(12) 特許協力条約に基づいて公開された国際出願

(19) 世界知的所有権機関
国際事務局

WIPO | PCT

(43) 国際公開日
2024年4月4日(04.04.2024)

(10) 国際公開番号
WO 2024/071352 A1

(51) 国際特許分類:
B21B 17/00 (2006.01) ***C22C 38/00*** (2006.01)
C21D 8/00 (2006.01) ***C22C 38/60*** (2006.01)
C21D 8/10 (2006.01) ***B22D 11/00*** (2006.01)
C21D 9/08 (2006.01)

(21) 国際出願番号： PCT/JP2023/035554

(22) 国際出願日： 2023年9月28日(28.09.2023)

(25) 国際出願の言語： 日本語

(26) 国際公開の言語： 日本語

(30) 優先権データ：
特願 2022-157170 2022年9月29日(29.09.2022) JP

(71) 出願人: ＪＦＥスチール株式会社(**JFE STEEL CORPORATION**) [JP/JP]; 〒1000011 東京都千代田区内幸町二丁目２番３号 Tokyo (JP).

(72) 発明者: 岡野 拓史(**OKANO Hiroshi**); 〒1000011 東京都千代田区内幸町二丁目２番３号ＪＦＥスチール株式会社知的財産部内 Tokyo (JP). 西原 佳宏(**NISHIHARA Yoshihiro**); 〒1000011 東京都千代田区内幸町二丁目２番３号ＪＦＥスチール株式会社知的財産部内 Tokyo (JP). 井上 奈穂(**INOUE Naho**); 〒1000011 東京都千代田区内幸町二丁目２番３号ＪＦＥスチール株式会社知的財産部内 Tokyo (JP).

(74) 代理人: 熊坂 晃, 外(**KUMASAKA Akira** et al.); 〒1000004 東京都千代田区大手町一丁目６番１号ＪＦＥテクノリサーチ株式会社知的財産事業部内 Tokyo (JP).

(81) 指定国(表示のない限り、全ての種類の国内保護が可能)：AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(54) Title: STEEL PIPE FOR LINE PIPE HAVING EXCELLENT HYDROGEN EMBRITTLEMENT RESISTANCE CHARACTERISTICS, METHOD OF MANUFACTURING SAME, STEEL MATERIAL FOR LINE PIPE, AND METHOD OF MANUFACTURING SAME

(54) 発明の名称： 耐水素脆化特性に優れたラインパイプ用鋼管、その製造方法、ラインパイプ用鋼材およびその製造方法

(57) **Abstract:** The purpose of the present invention is to provide a steel pipe for a line pipe and a method of manufacturing the same, and a steel material for a line pipe and a method of manufacturing the same, the steel pipe for a line pipe being suitable for steel structures that are used in a high-pressure hydrogen gas environment, such as a line pipe for 100% hydrogen gas or natural gas containing hydrogen with a hydrogen partial pressure of more than or equal to 1 MPa (natural gas is a gas having hydrocarbon, such as methane or ethane, as a major component), the steel pipe for a line pipe having high strength and excellent hydrogen embrittlement resistance characteristics in a high-pressure hydrogen gas environment. The steel pipe for a line pipe is characterized by having excellent hydrogen embrittlement resistance characteristics and a specific component composition and a specific structure, wherein the fatigue limit stress in hydrogen of more than or equal to 1 MPa is more than or equal to 200 MPa, and the value of the fatigue limit stress in hydrogen of more than or equal to 1 MPa over the fatigue limit stress in an inert gas environment is more than or equal to 0.90.

(57) 要約： １００％水素ガスまたは水素分圧が１ＭＰａ以上の水素を含む天然ガス（天然ガスはメタン、エタンなどの炭化水素を主な成分とするガス）用ラインパイプ等の、高圧水素ガス環境下で使用される鋼構造物用として好適な、高強度で、高圧水素ガス環境下における耐水素脆化特性に優れたラインパイプ用鋼管とその製造方法、ラインパイプ用鋼材およびその製造方法を提供することを目的とする。 特定の成分組成、特定の組織を有し、１ＭＰａ以上の水素中疲労限応力が２００ＭＰａ以上であり、かつ、１ＭＰａ以上の水素中疲労限応力／不活性ガス環境下の疲労限応力が０．９０以上であることを特徴とする耐水素脆化特性に優れたラインパイプ用鋼管。

WO 2024/071352 A1

［続葉有］

(84) 指定国(表示のない限り、全ての種類の広域保護が可能): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), ユーラシア (AM, AZ, BY, KG, KZ, RU, TJ, TM), ヨーロッパ (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

添付公開書類：

— 国際調査報告（条約第21条(3)）

DESCRIPTION

Title of Invention: STEEL PIPE FOR LINE PIPE WITH HIGH HYDROGEN EMBRITTLEMENT RESISTANCE AND METHOD FOR PRODUCING THE SAME, AND STEEL MATERIAL FOR LINE PIPE AND METHOD FOR PRODUCING THE SAME

Technical Field

[0001]

The present invention relates to a steel pipe for a line pipe with high hydrogen embrittlement resistance, a method for producing the steel pipe, a steel material for a line pipe, and a method for producing the steel material, 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 improve 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.

Citation List

Patent Literature

[0010]

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

[0011]

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

[0012]

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.

[0013]

In view of the problems of the related art, it is an object of the present invention to provide a steel pipe 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 pipe, a steel material for a line pipe, and a method for producing the steel material, 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).

[0014]

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°C ± 10°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. The natural gas containing hydrogen at a hydrogen partial pressure of 1 MPa or more, for example, has a hydrogen concentration of 30% or less by volume and a pressure of the entire gas of 30 MPa or less.

[0015]

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.

[0016]

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

[0017]

The present inventors have extensively studied conditions to be satisfied by a steel material for producing a steel pipe for a line pipe and a steel material for a line pipe with high hydrogen embrittlement resistance and have invented a new steel pipe for a line pipe and a new steel material for a line pipe. A steel pipe and a steel material 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.

[0018]

The gist of the present invention is as follows:

[1] 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: 0.10% to 0.45%,

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%,

Ti: 0% to 0.1%,

Ca: 0% to 0.005%,

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%, bainite or martensite presents at a quarter thickness position from an inner surface of the steel pipe with an area fraction of the bainite of 90% or more or an area fraction of the martensite of 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. [2] The steel pipe 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%,

Ti: 0.005% to 0.1%,

Ca: 0.0001% to 0.005%,

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 pipe for a line pipe, the method including:

a casting step of casting a steel raw material having the chemical composition according to [1] or [2] at a casting speed of 1.8 m/min or less;

a heating step of heating the steel raw material at 1350°C or less;

a hot rolling step of rolling the steel raw material heated in the heating step with a finish rolling temperature of 820°C or more to form a steel pipe shape;

a cooling step of, after holding a steel pipe produced in the hot rolling step at a temperature of an Ac_3 point or higher and 1000°C or less, cooling the steel pipe wherein a cooling condition is the following Group A or Group B; and

a tempering step of tempering the steel pipe produced in the cooling step at 400°C or more and an Ac_1 point or lower,

Group A:

cooling the steel pipe to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C in terms of a temperatuer at a quarter thickness position from an inner surface of the steel pipe and at an average cooling rate of 15°C/s or less from 550°C to 50°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe, and

Group B:

cooling the steel pipe to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe and at an average cooling rate of 5°C/s or less from 300°C to 50°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe.

