	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	787	Conforming steel
24	0.11	1.98	1.2	0.0062	0.0003	0.061	0.010	0.005	0.00055	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	780	Conforming steel
25	0.07	0.25	0.8	0.0115	0.0006	0.028	0.009	0.003	0.00077	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	824	Conforming steel
26	0.09	1.75	0.6	0.0008	0.0011	0.146	0.008	0.001	0.00021	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	834	Conforming steel
27	0.11	1.61	0.5	0.0093	0.0003	0.096	0.008	0.005	0.00017	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	836	Conforming steel
28	0.04	0.75	0.7	0.0138	0.0005	0.099	0.002	0.003	0.00051	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	842	Conforming steel
29	0.07	0.82	1.1	0.0073	0.0005	0.086	0.007	0.004	0.00001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	800	Conforming steel
30	0.09	1.08	1.4	0.0130	0.0011	0.145	0.009	0.004	0.00100	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	770	Conforming steel

*1 The remainder is composed of Fe and incidental impurities
Underline: outside the scope of the present invention.
-: no intended addition

[Table 1-2]

Type of steel	Chemical composition (% by mass) *1																											Ar3 point (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H	Nb	Ca	Ti	Ni	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb		
31	0.12	1.12	0.6	0.0042	0.0008	0.110	0.010	0.004	0.00023	0.051	0.0016	0.047	0.47	0.63	0.02	0.27	0.99	0.04	0.003	0.0042	0.0043	0.0009	0.1159	0.0018	0.0030	0.1307	0.1166	764	Conforming steel
32	0.14	1.94	1.1	0.0011	0.0013	0.145	0.006	0.004	0.00063	0.001	0.0017	0.062	0.65	0.70	0.60	0.54	0.70	0.04	0.010	0.0047	0.0045	0.0002	0.1236	0.1869	0.0007	0.1333	0.1766	677	Conforming steel
33	0.11	0.88	0.7	0.0074	0.0007	0.094	0.007	0.002	0.00057	0.100	0.0033	0.053	0.28	0.95	0.32	0.44	0.33	0.08	0.019	0.0097	0.0061	0.0002	0.1038	0.0162	0.0033	0.1555	0.0264	746	Conforming steel
34	0.06	1.80	0.7	0.0118	0.0012	0.078	0.006	0.003	0.00077	0.025	0.0026	0.044	1.35	0.77	0.79	0.13	0.46	0.09	0.023	0.0061	0.0051	0.0012	0.1060	0.1475	0.0028	0.0703	0.2265	724	Conforming steel
35	0.15	1.48	1.5	0.0127	0.0003	0.020	0.006	0.002	0.00075	0.034	0.0001	0.078	0.70	0.48	0.21	0.09	0.62	0.07	0.027	0.0040	0.0059	0.0011	0.0002	0.0845	0.0038	0.2622	0.1804	685	Conforming steel
36	0.06	1.57	1.3	0.0069	0.0013	0.144	0.010	0.004	0.00061	0.086	0.0050	0.037	1.58	0.14	0.94	0.20	0.61	0.05	0.041	0.0084	0.0051	0.0016	0.0573	0.0399	0.0007	0.2673	0.0969	668	Conforming steel
37	0.07	0.37	0.7	0.0115	0.0009	0.055	0.003	0.002	0.00065	0.076	0.0027	0.014	1.01	0.56	0.50	0.08	0.80	0.05	0.032	0.0033	0.0089	0.0019	0.1745	0.1963	0.0049	0.2993	0.1935	752	Conforming steel
38	0.11	0.41	1.4	0.0143	0.0013	0.070	0.009	0.005	0.00009	0.099	0.0041	0.055	0.01	0.33	0.83	0.45	0.14	0.02	0.040	0.0001	0.0054	0.0016	0.0180	0.1853	0.0047	0.1868	0.1743	706	Conforming steel
39	0.13	0.74	1.4	0.0083	0.0002	0.015	0.003	0.001	0.00081	0.059	0.0010	0.073	2.00	0.45	0.83	0.31	0.29	0.07	0.036	0.0085	0.0061	0.0005	0.0935	0.0533	0.0050	0.0531	0.0577	601	Conforming steel
40	0.05	0.79	1.4	0.0143	0.0014	0.091	0.005	0.002	0.00060	0.019	0.0015	0.053	1.12	0.86	0.57	0.24	0.42	0.06	0.020	0.0049	0.0093	0.0012	0.0024	0.0798	0.0027	0.1223	0.1887	676	Conforming steel
41	0.10	1.93	1.2	0.0137	0.0005	0.050	0.002	0.005	0.00097	0.014	0.0032	0.005	1.72	0.92	0.39	0.28	0.63	0.09	0.017	0.0096	0.0064	0.0010	0.0777	0.1606	0.0041	0.1832	0.1050	642	Conforming steel
42	0.02	0.91	0.7	0.0143	0.0004	0.107	0.008	0.004	0.00054	0.014	0.0039	0.100	1.93	0.81	0.55	0.12	0.25	0.01	0.040	0.0037	0.0006	0.0005	0.0272	0.1843	0.0045	0.1304	0.1009	708	Conforming steel
43	0.02	1.58	1.4	0.0144	0.0006	0.032	0.004	0.003	0.00077	0.005	0.0037	0.013	0.59	0.51	0.89	0.50	0.67	0.03	0.008	0.0069	0.0019	0.0019	0.1299	0.1314	0.0021	0.2635	0.1794	696	Conforming steel
44	0.08	0.58	1.1	0.0130	0.0008	0.122	0.001	0.002	0.00089	0.074	0.0050	0.073	0.48	0.01	0.33	0.46	0.97	0.04	0.050	0.0058	0.0076	0.0016	0.1088	0.0716	0.0031	0.0958	0.1501	729	Conforming steel
45	0.07	1.49	0.5	0.0147	0.0005	0.022	0.006	0.003	0.00027	0.039	0.0029	0.015	0.13	1.00	0.74	0.09	0.31	0.06	0.046	0.0093	0.0074	0.0002	0.1105	0.1035	0.0042	0.2342	0.2780	803	Conforming steel
46	0.14	1.71	0.8	0.0113	0.0006	0.055	0.005	0.002	0.00050	0.006	0.0047	0.008	0.73	0.65	0.51	0.48	0.14	0.05	0.009	0.0067	0.0029	0.0012	0.1776	0.1784	0.0017	0.2043	0.1598	703	Conforming steel
47	0.10	1.27	0.8	0.0016	0.0010	0.066	0.009	0.004	0.00077	0.081	0.0037	0.018	0.56	0.21	0.01	0.52	0.72	0.03	0.026	0.0018	0.0022	0.0018	0.0848	0.0792	0.0006	0.0990	0.0528	738	Conforming steel
48	0.15	1.51	0.7	0.0135	0.0013	0.106	0.005	0.004	0.00098	0.045	0.0036	0.047	1.32	0.56	1.00	0.20	0.27	0.04	0.048	0.0068	0.0052	0.0019	0.0562	0.1132	0.0026	0.2958	0.1011	693	Conforming steel
49	0.03	0.76	0.9	0.0026	0.0005	0.095	0.004	0.005	0.00074	0.089	0.0015	0.029	0.07	0.11	0.29	0.31	0.27	0.05	0.021	0.0064	0.0030	0.0013	0.1885	0.1833	0.0002	0.1650	0.1513	794	Conforming steel
50	0.12	0.35	1.0	0.0078	0.0011	0.135	0.009	0.002	0.00012	0.025	0.0030	0.098	1.04	0.68	0.28	0.01	0.35	0.10	0.033	0.0099	0.0054	0.0002	0.1632	0.1711	0.0010	0.0330	0.1459	717	Conforming steel
51	0.13	1.26	0.6	0.0092	0.0005	0.039	0.009	0.002	0.00086	0.056	0.0039	0.049	0.01	0.23	0.04	0.60	0.40	0.01	0.011	0.0086	0.0023	0.0015	0.1392	0.1436	0.0034	0.2239	0.0235	768	Conforming steel
52	0.07	0.76	0.6	0.0097	0.0004	0.028	0.007	0.004	0.00084	0.086	0.0029	0.026	0.29	0.09	0.54	0.54	0.51	0.06	0.017	0.0023	0.0094	0.0011	0.0446	0.0707	0.0030	0.2435	0.2559	771	Conforming steel
53	0.06	1.14	1.0	0.0045	0.0003	0.094	0.004	0.001	0.00069	0.116	0.0008	0.038	1.70	0.32	0.42	0.13	0.01	0.05	0.011	0.0084	0.0076	0.0007	0.0326	0.1861	0.0021	0.2800	0.0928	750	Conforming steel
54	0.08	1.76	0.9	0.0035	0.0007	0.130	0.007	0.002	0.00019	0.024	0.0030	0.022	1.52	0.11	0.40	0.15	1.00	0.09	0.040	0.0029	0.0089	0.0015	0.0659	0.1895	0.0036	0.0914	0.2015	709	Conforming steel
55	0.09	0.85	1.3	0.0130	0.0004	0.119	0.009	0.003	0.00053	0.017	0.0017	0.044	1.55	0.45	0.76	0.18	0.22	0.06	0.037	0.0069	0.0082	0.0002	0.0843	0.0255	0.0024	0.2298	0.0399	658	Conforming steel
56	0.10	0.15	1.4	0.0062	0.0004	0.041	0.007	0.003	0.00046	0.012	0.0031	0.051	1.47	0.41	0.06	0.23	0.25	0.01	0.020	0.0098	0.0079	0.0008	0.0309	0.1394	0.0016	0.1104	0.0437	659	Conforming steel
57	0.14	1.64	0.9	0.0141	0.0005	0.091	0.005	0.001	0.00049	0.044	0.0009	0.074	1.62	0.38	0.42	0.40	0.27	0.10	0.048	0.0068	0.0060	0.0003	0.0910	0.1729	0.0003	0.2417	0.2659	660	Conforming steel
58	0.07	1.34	0.7	0.0090	0.0008	0.038	0.002	0.002	0.00051	0.069	0.0007	0.016	0.29	0.69	0.91	0.06	0.71	0.08	0.025	0.0051	0.0043	0.0005	0.1617	0.0807	0.0049	0.1037	0.2029	784	Conforming steel
59	0.15	1.18	0.6	0.0048	0.0003	0.036	0.005	0.004	0.00050	0.070	0.0017	0.041	1.55	0.62	0.74	0.26	0.23	0.01	0.000	0.0055	0.0053	0.0005	0.1176	0.0914	0.0017	0.0908	0.1477	686	Conforming steel
60	0.03	1.66	0.9	0.0050	0.0004	0.077	0.007	0.003	0.00027	0.016	0.0043	0.009	1.82	0.96	0.88	0.16	0.43	0.06	0.050	0.0072	0.0002	0.0015	0.0711	0.0402	0.0020	0.2479	0.2952	683	Conforming steel