[4] The method for producing a steel pipe for a line pipe according to [3], including, before the tempering step, a quenching step of reheating the steel pipe to an Ac_3 point

or higher and 1000°C or less, and cooling the steel pipe wherein a cooling condition is the following Group A or Group B,

Group A:

cooling the steel pipe to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe and at an average cooling rate of 15°C/s or less from 550°C to 50°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe, and

Group B:

cooling the steel pipe to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe and at an average cooling rate of 5°C/s or less from 300°C to 50°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe.

[5] The method for producing a steel pipe for a line pipe according to [3] or [4], wherein the casting speed is 1.0 m/min or less.

[6] A steel material for a line pipe with high hydrogen embrittlement resistance, the steel material having a chemical composition containing:

on a mass percent basis,

C: 0.10% to 0.45%,

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%,

Ti: 0% to 0.1%,

Ca: 0% to 0.005%,

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%, bainite or martensite presents at a quarter thickness position of the steel material with an area fraction of the bainite of 90% or more or an area fraction of the martensite of 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.

[7] The steel material for a line pipe with high hydrogen embrittlement resistance according to [6], wherein the chemical composition contains, on a mass percent basis,

Nb: 0.001% to 0.10%,

Ti: 0.005% to 0.1%,

Ca: 0.0001% to 0.005%,

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%.

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

a casting step of casting a steel raw material having the chemical composition according to [6] or [7] at a casting speed of 1.8 m/min or less;

a heating step of heating the steel raw material at 1350°C or less;

a hot rolling step of rolling the steel raw material heated in the heating step with a finish rolling temperature of 820°C or more;

a cooling step of, after holding a steel material produced in the hot rolling step at a temperature of an Ac_3 point or higher and 1000°C or less, cooling the steel material wherein a cooling condition is the following Group A or Group B; and a tempering step of tempering the steel material produced in the cooling step at 400°C or more and an Ac_1 point or lower,

Group A:

cooling the steel material to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C in terms of a temperature at a quarter thickness position from a surface of the steel material and at an average cooling rate of 15°C/s or less from 550°C to 50°C in terms of a temperature at the quarter thickness position from the surface of the steel material, and

Group B:

cooling the steel material to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C in terms of a temperature at the quarter thickness position from the surface of the steel material and at an average cooling rate of 5°C/s or less from 300°C to 50°C in terms of a temperature at the quarter thickness position from the surface of the steel material.

[9] The method for producing a steel material for a line pip according to [8], including, before the tempering step, a quenching step of reheating the steel material to an Ac_3 point or higher and 1000°C or less, and cooling *the* steel material wherein a cooling condition is the following Group A or Group B,

Group A:

cooling the steel material to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C in terms of a temperature at the quarter thickness position from the surface of the steel material and at an average cooling rate of 15°C/s or less from 550°C to 50°C in terms of a temperature at the quarter thickness position from the surface of the steel material, and

Group B:

cooling the steel material to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C in terms of a temperatre at the quarter thickness position from the surface of the steel material and at an average cooling rate of 5°C/s or less from 300°C to 50°C in terms of a temperature at the quarter thickness position from the surface of the steel material.

[10] The method for producing a steel material for a line pipe according to [8] or [9], wherein the casting speed is 1.0 m/min or less.

Advantageous Effects of Invention

[0019]

The present invention can easily and simply produce a steel pipe and 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

[0020]

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.

[0021]

An implementation method for a steel pipe is more specifically described as a first embodiment, and then an implementation method for a steel material is more specifically described as a second embodiment.

[0022]

First Embodiment

[Chemical Composition]

The reasons for limiting the component composition (chemical composition) of a steel pipe (including a steel material) according to the present invention are described below. Unless otherwise specified, "%" in the following description refers to "% by mass".

[0023]

C: 0.10% to 0.45%

C is an element necessary to increase strength. Thus, the C content is 0.10% or more. The C content is preferably 0.13% or more. On the other hand, a C content of more than 0.45% may result in quenching crack during quenching, and the C content is therefore 0.45% or less. The C content is preferably 0.25% or less, more preferably 0.20% or less, still more preferably 0.17% or less.

[0024]

Si: 0.01% to 2.0%

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.

[0025]

Mn: 0.5% to 1.5%

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.

[0026]

P: 0.0001% to 0.015%

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.

[0027]

S: 0.0002% to 0.0015%

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.

[0028]

Al: 0.005% to 0.15%

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.

[0029]

O: 0.01% or less

O can form an oxide inclusion, and a lower O content is more preferred, but an O content of 0.01% or less causes no problem. Thus, the O content is 0.01% or less. The O content is preferably 0.005% or less. The O content is more preferably less than 0.003%. 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.

[0030]

N: 0.010% or less

N has a small influence on the fatigue property of a steel pipe, 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.

[0031]

H: 0.0010% or less

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 pipe. 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 pipe, the chemical composition in the present disclosure may optionally contain at least one selected from Nb, Ti, Ca, Ni, Cu, Cr, Mo, W, V, Zr, REM, Mg, B, Hf, Ta, Re, Sn, and Sb in the following ranges.

[0033]

Nb: 0% to 0.10% and Ti: 0% to 0.1%

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.

[0034]

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.

[0035]

Ca: 0% to 0.005%

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.

[0036]

Ni: 0% to 2.0%

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.

[0037]

Cu: 0% to 1.0%

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.

[0038]

Cr: 0% to 1.0%

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.

[0039]

Mo: 0% to 0.60%

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, more preferably 0.50% or less, still 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.

[0040]

W: 0% to 1.0%

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.

[0041]

V: 0% to 0.10%

V is an element that can be optionally contained to increase the strength and toughness of a steel pipe, 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.

[0042]

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

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.

[0043]

B: 0% to 0.0020%

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.

[0044]

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

These elements contribute to an increase in the strength of a steel pipe, 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 effect. Thus, 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.

[0045]

Re: 0% to 0.005%

Re contributes to an increase in the strength of a steel pipe, 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 effect. 0.001% or more is more preferred.

[0046]

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

These elements contribute to an increase in the strength of a steel pipe 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. Thus, 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 pipe, the remainder other than these components (elements) is composed of Fe and an incidental impurity element.

[0048]

The metallic microstructure of a steel pipe according to the present invention is described below.

[0049]

Metallic Microstructure

Area fraction Retained austenite: 0% to 3%

Austenite remaining in a steel pipe 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, area fraction of retained austenite is 3% or less to reduce the fatigue crack growth rate. Retained austenite is preferably 2% or less, more preferably 1% or less. The retained austenite may be 0%.

[0050]

Bainite or martensite presents at a quarter thickness position from the inner surface of a steel pipe (for a steel material, a quarter thickness position from a surface of the steel material), and area fraction of bainite is 90% or more or area fraction of martensite is 90% or more

To increase the tensile strength to 520 MPa or more, the steel microstructure needs to be a bainite or martensite microstructure. On the other hand, when a steel pipe has a soft phase and a hard phase, fatigue damage preferentially accumulates in the soft phase and is likely to cause cracking, thus reducing the 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 in hydrogen/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. Thus, the metallic microstructure needs to be a single microstructure of bainite or martensite and, therefore, defined to be containing either one of bainite or martensite with an area fraction of the microstructure of 90% or more. Preferably, the area fraction of the bainite or martensite microstructure is 92% or more, more preferably 95% or more, still more preferably 98% or more. The upper limit may be, but is not limited to, 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.

[0051]

The bainite microstructure includes bainitic ferrite or granular bainite that transforms during or after cooling (accelerated cooling or quenching) contributing to transformation strengthening, and also includes tempered bainite. A different microstructure, such as ferrite, martensite, pearlite, a martensite-austenite constituent (MA), or retained austenite, in the bainite microstructure reduces the strength or toughness, and the volume fraction of a microstructure other than the bainite phase is therefore preferably as small as possible. The martensite microstructure includes tempered martensite.

[0052]

Furthermore, the bainite and martensite microstructures can be tempered to precipitate a carbide, such as cementite. A fine carbide can be precipitated to inhibit the straightness of a fatigue crack propagation path in hydrogen and further reduce the fatigue crack growth rate. Thus, a tempered bainite or tempered martensite microstructure is preferred. Furthermore, it is preferable to finely disperse and precipitate carbides. Thus, carbides preferably have an average size of 200 nm or less, more preferably 50 nm or less. The average size X of carbides is defined by $X = \sqrt{(a^2 + b^2)/2}$, wherein a denotes the long side, and b denotes the short side.

[0053]

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

To design a steel structure for hydrogen, such as a long-life line pipe, in a thickness range that is available by a process within the scope of the present invention, a steel pipe needs to have a fatigue limit stress of 200 MPa or more in hydrogen at 1 MPa 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. Furthermore, the fatigue limit stress in hydrogen at 1 MPa or more/fatigue limit stress in an inert gas environment in a steel pipe needs to be 0.90 or more. 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 1.10 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 suppress the toughness degradation in a high-pressure hydrogen atmosphere 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 is preferably 5 mm or more, preferably 30 mm or less.

[0056]

[Production Method]

Next, a method for producing a steel pipe according to the present invention is described below. Although a production method in the following description is described by taking a seamless steel pipe as an example of the steel pipe, it is needless to say that an electric-resistance-welded pipe or a UOE steel pipe can be produced by performing the treatment so as to have the same thermal history.

[0057]

A steel pipe according to the present invention can be produced by sequentially performing the following steps (1) to (3).

(1) A step of casting a steel raw material after component adjustment

(2) A hot rolling step of heating and rolling a cast material into a steel pipe

(3) A step of cooling (accelerated cooling) and tempering the steel pipe produced in the hot rolling step (including reheating and quenching before the tempering step)

Each of the steps is described below. 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.

[0058]

[Casting Step]

Casting speed: 1.8 m/min or less

A lower casting speed results in a decrease in the hydrogen concentration and inclusions in the steel, and the effects are remarkable at 1.8 m/min or less. Thus, the casting speed is 1.8 m/min or less, preferably 1.5 m/min or less, more preferably 1.0/min or less, still more preferably

0.5 m/min or less, most preferably 0.1 m/min or less. Although the lower limit is not particularly limited, the casting speed may be more than 0 m/min.

[0059]

[Heating Step]

To perform hot rolling, a steel raw material with the chemical composition described above is heated. The steel raw material can be, for example, but is not limited to, a billet or the like produced by an ordinary continuous casting method.

[0060]

Heating to temperature of 1350°C or less

A heating temperature of more than 1350°C in the heating step results in prior austenite grains with an excessively large average grain size and a degradation of various characteristics. Thus, the heating temperature is 1350°C or less. The heating temperature is preferably 1300°C or less, more preferably 1250°C or less, most preferably 1200°C or less. On the other hand, the heating temperature is preferably lowered to reduce the amount of hydrogen in the steel, but an excessively low heating temperature results in a decrease in the finish rolling temperature and makes rolling difficult. Thus, the heating temperature is preferably 950°C or more. The heating temperature is more preferably 1000°C or more. Although the heating time is not particularly specified, an excessively long heating time increases the risk of increasing the amount of hydrogen introduced into a steel pipe, so that 180 minutes or less is preferred. The heating time is more preferably 150 minutes or less, still more preferably 120 minutes or less. Although the lower limit is not particularly limited, the heating time is preferably 30 minutes or more, more preferably 60 minutes or more.

[0061]

[Rolling Step]

Next, the steel raw material heated in the heating step is rolled into a steel pipe shape. The rolling can be hot rolling including piercing and rolling of an ordinary Mannesmann-plug mill process or Mannesmann-mandrel mill process.

[0062]

Finish rolling temperature: 820°C or more

A finish rolling temperature of less than 820°C results in excessively large rolling force and a higher risk of occurrence of rolling trouble. Thus, the finish rolling temperature is 820°C or more. The finish rolling temperature is preferably 850°C or more, more preferably 900°C or more. On the other hand, although the upper limit of the finish rolling temperature is not particularly limited, an excessively high temperature tends to result in a nonuniform metallic microstructure. Thus, the finish rolling temperature is preferably 1200°C or less. The finish rolling temperature is more preferably 1150°C or less, still more preferably 1100°C or less.

[0063]

[Cooling Step (Accelerated Cooling Step)]

In the cooling step, a steel material with the chemical composition described above is heated and held at a temperature of the Ac_3 point or higher and 1000°C or less as it is or after being processed into a steel pipe, and is cooled under the cooling conditions of the following Group A or Group B. The temperature is preferably held for 10 minutes or more, more preferably 15 minutes or more, still more preferably 20 minutes or more. Although the upper limit is not particularly limited, the temperature is preferably held for 60 minutes or less, more preferably 45 minutes or less.

[0064]

Heating temperature after processing into steel pipe: Ac_3 point or higher and 1000°C or less

A heating temperature lower than the Ac_3 point in the cooling step results in ferrite remaining in the steel after cooling, a decrease in the strength of a steel pipe, and a decrease in the fatigue limit stress in hydrogen. Thus, the heating temperature is the Ac_3 point or higher. The heating temperature is preferably the Ac_3 point + 30°C or more, more preferably the Ac_3 point + 50°C or more. However, the Ac_3 point + 30°C or more or the Ac_3 point + 50°C or more is not applied to a composition system in which the Ac_3 point + 30°C or the Ac_3 point + 50°C exceeds 1000°C. On the other hand, a heating temperature of more than 1000°C may result in coarse austenite grains and a decrease in the impact absorbed energy and toughness of the material after heat treatment. Thus, the heating temperature is 1000°C or less. The heating temperature is preferably 950°C or less, more preferably 900°C or less. However, 950°C or less or 900°C or less described above is not applied to a composition system in which 950°C or 900°C is lower than the Ac_3 point.