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[Table 1-3]

Type of steel	Chemical composition (% by mass) ^{*1}																											Ar3 point (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H	Nb	Ca	Ti	Ni	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb		
61	0.07	0.93	1.0	0.0096	0.0002	0.062	0.001	0.001	0.00064	0.091	0.0014	0.015	1.98	0.90	0.93	0.14	0.39	0.08	0.026	0.0061	0.0014	0.0011	0.0154	0.0490	0.0015	0.1405	0.0398	656	Conforming steel
62	0.10	0.71	0.6	0.0006	0.0012	0.018	0.005	0.005	0.00013	0.071	0.0012	0.071	0.59	0.86	0.50	0.59	0.87	0.09	0.045	0.0044	0.0065	0.0001	0.1798	0.1841	0.0005	0.1620	0.2678	727	Conforming steel
63	0.02	1.55	1.5	0.0064	0.0006	0.031	0.010	0.004	0.00054	0.054	0.0033	0.074	0.78	0.24	0.04	0.40	0.77	0.02	0.033	0.0041	0.0089	0.0020	0.0540	0.1726	0.0025	0.1407	0.0867	704	Conforming steel
64	0.03	0.19	1.2	0.0047	0.0007	0.150	0.002	0.002	0.00100	0.069	0.0020	0.057	0.59	0.52	0.03	0.56	0.44	0.06	0.015	0.0051	0.0083	0.0020	0.0069	0.0202	0.0038	0.0661	0.2699	717	Conforming steel
65	0.05	0.78	1.2	0.0021	0.0012	0.067	0.003	0.003	0.00084	0.064	0.0014	0.089	0.47	0.56	0.93	0.22	0.83	0.01	0.016	0.0001	0.0073	0.0003	0.0536	0.1205	0.0034	0.0355	0.2455	730	Conforming steel
66	0.14	1.63	1.1	0.0079	0.0013	0.080	0.006	0.002	0.00031	0.046	0.0002	0.011	0.45	0.96	0.47	0.18	0.70	0.07	0.042	0.0100	0.0088	0.0007	0.0111	0.0872	0.0014	0.1042	0.1110	713	Conforming steel
67	0.09	1.85	1.0	0.0008	0.0015	0.031	0.005	0.004	0.00077	0.018	0.0023	0.050	0.48	0.73	0.29	0.10	0.76	0.01	0.001	0.0092	0.0051	0.0010	0.1055	0.1179	0.0021	0.0202	0.1551	749	Conforming steel
68	0.07	1.30	1.3	0.0119	0.0005	0.143	0.006	0.003	0.00098	0.050	0.0049	0.056	1.11	0.53	0.65	0.56	0.06	0.04	0.028	0.0041	0.0001	0.0017	0.0303	0.1211	0.0050	0.0844	0.1089	658	Conforming steel
69	0.12	1.85	0.9	0.0022	0.0003	0.054	0.004	0.001	0.00079	0.006	0.0038	0.049	1.12	0.80	0.41	0.18	0.69	0.02	0.029	0.0087	0.0100	0.0017	0.0616	0.1579	0.0025	0.1688	0.0856	703	Conforming steel
70	0.02	1.30	1.3	0.0119	0.0005	0.143	0.006	0.003	0.00098	0.050	0.0049	0.056	1.11	0.53	0.65	0.56	0.06	0.04	0.028	0.0041	0.0001	0.0017	0.0303	0.1211	0.0050	0.0844	0.1089	674	Conforming steel
71	0.15	1.42	0.6	0.0109	0.0012	0.037	0.010	0.002	0.00041	0.026	0.0025	0.093	0.03	0.93	0.11	0.53	0.74	0.06	0.019	0.0039	0.0096	0.0013	0.1126	0.0220	0.0023	0.0234	0.2453	751	Conforming steel
72	0.12	1.89	1.2	0.0013	0.0002	0.106	0.004	0.004	0.00093	0.027	0.0007	0.099	1.50	0.60	0.70	0.43	1.00	0.08	0.014	0.0056	0.0042	0.0005	0.1074	0.0400	0.0049	0.0980	0.0655	637	Conforming steel
73	0.13	0.75	0.6	0.0137	0.0007	0.035	0.002	0.002	0.00063	0.090	0.0016	0.084	0.52	0.26	0.60	0.23	0.62	0.07	0.041	0.0073	0.0070	0.0014	0.1369	0.0924	0.0039	0.2183	0.2483	761	Conforming steel
74	0.09	1.23	1.0	0.0033	0.0005	0.057	0.008	0.003	0.00088	0.050	0.0040	0.059	0.49	0.51	0.52	0.02	0.48	0.07	0.011	0.0022	0.0070	0.0006	0.1001	0.1241	0.0044	0.0803	0.0726	756	Conforming steel
75	0.04	1.20	1.2	0.0142	0.0014	0.064	0.001	0.004	0.00008	0.063	0.0027	0.060	1.43	0.73	0.35	0.06	0.04	0.03	0.047	0.0091	0.0052	0.0002	0.0001	0.0433	0.0021	0.0397	0.0491	698	Conforming steel
76	0.03	0.12	1.2	0.0064	0.0002	0.076	0.009	0.004	0.00017	0.075	0.0013	0.020	1.39	0.80	0.25	0.31	0.09	0.04	0.016	0.0023	0.0016	0.0020	0.2000	0.1732	0.0025	0.2471	0.0935	684	Conforming steel