[0065]

In the cooling process, when the temperature after the completion of rolling satisfies the heating conditions, cooling may be performed as it is, or the completion of rolling may be followed by reheating again and cooling. When a steel sheet is cooled by natural cooling once, the steel sheet may be heated again to a temperature of the Ac_3 point or higher and 1000°C or less and may be cooled under the cooling conditions of the following Group A or Group B. In the present invention, the Ac_3 point (°C) is calculated using the following formula.

$$Ac_3\ (°C) = 910 - 203[C]1/2 - 30[Mn] + 44.7[Si] + 700[P]$$

$+ 100[Al] + 31.5[Mo] - 11[Cr] - 15.2[Ni] - 20[Cu] + 104[V]$

In the formula, [M] denotes the element M content (% by mass).

[0066]

Average Cooling Rate

Group A: cooling to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C and at an average cooling rate of 15°C/s or less from 550°C to 50°C at the quarter thickness position from the inner surface of a steel pipe

When the average cooling rate from 800°C to 550°C at the quarter thickness position from the inner surface of a steel pipe is less than 15°C/s, a bainite microstructure with an area fraction of 90% or more cannot be formed, and the strength decreases. Thus, the average cooling rate at the quarter thickness position from the inner surface of a steel pipe is 15°C/s or more. From the perspective of reducing variations in microstructure, the average cooling rate is preferably 17°C/s or more. The average cooling rate from 800°C to 550°C is more preferably 20°C/s or more, most preferably 22°C/s or more. On the other hand, to reduce variations in grain size, the average cooling rate is preferably 50°C/s or less, more preferably 45°C/s or less, still more preferably 40°C/s or less. Furthermore, cooling to 50°C or less at an average cooling rate of 15°C/s or less from 550°C to 50°C can decrease retained austenite and reduce the amount of hydrogen in the steel. Thus, the average cooling rate from 550°C to 50°C is 15°C/s or less. The average cooling rate from 550°C to 50°C is preferably 12°C/s or less, more preferably 10°C/s or less. Although the lower limit is not particularly limited, the average cooling rate from 550°C to 50°C is preferably 1°C/s or more. The cooling method is not particularly limited, and an arbitrary method, such as water cooling, oil cooling, or natural cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 550°C, and natural cooling is preferred from 550°C to 50°C.

[0067]

Group B: cooling to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C and at an average cooling rate of 5°C/s or less from 300°C to 50°C at the quarter thickness position from the inner surface of a steel pipe

When the average cooling rate from 800°C to 300°C at the quarter thickness position from the inner surface of a steel pipe is less than 10°C/s, 90% or more of a martensite microstructure cannot be formed, mixing with a bainite microstructure occurs, and the fatigue limit stress in hydrogen decreases. Thus, the average cooling rate at the quarter thickness position from the inner surface of a steel pipe is 10°C/s or more. From the perspective of reducing variations in microstructure, the average cooling rate from 800°C to 300°C is preferably 12°C/s or more, more preferably 15°C/s or more, still more preferably 17°C/s or more. Although the upper limit is not particularly limited, the average cooling rate is preferably 60°C/s or less. Furthermore, cooling to 50°C or less at an average cooling rate of 5°C/s or less from 300°C to 50°C can reduce the amount of hydrogen in the steel. Thus, the average cooling rate from 300°C to 50°C is 5°C/s or less. The average cooling rate from 300°C to 50°C is preferably 1°C/s or less. The lower limit is preferably, but not limited to, 0.1°C/s or more. The cooling method is not particularly limited, and an arbitrary method, such as water cooling, oil cooling, or natural cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 300°C, and natural cooling is preferred from 300°C to 50°C.

[0068]

[Reheating and Quenching Step (Suitable Conditions)]

Reheating temperature before tempering: Ac_3 point or higher and 1000°C or less

When the temperature at the middle of the sheet thickness is lower than the Ac_3 point, non-transformed austenite partially remains, and a desired steel microstructure cannot be formed after hot rolling, quenching, and tempering described later. Thus, the heating temperature before quenching at the time of reheating is preferably the Ac_3 point or higher, preferably higher than the Ac_3 point. To suppress an excessive increase in the initial austenite grain size and improve the production efficiency, the heating temperature before quenching is preferably 1000°C or less, more preferably 980°C or less, still more preferably 960°C or less, most preferably 950°C or less. A reheating temperature before quenching on the low temperature side in the range of the Ac_3 point or higher can result in a decrease in the initial austenite grain size and a decrease in the fatigue limit stress in hydrogen.

[0069]

Average cooling rate during quenching: the following Group A or Group B

Group A: cooling to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C and at an average cooling rate of 15°C/s or less from 550°C to 50°C at the quarter thickness position from the inner surface of a steel pipe

When the average cooling rate from 800°C to 550°C at the quarter thickness position from the inner surface of a steel pipe is less than 15°C/s, a bainite microstructure with an area fraction of 90% or more cannot be formed, and the strength decreases. Thus, the average cooling rate at the quarter thickness position from the inner surface of a steel pipe is 15°C/s or more. From the perspective of reducing variations in microstructure, the average cooling rate is preferably 17°C/s or more, more preferably 20°C/s or more, still more preferably 22°C/s or more. On the other hand, to reduce variations in grain size, the average cooling rate is preferably 50°C/s or less, more preferably 47°C/s or less, still more preferably 45°C/s or less. Furthermore, cooling to 50°C or less at an average cooling rate of 15°C/s or less from 550°C to 50°C can decrease retained austenite and reduce the amount of hydrogen in the steel. Thus, the average cooling rate from 550°C to 50°C is 15°C/s or less. The average cooling rate from 550°C to 50°C is preferably 12°C/s or less, more preferably 10°C/s or less. Although the lower limit is not particularly limited, the average cooling rate from 550°C to 50°C is preferably 1°C/s or more. The cooling method is not particularly limited, and an arbitrary method, such as water cooling, oil cooling, or natural cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 550°C, and natural cooling is preferred from 550°C to 50°C.