77	0.04	1.08	0.6	0.0102	0.0002	0.080	0.002	0.004	0.00015	0.047	0.0017	0.064	1.81	0.08	0.27	0.37	0.05	0.06	0.040	0.0007	0.0041	0.0005	0.1664	0.1001	0.0041	0.2919	0.1438	715	Conforming steel
78	0.08	1.34	0.7	0.0047	0.0004	0.035	0.003	0.002	0.00064	0.097	0.0041	0.097	1.58	0.88	0.87	0.41	0.46	0.03	0.026	0.0077	0.0005	0.0009	0.0604	0.0001	0.0041	0.2381	0.2020	679	Conforming steel
79	0.11	0.80	0.7	0.0031	0.0003	0.042	0.002	0.005	0.00017	0.033	0.0035	0.069	0.07	0.94	0.49	0.26	0.57	0.02	0.044	0.0058	0.0048	0.0010	0.1031	0.2000	0.0006	0.1247	0.2682	769	Conforming steel
80	0.11	0.03	1.2	0.0089	0.0007	0.089	0.001	0.003	0.00031	0.035	0.0014	0.091	1.39	0.72	0.04	0.25	0.88	0.01	0.038	0.0025	0.0068	0.0005	0.0420	0.1515	0.0026	0.1850	0.2511	668	Conforming steel
81	0.05	0.46	1.0	0.0095	0.0014	0.100	0.005	0.003	0.00022	0.005	0.0026	0.051	0.42	0.12	0.66	0.50	0.84	0.03	0.036	0.0074	0.0097	0.0012	0.0384	0.0686	0.0001	0.0733	0.2749	739	Conforming steel
82	0.13	0.06	1.0	0.0140	0.0006	0.027	0.003	0.001	0.00052	0.066	0.0041	0.030	0.62	0.29	0.80	0.28	0.46	0.05	0.043	0.0077	0.0034	0.0020	0.1999	0.1736	0.0050	0.0925	0.1159	715	Conforming steel
83	0.06	0.80	1.1	0.0091	0.0015	0.142	0.006	0.003	0.00031	0.079	0.0029	0.053	0.83	0.64	0.51	0.39	0.88	0.03	0.017	0.0011	0.0038	0.0004	0.1270	0.0706	0.0048	0.1501	0.0312	706	Conforming steel
84	0.13	1.49	1.3	0.0022	0.0009	0.125	0.003	0.004	0.00088	0.091	0.0040	0.035	1.26	0.08	0.92	0.40	0.32	0.03	0.034	0.0043	0.0042	0.0007	0.0526	0.0539	0.0010	0.0001	0.0808	649	Conforming steel
85	0.11	0.10	1.3	0.0127	0.0013	0.100	0.002	0.001	0.00084	0.079	0.0018	0.077	1.33	0.24	0.67	0.59	0.37	0.02	0.013	0.0080	0.0046	0.0013	0.0317	0.1650	0.0032	0.3000	0.2964	637	Conforming steel
86	0.04	0.65	1.3	0.0050	0.0011	0.110	0.002	0.005	0.00009	0.034	0.0004	0.036	1.12	0.50	0.62	0.30	0.11	0.03	0.030	0.0034	0.0037	0.0008	0.0161	0.0383	0.0025	0.2647	0.1501	689	Conforming steel
87	0.04	1.44	1.3	0.0018	0.0006	0.052	0.008	0.001	0.00087	0.043	0.0048	0.052	0.72	0.19	0.16	0.17	0.60	0.08	0.027	0.0051	0.0072	0.0011	0.0139	0.0735	0.0036	0.0268	0.0001	734	Conforming steel
88	0.14	0.45	1.5	0.0130	0.0002	0.005	0.009	0.003	0.00021	0.018	0.0031	0.017	1.24	0.46	0.14	0.23	0.84	0.02	0.030	0.0026	0.0082	0.0008	0.0077	0.1925	0.0043	0.1787	0.3000	649	Conforming steel
89	0.12	0.13	1.1	0.0070	0.0010	0.031	0.004	0.003	0.00080	0.050	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	785	Conforming steel
90	0.12	0.13	0.8	0.0076	0.0014	0.031	0.004	0.003	0.00021	-	-	-	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	802	Conforming steel
91	0.04	0.15	0.9	0.0050	0.0014	0.036	0.005	0.005	0.00031	-	-	-	-	0.16	-	-	-	-	-	-	-	-	-	-	-	-	-	823	Conforming steel
92	0.05	0.16	1.0	0.0076	0.0004	0.027	0.004	0.003	0.00088	-	0.0015	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	815	Conforming steel
93	0.07	0.14	1.1	0.0050	0.0010	0.044	0.004	0.005	0.00080	-	-	0.010	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	800	Conforming steel
94	0.05	0.13	1.0	0.0076	0.0004	0.027	0.004	0.003	0.00088	-	-	-	-	-	0.04	-	-	-	-	-	-	-	-	-	-	-	-	814	Conforming steel
95	0.03	0.16	1.0	0.0076	0.0004	0.027	0.004	0.003	0.00031	-	-	-	-	-	-	-	-	0.01	-	-	-	-	-	-	-	-	-	821	Conforming steel

*1. The remainder is composed of Fe and incidental impurities
 Underline: outside the scope of the present invention.
 -: no intended addition

[Table 2-1]

Steel material No.	Steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)	
1	1	1	42	312	O	Y	0.0	98	622	311	0.97	Inventive example
2	2	2	40	360	O	Y	0.3	92	569	296	0.94	Inventive example
3	3	3	35	278	O	Y	2.3	95	654	340	0.98	Inventive example
4	4	4	48	95	X	=	0.3	92	622	334	0.82	Comparative example
5	5	5	50	316	O	Y	0.5	95	554	283	0.96	Inventive example
6	6	6	46	95	O	Y	0.1	80	619	334	0.85	Comparative example
7	7	7	45	323	O	Y	0.9	91	571	257	1.00	Inventive example
8	8	8	44	80	X	=	5.0	92	622	334	0.85	Comparative example
9	9	9	44	402	O	Y	1.3	97	618	315	0.94	Inventive example
10	10	10	5	332	O	Y	1.7	60	676	338	0.75	Comparative example
11	11	11	45	465	O	Y	2.2	97	680	360	1.00	Inventive example
12	12	12	45	544	O	Y	1.3	97	360	185	1.00	Comparative example

(continued)

Steel material No.	Steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)	
13	13	13	40	309	O	Y	1.1	96	620	310	0.90	Inventive example
14	14	14	38	265	O	Y	0.1	92	664	332	1.00	Inventive example
15	15	15	40	465	O	Y	2.0	96	555	272	0.95	Inventive example
16	16	16	46	433	O	Y	0.5	94	532	282	0.96	Inventive example
17	17	17	38	259	O	Y	2.4	95	637	306	1.00	Inventive example
18	18	18	40	270	O	Y	2.2	96	687	316	0.92	Inventive example
19	19	19	46	335	O	Y	0.6	92	572	303	0.93	Inventive example
20	20	20	38	260	O	Y	2.9	94	529	291	0.90	Inventive example
21	21	21	40	295	O	Y	0.9	93	687	323	0.90	Inventive example
22	22	22	42	295	O	Y	0.7	96	586	281	0.90	Inventive example
23	23	23	38	380	O	Y	0.2	91	605	315	0.92	Inventive example
24	24	24	42	295	O	Y	0.1	92	554	277	0.97	Inventive example

(continued)

Steel material No.	Steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)	
25	25	25	39	309	O	Y	1.4	93	570	257	0.93	Inventive example
26	26	26	40	380	O	Y	2.9	96	662	357	0.90	Inventive example
27	27	27	46	295	O	Y	1.4	92	693	333	0.94	Inventive example
28	28	28	42	278	O	Y	2.8	96	534	240	0.95	Inventive example
29	29	29	39	392	O	Y	0.2	98	562	298	1.00	Inventive example
30	30	30	40	451	O	Y	0.1	94	663	345	0.96	Inventive example
Underline: outside the scope of the present invention. γ : austenite, B: bainite Dehydrogenation treatment temperature: Y indicates room temperature to 550°C, N indicates more than 550°C												

[Table 2-2]

Steel material No.	steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)	
31	31	31	42	380	O	Y	2.7	91	650	299	0.93	Inventive example
32	32	32	46	295	O	Y	2.3	90	553	271	0.96	Inventive example
33	33	33	39	392	O	Y	2.5	91	530	249	0.91	Inventive example
34	34	34	40	433	O	Y	0.7	97	520	265	0.94	Inventive example
35	35	35	39	380	O	Y	2.3	96	548	296	0.94	Inventive example
36	36	36	46	380	O	Y	1.2	98	553	304	0.95	Inventive example
37	37	37	40	392	O	Y	2.3	93	665	339	0.99	Inventive example
38	38	38	42	451	O	Y	2.7	91	553	260	0.92	Inventive example
39	39	39	39	309	O	Y	2.7	91	646	336	1.00	Inventive example
40	40	40	46	278	O	Y	1.0	94	524	241	0.97	Inventive example
41	41	41	39	295	O	Y	0.7	93	619	340	0.95	Inventive example
42	42	42	40	451	O	Y	0.3	96	664	319	0.94	Inventive example

(continued)

Steel material No.	steel pipe No	Steel No.	Method for producing steel sheet					Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)		
43	43	43	39	433	O	Y	2.1	96	546	273	0.90	Inventive example	
44	44	44	40	380	O	Y	0.5	96	656	295	0.96	Inventive example	
45	45	45	46	392	O	Y	0.1	99	663	338	0.99	Inventive example	
46	46	46	39	433	O	Y	2.6	96	663	338	0.90	Inventive example	
47	47	47	38	380	O	Y	2.3	95	695	368	0.97	Inventive example	
48	48	48	39	451	O	Y	1.7	97	578	295	0.99	Inventive example	
49	49	49	38	309	O	Y	2.4	91	571	268	0.97	Inventive example	
50	50	50	46	295	O	Y	1.5	97	578	295	0.94	Inventive example	
51	51	51	40	309	O	Y	0.9	98	625	325	0.91	Inventive example	
52	52	52	39	278	O	Y	1.6	97	636	293	0.92	Inventive example	
53	53	53	46	392	O	Y	2.6	98	679	360	0.93	Inventive example	
54	54	54	42	451	O	Y	0.8	92	585	316	0.97	Inventive example	