[0070]

Group B: cooling to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C and at an average cooling rate of 5°C/s or less from 300°C to 50°C at the quarter thickness position from the inner surface of a steel pipe

When the average cooling rate from 800°C to 300°C at the quarter thickness position from the inner surface of a steel pipe is less than 10°C/s, 90% or more of a martensite microstructure cannot be formed, mixing with a bainite microstructure occurs, and the fatigue limit stress in hydrogen decreases. Thus, the average cooling rate at the quarter thickness position from the inner surface of a steel pipe is 10°C/s or more. From the perspective of reducing variations in microstructure, the average cooling rate is preferably 17°C/s or more, more preferably 20°C/s or more, still more preferably 25°C/s or more. On the other hand, although the average cooling rate may have any upper limit, when the average cooling rate is more than 60°C/s, a large amount of hard microstructure is formed on the surface of a steel sheet, a steel microstructure with the microstructure intended in the present invention is not formed, and the fatigue property in hydrogen deteriorates. Thus, the average cooling rate is preferably 60°C/s or less. Furthermore, cooling to 50°C or less at an average cooling rate of 5°C/s or less from 300°C to 50°C can reduce the amount of hydrogen in the steel. Thus, the average cooling rate from 300°C to 50°C is 5°C/s or less. The average cooling rate is preferably 3°C/s or less, more preferably 1°C/s or less. The lower limit is preferably, but not limited to, 0.1°C/s or more. The cooling method is not particularly limited, and an arbitrary method, such as water cooling, oil cooling, or natural cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 300°C, and natural cooling is preferred from 300°C to 50°C.

[0071]

Cooling stop temperature during quenching: 50°C or less

When the cooling stop temperature is more than 50°C, the transformation is not completed, and a desired steel microstructure cannot be formed after tempering. Thus, quenching is performed to a temperature of 50°C or less. The cooling stop temperature is preferably 45°C or less, more preferably 40°C or less. Although the lower limit is not particularly limited, the cooling stop temperature is preferably 25°C or more.

[0072]

[Tempering Step]

Heating to 400°C or more and Ac_1 point or lower

A tempering temperature of 400°C or more can result in a decrease in retained austenite and a decrease in hydrogen in the steel. The tempering temperature is preferably 450°C or more, more preferably 500°C or more. On the other hand, heating to a temperature higher than the Ac_1 point may result in an increase in retained austenite and an increase in hydrogen in the steel. Thus, the tempering temperature is the Ac_1 point or lower, preferably, (Ac_1 - 30)°C or less. The upper limit of the average heating rate during tempering is preferably, but not limited to, 1°C/s or less. The tempering time is preferably, but not limited to, 60 minutes or more because retained austenite and hydrogen in a steel pipe decreases as the tempering time increases. The tempering time is more preferably 80 minutes or more, still more preferably 100 minutes or more. An excessively long tempering time results in an excessive decrease in the material strength and saturation of the effects. Thus, the tempering time is preferably 180 minutes or less.

[0073]

In the present invention, the Ac_1 point (°C) is calculated using the following formula.

$$Ac_1 = 723 - 14Mn + 22Si - 14.4Ni + 23.3Cr$$

Each element symbol in the formula represents the element content (% by mass) of the steel and is 0 for an element not contained.

[0074]

[Dehydrogenation Treatment Step]

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 (h) is preferably determined from the sheet thickness or the wall thickness t (mm) of a steel pipe and the hydrogen diffusion coefficient D ($mm\cdot s^{-2}$) in the steel at room temperature using the following formula (A).

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

The hydrogen diffusion coefficient varies depending on a component contained and the metallic microstructure and may range from, for example, 1×10^{-11} to 5×10^{-9} m^2/s, more preferably 5×10^{-10} m^2/s or less.

[0075]

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 in the dehydrogenation step results in a significant decrease in the material strength, and the dehydrogenation treatment temperature is preferably 550°C or less. The dehydrogenation treatment temperature T is more preferably 500°C or less. The dehydrogenation treatment temperature T is still more preferably 400°C or less, most preferably 300°C or less. Furthermore, the dehydrogenation treatment temperature T is preferably room temperature or higher for the reason that the dehydrogenation treatment at a temperature lower than room temperature increases the treatment time and cost. The dehydrogenation treatment temperature T is more preferably 50°C or more. The dehydrogenation treatment temperature T is still more preferably 100°C or more, most preferably 150°C or more. The dehydrogenation treatment temperature T herein is the temperature of the ambient in the dehydrogenation treatment step. The room temperature refers to 20°C ± 10°C.

[0076]

In particular, when heating, it takes time for the temperature Tc 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 Tc at the middle of the sheet thickness reaches a target dehydrogenation treatment temperature T. Furthermore, to achieve a predetermined crack growth rate in hydrogen gas, it is necessary to appropriately adjust the amount of hydrogen in a steel material in a surface layer portion and at the 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 the holding time R (s) or more after the temperature Tc at the middle of the sheet thickness reaches the target dehydrogenation treatment temperature T. In other words, at least the former can appropriately control the amount of hydrogen in the steel material in the surface layer portion of the steel material or the steel pipe, and when the latter is also performed, the amount of hydrogen in the steel material from the surface layer portion to the middle of the sheet thickness of the steel material or the steel pipe can be appropriately controlled. The temperature Tc 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.

[0077]

Furthermore, the scale on the steel surface inhibits dehydrogenation and is therefore preferably removed before the dehydrogenation treatment. The scale 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. Although the thickness of scale to be removed is not particularly limited, the scale removal effect can be obtained when the scale is removed by approximately 100 μm.

[0078]

Second Embodiment

A steel material according to the present invention is more specifically described below. The chemical composition, metallic microstructure, and fatigue limit stress of the steel material are the same as those described for the steel pipe, and the steps other than the rolling step and the cooling step (the casting step, the heating step, the reheating and quenching step, the tempering step, and the dehydrogenation treatment step) in the production method are performed in the same manner as described for the steel pipe. The rolling step and the cooling step are performed as described below.

[0079]

[Rolling Step]

Finish rolling temperature: 820°C or more

A finish rolling temperature of less than 820°C results in excessively large rolling force and a higher risk of occurrence of rolling trouble. Thus, the finish rolling temperature is 820°C or more. The finish rolling temperature is preferably 850°C or more, more preferably 900°C or more. On the other hand, although the upper limit of the finish rolling temperature is not particularly limited, an excessively high temperature tends to result in a nonuniform metallic microstructure, so that the finish rolling temperature is preferably 1200°C or less. The finish rolling temperature is more preferably 1150°C or less, still more preferably 1100°C or less.

[0080]

[Cooling Step (Accelerated Cooling Step)]

In the cooling step, after the hot-rolling, the hot-rolled steel material with the chemical composition described above is heated, and held at a temperature of the Ac_3 point or higher and 1000°C or less, and is cooled under the cooling conditions of the following Group A or Group B. The temperature is preferably held for 10 minutes or more, more preferably 15 minutes or more, still more preferably 20 minutes or more. Although the upper limit is not particularly limited, the temperature is preferably held for 60 minutes or less, more preferably 45 minutes or less.

[0081]

Heating temperature after hot rolling: Ac_3 point or higher and 1000°C or less

A heating temperature lower than the Ac_3 point in the cooling step results in ferrite remaining in the steel after cooling, a decrease in the strength of a steel material, and a decrease in the fatigue limit stress in hydrogen. Thus, the heating temperature is the Ac_3 point or higher. The heating temperature is preferably the Ac_3 point + 30°C or more, more preferably the Ac_3 point + 50°C or more. However, the Ac_3 point + 30°C or more or the Ac_3 point + 50°C or more is not applied to a composition system in which the Ac_3 point + 30°C or the Ac_3 point + 50°C exceeds 1000°C. On the other hand, a heating temperature of more than 1000°C may result in coarse austenite grains and a decrease in the impact absorbed energy and toughness of the material after heat treatment. Thus, the heating temperature is 1000°C or less, preferably 950°C or less, more preferably 900°C or less. However, 950°C or less or 900°C or less described above is not applied to a composition system in which 950°C or 900°C is lower than the Ac_3 point.

[0082]

In the cooling process, when the temperature after the completion of rolling satisfies the heating conditions, cooling may be performed as it is, or the completion of rolling may be followed by reheating again and cooling. When a steel sheet is cooled by natural cooling once, the steel sheet may be heated again to a temperature of the Ac_3 point or higher and 1000°C or less and may be cooled under the cooling conditions of the following Group A or Group B (in this case, referred to as quenching). In the present invention, the Ac_3 point (°C) is calculated using the following formula.

Ac_3 (°C) = 910 - 203[C]1/2 - 30[Mn] + 44.7[Si] + 700[P] + 100[Al] + 31.5[Mo] - 11[Cr] - 15.2[Ni] - 20[Cu] + 104[V]

In the formula, [M] denotes the element M content (% by mass).

[0083]

Average Cooling Rate

Group A: cooling to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C and at an average cooling rate of 15°C/s or less from 550°C to 50°C at the quarter thickness position from a surface of a steel material

When the average cooling rate from 800°C to 550°C at the quarter thickness position from a surface of a steel material is less than 15°C/s, a bainite microstructure with an area fraction of 90% or more cannot be formed, and the strength decreases. Thus, the average cooling rate at the quarter thickness position from the surface of a steel material is 15°C/s or more. From the perspective of reducing variations in microstructure, the average cooling rate is preferably 17°C/s or more, more preferably 20°C/s or more, still more preferably 22°C/s or more. On the other hand, to suppress variations in grain size, the average cooling rate is 50°C/s or less, preferably 47°C/s or less, more preferably 45°C/s or less. Furthermore, cooling to 50°C or less at an average cooling rate of 15°C/s or less from 550°C to 50°C can decrease retained austenite and reduce the amount of hydrogen in the steel. Thus, the average cooling rate from 550°C to 50°C is 15°C/s or less. Although the lower limit is not particularly limited, the average cooling rate from 550°C to 50°C is preferably 1°C/s or more. The cooling method is not particularly limited, and an arbitrary method, such as water cooling, oil cooling, or natural cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 550°C, and natural cooling is preferred from 550°C to 50°C.

[0084]

Group B: cooling to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C and at an average cooling rate of 5°C/s or less from 300°C to 50°C at the quarter thickness position from a surface of a steel material

When the average cooling rate from 800°C to 300°C at the quarter thickness position from a surface of a steel material is less than 10°C/s, 90% or more of a martensite microstructure cannot be formed, mixing with a bainite microstructure occurs, and the fatigue limit stress in hydrogen decreases. Thus, the average cooling rate at the quarter thickness position from a surface of a steel material is 10°C/s or more. From the perspective of reducing variations in microstructure, 12°C/s or more is more preferred. The average cooling rate is still more preferably 15°C/s or more, still more preferably 17°C/s or more. On the other hand, although the average cooling rate may have any upper limit, when the average cooling rate is more than 60°C/s, a large amount of hard microstructure is formed on the surface of a steel sheet, a steel microstructure with the microstructure intended in the present invention is not formed, and the fatigue property in hydrogen deteriorates. Thus, the average cooling rate is preferably 60°C/s or less. Furthermore, cooling to 50°C or less at an average cooling rate of 5°C/s or less from 300°C to 50°C can reduce the amount of hydrogen in the steel. Thus, the average cooling rate from 300°C to 50°C is 5°C/s or less. The average cooling rate is preferably 1°C/s or less, more preferably 0.8°C/s or less. The lower limit is preferably, but not limited to, 0.1°C/s or more. The cooling method is not particularly limited, and an arbitrary method, such as water cooling, oil cooling, or natural cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 300°C, and natural cooling is preferred from 300°C to 50°C.

[0085]

After the cooling, a steel sheet is preferably coiled, although it is not necessary for a thick sheet.

EXAMPLE 1

[0086]

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.

[0087]

Steel pipes made of steel materials with the chemical compositions shown in Tables 1-1, 1-2, 1-3, 2-1, and 2-2 were produced. The production procedure is described below. First, billets with the chemical compositions shown in Tables 1-1, 1-2, 1-3, 2-1, and 2-2 were produced. The billets shown in Tables 1-1, 1-2, 1-3, and 2-1 were produced at a casting speed in the range of 0.05 to 0.2 m/min. The billets shown in Table 2-2 were cast at a casting speed in the range of 1.1 to 1.5 m/min. The billets were heated to 1000°C to 1100°C and were hot-rolled. The product was expanded by a Mannesmann-plug mill process or a Mannesmann-mandrel mill process to produce a seamless steel pipe with a finish rolling temperature of 850°C or more. The seamless steel pipe was then slowly cooled by natural cooling. The steel pipes produced by the above method were heated and held at 950°C for steel pipes with an Ac_3 point of 950°C or less or at 1000°C for steel pipes with an Ac_3 point of more than 950°C and were then cooled to 50°C or less at an average cooling rate shown in Tables 3-1, 3-2, 3-3, 4-1, and 4-2. Tempering was then performed, the steel pipes Nos. 16, 29, 35, 37, and 39 were subjected to dehydrogenation treatment, and the metallic microstructure and mechanical properties were evaluated. The tempering temperature was adjusted in the range of 400°C to 680°C so that the tensile strength of the material ranged from 520 MPa to 700 MPa. In the dehydrogenation treatment of Example 1, after it was confirmed that the temperature Tc at the middle of the sheet thickness reached room temperature as the target temperature, held for R (s) to satisfy the formula (A). Tables 3-1, 3-2, 3-3, 4-1, and 4-2 show evaluation results. The evaluation method is described below. A steel material taken from a central portion in the longitudinal direction of a steel pipe was treated as a steel material of the present invention.

[0088]

Retained Austenite Measurement

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 Co-Kα radiation source was used for an incident X-ray, and the area fraction of retained austenite was calculated from the intensity ratios of the (200), (211), and (220) planes of ferrite to the (200), (220), and (311) planes of austenite.