(continued)

Steel material No.	steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)	
55	55	55	38	380	O	Y	1.2	91	695	348	0.95	Inventive example
56	-	56	39	295	O	Y	2.2	90	534	283	0.96	Inventive example
57	-	57	46	309	O	Y	1.5	94	609	335	0.97	Inventive example
58	-	58	40	380	O	Y	0.7	92	533	245	0.97	Inventive example
59	-	59	42	295	O	Y	0.1	92	634	298	0.95	Inventive example
60	-	60	38	433	O	Y	1.8	91	684	342	0.98	Inventive example
Underline: outside the scope of the present invention. γ : austenite, B: bainite Dehydrogenation treatment: Y indicates room temperature to 550°C, N indicates more than 550°C												

[Table 2-3]

Steel material No.	steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)	
61	-	61	39	295	O	Y	0.2	98	526	289	0.94	Inventive example
62	-	62	39	309	O	Y	1.8	97	587	311	0.99	Inventive example
63	-	63	40	278	O	Y	0.2	96	587	323	0.97	Inventive example
64	-	64	39	451	O	Y	2.1	91	600	306	0.93	Inventive example
65	-	65	40	387	O	Y	0.1	91	610	305	0.93	Inventive example
66	-	66	42	380	O	Y	1.1	97	619	303	0.90	Inventive example
67	-	67	38	350	O	Y	1.0	99	579	278	0.92	Inventive example
68	-	68	46	309	O	Y	1.5	97	530	292	0.90	Inventive example
69	-	69	39	380	O	Y	1.1	93	684	315	0.94	Inventive example
70	-	70	<u>10</u>	433	O	Y	1.5	<u>50</u>	520	<u>195</u>	<u>088</u>	Comparative example
71	-	71	42	392	O	Y	1.7	91	678	319	0.93	Inventive example
72	-	72	33	309	O	Y	0.2	95	629	327	0.90	Inventive example

(continued)

Steel material No.	steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)	
73	-	73	40	451	O	Y	1.4	94	600	306	0.94	Inventive example
74	-	74	39	380	O	Y	2.1	91	592	314	0.97	Inventive example
75	-	75	42	295	O	Y	1.7	92	597	275	0.92	Inventive example
76	-	76	40	380	O	Y	2.8	95	673	316	1.00	Inventive example
77	-	77	33	380	O	Y	1.0	94	521	234	0.96	Inventive example
78	-	78	38	451	O	Y	0.1	95	577	277	0.90	Inventive example
79	-	79	33	380	O	Y	1.8	90	602	307	0.94	Inventive example
80	-	80	46	295	O	Y	2.4	97	557	279	1.00	Inventive example
81	-	81	40	451	O	Y	0.5	96	549	264	0.91	Inventive example
82	-	82	17	550	O	Y	1.9	94	520	281	0.91	Inventive example
83	-	83	42	380	O	Y	0.1	92	683	362	0.92	Inventive example
84	-	84	40	433	O	Y	2.4	91	598	287	0.94	Inventive example

(continued)

Steel material No.	steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	
85	-	85	38	380	O	Y	2.4	93	696	327	0.99	Inventive example
86	-	86	46	309	O	Y	0.3	97	542	255	0.98	Inventive example
87	-	87	33	545	O	Y	2.5	96	532	261	0.99	Inventive example
88	-	88	38	451	O	Y	2.0	93	560	280	0.92	Inventive example
89	-	14	38	<u>215</u>	O	Y	<u>5.2</u>	92	622	334	<u>0.88</u>	Comparative example
90	-	14	40	<u>680</u>	O	Y	0.3	97	407	<u>183</u>	0.91	Comparative example
91	-	14	45	380	O	N	0.3	97	431	<u>194</u>	0.92	Comparative example
92	92	89	38	316	O	Y	0.1	98	596	274	0.93	Inventive example
93	93	90	39	321	O	Y	0.2	97	549	258	0.96	Inventive example
94	94	91	42	358	O	Y	0.1	98	592	278	0.95	Inventive example
95	95	92	50	362	O	Y	0.0	96	549	245	0.96	Inventive example
96	96	93	49	318	O	Y	0.0	95	523	241	0.94	Inventive example

(continued)

Steel material No.	steel pipe No	Steel No.	Method for producing steel sheet				Microstructure of steel sheet and steel pipe		Characteristics of steel sheet and steel pipe			Notes
			Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)	Dehydrogenation treatment	Dehydrogenation treatment temperature	r ratio (%)	B fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment)	
97	97	94	46	325	O	Y	0.0	97	549	262	0.98	Inventive example
98	98	95	43	338	O	Y	0.0	98	563	246	0.99	Inventive example
Underline: outside the scope of the present invention. γ : austenite, B: bainite Dehydrogenation treatment temperature: Y indicates room temperature to 550°C, N indicates more than 550°C												

[Table 3]