[0089]

Measurement of Area Fraction of Bainite and Martensite

The metallic microstructure at a quarter thickness position on the inner side of each steel pipe was evaluated as described below. A test specimen was taken from the steel pipe such that the quarter thickness position on the inner side and the center position of the wall thickness in the center in the longitudinal direction of the steel pipe were observation positions. A cross section of the taken test specimen was etched using a 3% by volume nital solution. A scanning electron microscope photograph was taken at an appropriate magnification in the range of 1000 to 5000 times, and tempered martensite, ferrite, bainite, and pearlite were observed. Martensite, ferrite, bainite, and pearlite were visually identified by comparison with microstructure photographs of Non Patent Literature 2. The microstructure fractions were determined as area fractions of respection phases from an image obtained by dividing the SEM photograph into regions based on the above identification by image analysis (for example, to calculate the fraction of bainite, the bainite and the other region were binarized to determine the fraction of bainite).

[0090]

Tensile Strength (TS)

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 pipes and the steel materials thus produced, and the tensile strength was measured.

[0091]

Hydrogen Temperature-Programmed Analysis

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, 1-3, 2-1, and 2-2 before being subjected to a high-pressure hydrogen fatigue test as explained in the item described later.

[0092]

Fatigue Test

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.

[0093]

High-Pressure Hydrogen Fatigue Test

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.

[0094]

In all of Inventive examples of the present invention, as shown in Tables 3-1, 3-2, 3-3, 4-1, and 4-2, 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, the tensile strength was 520 MPa or more, and high hydrogen embrittlement resistance was satisfied.

[0095]

[Table 1-1]

Steel No.	Chemical composition (% by mass) *1																											Ac3 point (°C)	Ac1 point (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H	Nb	Ti	Ca	Ni	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb			
1	0.28	1.49	1.4	0.00160	0.0003	0.037	0.008	0.003	0.00083																			912	736	Conforming steel
2	0.10	1.73	1.2	0.01480	0.0005	0.060	0.003	0.001	0.00069																			958	744	Conforming steel
3	0.45	1.97	1.0	0.01290	0.0011	0.146	0.008	0.001	0.00041																			946	752	Conforming steel
4	0.12	0.73	1.2	0.00560	0.0010	0.121	0.007	0.004	0.00200																			910	722	Comparative steel
5	0.40	1.01	1.4	0.00230	0.0003	0.131	0.008	0.006	0.00032																			887	726	Conforming steel
6	0.40	0.10	0.9	0.01330	0.0011	0.095	0.003	0.004	0.00092																			866	713	Conforming steel
7	0.35	2.00	1.0	0.00780	0.0012	0.042	0.008	0.003	0.00034																			944	753	Conforming steel
8	0.10	1.01	0.9	0.00680	0.0012	0.128	0.003	0.004	0.04360																			935	733	Comparative steel
9	0.24	0.48	1.2	0.00890	0.0004	0.029	0.008	0.004	0.00044																			882	717	Conforming steel
10	0.26	0.59	0.5	0.00980	0.0012	0.126	0.006	0.004	0.00050																			914	729	Conforming steel
11	0.29	1.54	1.3	0.00700	0.0005	0.058	0.005	0.004	0.00035																			921	739	Conforming steel
12	0.13	1.73	0.5	0.00200	0.0011	0.045	0.008	0.006	0.00079																			965	754	Conforming steel
13	0.38	0.25	0.6	0.00755	0.0007	0.035	0.008	0.002	0.00039																			873	720	Conforming steel
14	0.15	0.53	1.6	0.00010	0.0009	0.094	0.003	0.005	0.00097																			880	712	Conforming steel
15	0.20	0.53	0.6	0.01500	0.0008	0.050	0.006	0.006	0.00072																			911	726	Conforming steel
16	0.20	1.50	1.0	0.00670	0.0009	0.059	0.008	0.005	0.00003																			937	742	Conforming steel
17	0.40	0.42	1.3	0.00030	0.0002	0.080	0.002	0.001	0.00026																			857	714	Conforming steel
18	0.41	0.08	1.2	0.00440	0.0015	0.047	0.009	0.005	0.00021																			844	708	Conforming steel
19	0.26	1.20	0.9	0.01470	0.0003	0.078	0.010	0.005	0.00041																			928	737	Conforming steel
20	0.39	0.44	0.5	0.00040	0.0004	0.005	0.003	0.006	0.00033																			876	726	Conforming steel
21	0.20	0.52	1.3	0.00780	0.0003	0.150	0.009	0.004	0.00029																			894	716	Conforming steel
22	0.23	0.38	0.8	0.00580	0.0012	0.048	0.006	0.005	0.00045																			889	720	Conforming steel
23	0.36	0.81	1.4	0.00790	0.0010	0.081	0.003	0.002	0.00031																			881	721	Conforming steel
24	0.16	0.43	0.8	0.01270	0.0011	0.098	0.008	0.002	0.00057																			908	721	Conforming steel
25	0.10	1.93	1.0	0.00550	0.0004	0.100	0.004	0.003	0.00053																			970	751	Conforming steel
26	0.27	0.21	1.1	0.00270	0.0006	0.006	0.005	0.001	0.00093																			861	712	Conforming steel
27	0.14	0.28	0.9	0.01320	0.0011	0.137	0.002	0.005	0.00058																			904	717	Conforming steel
28	0.23	1.39	1.5	0.00700	0.0012	0.034	0.003	0.003	0.00051																			912	733	Conforming steel
29	0.15	0.56	1.1	0.00390	0.0008	0.070	0.006	0.002	0.00001																			897	720	Conforming steel
30	0.43	1.77	1.2	0.00950	0.0007	0.073	0.009	0.002	0.00100																			923	745	Conforming steel

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

[0096]

[Table 1-2]