Steel No.	Steel material No.	Steel pipe No.	Casting speed (m/min)	Cooling step		Dehydrogenation treatment step		Microstructure of steel material and steel pipe		TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	Notes
				Cooling rate of controlled cooling (°C/s)	Cooling stop temperature (°C)			r ratio (%)	B fraction (%)				
15	15-1	-	0.8	41	315	O	Y	0.6	95	587	282	0.92	Inventive example
15	15-11	15-11	0.8	41	286	O	Y	0.2	96	575	276	0.93	Inventive example
15	15-2	-	1.2	40	257	O	Y	0.1	94	592	284	0.95	Inventive example
15	15-12	15-12	1.2	40	316	O	Y	0.1	92	567	272	0.96	Inventive example
15	15-3	-	1.8	38	295	O	Y	0.3	93	588	282	0.97	Inventive example
15	15-13	15-13	1.8	38	350	O	Y	0.5	98	568	273	0.91	Inventive example
56	56-1	-	0.8	40	315	O	Y	0.1	90	599	285	0.94	Inventive example
56	56-11	56-11	0.8	40	362	O	Y	0.3	91	563	267	0.93	Inventive example
56	56-2	-	1.2	37	331	O	Y	0.1	95	587	279	0.95	Inventive example
56	56-12	56-12	1.2	37	295	O	Y	0.3	97	569	270	0.94	Inventive example
56	56-3	-	1.8	40	356	O	Y	0.2	92	546	259	0.96	Inventive example
56	56-13	56-13	1.8	40	345	O	Y	0.1	95	563	267	0.96	Inventive example

Underline: outside the scope of the present invention. γ: austenite, B: bainite
Dehydrogenation treatment temperature: Y indicates room temperature to 550°C

EXAMPLE 2

[0094] Examples that have verified the advantages of the present invention are described below. In the following Examples, steel pipes were produced under the following production conditions and were characterized. The steel Nos. 1, 15, and 56 shown in Tables 1-1 and 1-2 were used to produce steel pipes under the same conditions as the steel materials Nos. 1, 15, 56, 15-12, and 56-12 shown in Tables 2-1, 2-2, and 3 up to the controlled cooling step. The characteristics were evaluated while varying the dehydrogenation treatment conditions. The steel pipes were formed in the same manner as in Example 1. Table 4 shows the results.

[0095] In Inventive examples, for the steel pipes and steel materials Nos. 1A, 15A, 56A, 15-12A, and 56-12A, the dehydrogenation treatment temperature T (ambient temperature) was 50°C, and the holding time t_c after the temperature Tc at the middle of the sheet thickness reached 50°C satisfied the formula (A). For the steel pipes and steel materials Nos. 1B, 15B, 56B, 15-12B, and 56-12B, the dehydrogenation treatment temperature T (ambient temperature) was 50°C, and the holding time t_c satisfied the formula (A) at a dehydrogenation treatment temperature T of 50°C, but the holding time t_c after the temperature Tc at the middle of the sheet thickness reached 50°C did not satisfy the formula (A). For the steel pipes and steel materials Nos. 1C, 15C, 56C, 15-12C, and 56-12C, the dehydrogenation treatment temperature T (ambient temperature) is 50°C, but neither the holding time t at the ambient temperature nor the holding time t_c after the temperature Tc at the middle of the sheet thickness reaches 50°C satisfy the formula (A).

[0096] In Table 4, "Y" in "Dehydrogenation holding time t" means that the dehydrogenation treatment temperature T (ambient temperature) is 50°C and the holding time t satisfies the formula (A), and "N" in "Dehydrogenation holding time t" means that the dehydrogenation treatment temperature T (ambient temperature) is 50°C, but the holding time t does not satisfy the formula (A). Furthermore, "Y" in "Holding time t_c at steel material center temperature Tc" means that the holding time t_c after the temperature Tc at the middle of the sheet thickness reaches 50°C satisfies the formula (A), and "N" in "Holding time t_c at steel material center temperature Tc" means that the temperature Tc at the middle of the sheet thickness reaches 50°C, but the holding time t_c after Tc reaches 50°C does not satisfy the formula (A).

[0097] Various evaluations were performed by the methods described in Example 1.

[0098] In all of Inventive examples of the present invention, the fatigue limit stress in hydrogen was 200 MPa or more, and its ratio to the fatigue limit strength in an inert gas atmosphere, that is, the fatigue limit stress in hydrogen/fatigue limit stress in an inert gas environment, was 0.90 or more. Furthermore, the tensile strength satisfied 520 MPa or more. Among them, the fatigue property was better when the dehydrogenation treatment was performed under more suitable conditions.

[Table 4]

Steel No.	Steel material No.	Steel pipe No.	Dehydrogenation holding time t	Holding time tc at steel material center temperature Tc	Microstructure of steel material and steel pipe		TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/ fatigue limit stress in inert gas environment	Notes
					r ratio (%)	B fraction (%)				
1	1	1A	Y	Y	0.0	98	612	306	0.98	Inventive example
1	1	1B	Y	N	0.0	98	622	311	0.97	Inventive example
1	1	1C	N	N	0.0	98	629	315	0.96	Inventive example
15	15-12	15-12A	Y	Y	0.1	92	592	284	0.98	Inventive example
15	15-12	15-12B	Y	N	0.1	92	567	272	0.96	Inventive example
15	15-12	15-12C	N	N	0.1	92	568	273	0.93	Inventive example
15	15	15 A	Y	Y	2.0	96	562	275	0.96	Inventive example
15	15	15 B	Y	N	2.0	96	555	272	0.95	Inventive example
15	15	15 C	N	N	2.0	96	562	275	0.92	Inventive example
56	56-12	56-12A	Y	Y	0.3	97	578	275	0.98	Inventive example
56	56-12	56-12B	Y	N	0.3	97	569	270	0.94	Inventive example
56	56-12	56-12C	N	N	0.3	97	556	264	0.94	Inventive example
56	56	56A	Y	Y	2.2	90	558	296	0.97	Inventive example
56	56	56B	Y	N	2.2	90	534	283	0.96	Inventive example
56	56	56C	N	N	2.2	90	549	291	0.93	Inventive example
Underline: outside the scope of the present invention. γ: austenite, B: bainite Dehydrogenation treatment temperature: Y indicates room temperature to 550°C, N indicates more than 550°C										

Claims

1. A steel material for a line pipe with high hydrogen embrittlement resistance, the steel material comprising 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 1.5%,

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: 0.0010% or less, and
optionally at least one selected from

Nb: 0% to 0.10%,

Ca: 0% to 0.005%,

Ti: 0% to 0.1%,

Ni: 0% to 2.0%,

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 0.050%,

Mg: 0% to 0.050%,

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 an area fraction of retained austenite in the steel material is 0% to 3%, an area fraction of bainite at a quarter thickness position of the steel material, is 90% or more, fatigue limit stress of the steel material in hydrogen at 1 MPa or more is 200 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is 0.90 or more.

2. The steel material for a line pipe with high hydrogen embrittlement resistance according to Claim 1, wherein the chemical composition contains, on a mass percent basis,

Nb: 0.001% to 0.10%,

Ca: 0.0001% to 0.005%,

Ti: 0.005% to 0.1%,

Ni: 0.01% to 2.0%,

Cu: 0.01% to 1.0%,

Cr: 0.01% to 1.0%,

Mo: 0.01% to 0.60%,

W: 0.01% to 1.0%,

V: 0.01% to 0.10%,

Zr: 0.0001% to 0.050%,

REM: 0.0001% to 0.050%,

Mg: 0.0001% to 0.050%,

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

a heating step of heating a steel raw material having 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 with a finish rolling temperature of an Ar_3 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 point or higher in terms of a temperature at a surface of the steel sheet, a cooling start time difference between a front end and a rear end of the hot-rolled steel sheet is 50 seconds or less, an average cooling rate from 750°C to 550°C ranges from 15°C/s to 50°C/s in terms of a temperature at a middle of a thickness of the steel sheet, and a cooling stop temperature ranges from 250°C to 650°C; and
 a dehydrogenation treatment step of holding the steel sheet produced in the controlled cooling step in the range of room temperature to 550°C.

4. A steel pipe for a line pipe with high hydrogen embrittlement resistance, the steel pipe comprising 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 1.5%,
 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: 0.0010% or less, and
 optionally at least one selected from
 Nb: 0% to 0.10%,
 Ca: 0% to 0.005%,
 Ti: 0% to 0.1%,
 Ni: 0% to 2.0%,
 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 0.050%,
 Mg: 0% to 0.050%,
 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 an area fraction of retained austenite in the steel pipe is 0% to 3%, an area fraction of bainite at a quarter thickness position from an inner surface of the steel pipe is 90% or more, fatigue limit stress of the steel pipe in hydrogen at 1 MPa or more is 200 MPa or more, and the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment is 0.90 or more.

5. The steel pipe for a line pipe with high hydrogen embrittlement resistance according to Claim 4, wherein the chemical composition contains, on a mass percent basis,

Nb: 0.001% to 0.10%,
 Ca: 0.0001% to 0.005%,
 Ti: 0.005% to 0.1%,
 Ni: 0.01% to 2.0%,
 Cu: 0.01% to 1.0%,
 Cr: 0.01% to 1.0%,
 Mo: 0.01% to 0.60%,
 W: 0.01% to 1.0%,
 V: 0.01% to 0.10%,
 Zr: 0.0001% to 0.050%,
 REM: 0.0001% to 0.050%,
 Mg: 0.0001% to 0.050%,
 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%.

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

a heating step of heating a steel raw material having the chemical composition according to Claim 4 or 5 at 1000°C to 1250°C;
 a hot rolling step of rolling the steel raw material heated in the heating step with a finish rolling temperature of an Ar_3 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 point or higher in terms of a temperature at a surface of the steel sheet, a cooling start time difference between a front end and a rear end of the hot-rolled steel sheet is 50 seconds or less, an average cooling rate from 750°C to 550°C ranges from 15°C/s to 50°C/s in terms of a temperature at a middle of a thickness of the steel sheet, 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
 a dehydrogenation treatment step of holding a steel pipe produced in the pipe production step in the range of room temperature to 550°C.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/035558

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)

C22C38/00-38/60; 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.
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A	JP 2022-68942 A (JFE STEEL CORPORATION) 11 May 2022 (2022-05-11) claims	1-6
A	WO 2014/156187 A1 (JFE STEEL CORPORATION) 02 October 2014 (2014-10-02) claims	1-6
A	JP 2012-122103 A (SUMITOMO METAL IND LTD) 28 June 2012 (2012-06-28) claims	1-6
A	WO 2022/030818 A1 (POSCO) 10 February 2022 (2022-02-10) claims	1-6
A	JP 2018-12855 A (NIPPON STEEL & SUMITOMO METAL CORP) 25 January 2018 (2018-01-25) claims	1-6

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

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"O" document referring to an oral disclosure, use, exhibition or other means	
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/035558

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 2022/209896 A1 (JFE STEEL CORPORATION) 06 October 2022 (2022-10-06) claims	1-6

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/035558

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