Steel No.	Chemical composition (% by mass) *1																											Ac3 point (°C)	Ac1 point (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H	Nb	Ti	Ca	Ni	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb			
31	0.24	0.64	1.1	0.00540	0.0009	0.011	0.008	0.002	0.00074	0.051	0.023	0.0021	0.60	0.16	0.72	0.16	0.63	0.04	0.018	0.0062	0.0004	0.0011	0.116	0.045	0.001	0.293	0.0706	875	730	Conforming steel
32	0.39	0.90	0.6	0.01470	0.0003	0.066	0.005	0.002	0.00064	0.001	0.072	0.0049	1.08	0.34	0.62	0.55	0.22	0.03	0.038	0.0032	0.0051	0.0004	0.030	0.017	0.004	0.124	0.0714	900	733	Conforming steel
33	0.45	1.54	1.6	0.01160	0.0010	0.133	0.008	0.003	0.00089	0.100	0.030	0.0016	0.61	0.66	0.74	0.35	0.17	0.03	0.044	0.0072	0.0007	0.0002	0.169	0.198	0.001	0.041	0.0030	890	743	Conforming steel
34	0.28	1.99	0.8	0.00400	0.0012	0.123	0.002	0.003	0.00025	0.055	0.041	0.0026	1.02	0.97	0.17	0.10	0.16	0.08	0.019	0.0050	0.0038	0.0006	0.017	0.136	0.002	0.062	0.1711	936	745	Conforming steel
35	0.17	1.30	1.2	0.00390	0.0006	0.128	0.003	0.002	0.00007	0.044	0.088	0.0001	1.91	0.11	0.09	0.30	0.08	0.09	0.033	0.0023	0.0053	0.0011	0.177	0.050	0.002	0.030	0.0414	917	709	Conforming steel
36	0.15	0.38	0.6	0.00880	0.0007	0.098	0.007	0.002	0.00060	0.079	0.019	0.0050	0.68	0.02	0.91	0.17	0.17	0.06	0.016	0.0073	0.0057	0.0016	0.022	0.063	0.001	0.063	0.0614	901	734	Conforming steel
37	0.31	0.42	1.0	0.00380	0.0007	0.083	0.007	0.002	0.00004	0.075	0.084	0.0023	1.01	0.14	0.72	0.03	0.67	0.04	0.029	0.0086	0.0028	0.0001	0.166	0.076	0.001	0.200	0.1894	857	721	Conforming steel
38	0.42	1.74	1.1	0.01080	0.0002	0.142	0.007	0.003	0.00053	0.094	0.086	0.0037	0.01	0.71	0.30	0.15	0.05	0.04	0.028	0.0017	0.0047	0.0009	0.072	0.141	0.001	0.183	0.1685	925	753	Conforming steel
39	0.28	0.68	1.1	0.01170	0.0014	0.073	0.002	0.002	0.00009	0.098	0.084	0.0042	2.00	0.24	0.64	0.07	0.18	0.04	0.035	0.0041	0.0060	0.0018	0.195	0.054	0.002	0.115	0.2546	859	709	Conforming steel
40	0.30	1.50	0.8	0.00560	0.0013	0.074	0.004	0.001	0.00023	0.013	0.053	0.0044	1.41	0.41	0.15	0.58	0.92	0.09	0.028	0.0006	0.0099	0.0009	0.192	0.124	0.004	0.198	0.2438	930	728	Conforming steel
41	0.40	0.14	0.6	0.01430	0.0015	0.021	0.006	0.002	0.00081	0.035	0.005	0.0004	0.46	0.25	0.14	0.17	0.71	0.04	0.045	0.0002	0.0081	0.0020	0.034	0.192	0.003	0.197	0.1243	866	714	Conforming steel
42	0.37	1.25	0.7	0.00620	0.0010	0.103	0.010	0.003	0.00096	0.014	0.100	0.0019	0.16	0.85	0.03	0.38	0.90	0.04	0.008	0.0008	0.0035	0.0004	0.027	0.169	0.002	0.084	0.0391	918	739	Conforming steel
43	0.21	0.49	0.9	0.00150	0.0006	0.042	0.010	0.004	0.00081	0.039	0.097	0.0037	1.88	0.51	0.49	0.24	0.82	0.03	0.012	0.0034	0.0018	0.0002	0.014	0.134	0.001	0.211	0.0818	855	706	Conforming steel
44	0.30	1.18	0.6	0.00960	0.0012	0.137	0.005	0.003	0.00004	0.007	0.054	0.0048	0.81	0.01	0.76	0.12	0.57	0.07	0.002	0.0080	0.0069	0.0016	0.064	0.014	0.003	0.088	0.1192	925	747	Conforming steel
45	0.20	0.10	1.2	0.00140	0.0011	0.039	0.004	0.001	0.00011	0.003	0.069	0.0035	0.58	1.00	0.23	0.15	0.74	0.07	0.030	0.0094	0.0033	0.0005	0.147	0.131	0.001	0.045	0.0484	844	705	Conforming steel
46	0.39	1.33	1.0	0.01390	0.0009	0.079	0.003	0.004	0.00061	0.092	0.084	0.0035	0.86	0.59	0.51	0.22	0.73	0.06	0.039	0.0071	0.0042	0.0017	0.159	0.053	0.005	0.099	0.1414	900	738	Conforming steel
47	0.14	1.92	1.2	0.00200	0.0014	0.026	0.006	0.004	0.00080	0.072	0.062	0.0032	1.12	0.90	0.01	0.24	0.36	0.07	0.023	0.0019	0.0049	0.0007	0.086	0.197	0.003	0.086	0.1545	929	733	Conforming steel
48	0.40	1.08	0.5	0.01480	0.0010	0.128	0.003	0.003	0.00030	0.092	0.011	0.0035	0.60	0.29	1.00	0.45	0.92	0.04	0.001	0.0016	0.0044	0.0015	0.096	0.017	0.004	0.043	0.0112	918	754	Conforming steel
49	0.24	0.89	1.5	0.00150	0.0007	0.067	0.003	0.002	0.00051	0.031	0.011	0.0042	0.76	0.19	0.95	0.31	0.70	0.01	0.049	0.0034	0.0039	0.0007	0.169	0.093	0.000	0.271	0.0584	873	733	Conforming steel
50	0.19	1.16	1.5	0.00080	0.0010	0.125	0.001	0.002	0.00092	0.063	0.050	0.0049	0.97	0.06	0.40	0.01	0.21	0.07	0.007	0.0027	0.0021	0.0002	0.085	0.041	0.001	0.140	0.1536	898	723	Conforming steel
51	0.24	0.27	1.1	0.01000	0.0009	0.007	0.009	0.002	0.00045	0.040	0.066	0.0010	1.38	0.26	0.69	0.60	0.55	0.07	0.007	0.0096	0.0093	0.0014	0.174	0.045	0.004	0.260	0.1859	865	710	Conforming steel
52	0.20	0.05	1.5	0.01300	0.0014	0.095	0.005	0.002	0.00060	0.076	0.044	0.0011	0.79	0.19	0.14	0.19	0.51	0.03	0.015	0.0094	0.0096	0.0005	0.155	0.141	0.000	0.204	0.2213	857	695	Conforming steel
53	0.37	1.08	1.2	0.01270	0.0006	0.120	0.006	0.001	0.00050	0.015	0.075	0.0017	1.85	0.13	0.42	0.11	0.01	0.02	0.038	0.0013	0.0020	0.0008	0.182	0.192	0.002	0.283	0.1160	876	713	Conforming steel
54	0.43	1.53	0.5	0.00380	0.0005	0.053	0.008	0.001	0.00015	0.044	0.090	0.0041	1.56	0.64	0.43	0.18	1.00	0.09	0.050	0.0022	0.0085	0.0001	0.048	0.142	0.005	0.128	0.0100	901	737	Conforming steel
55	0.18	1.16	1.4	0.00720	0.0005	0.060	0.006	0.004	0.00030	0.087	0.018	0.0030	0.26	0.25	0.66	0.21	0.91	0.06	0.037	0.0030	0.0095	0.0004	0.022	0.141	0.002	0.035	0.1932	909	741	Conforming steel
56	0.30	0.23	0.8	0.00070	0.0013	0.070	0.005	0.004	0.00056	0.038	0.064	0.0013	0.62	0.72	0.65	0.15	0.97	0.01	0.032	0.0005	0.0016	0.0011	0.008	0.081	0.005	0.235	0.0598	848	723	Conforming steel
57	0.39	0.92	1.4	0.01330	0.0008	0.088	0.002	0.004	0.00046	0.002	0.084	0.0007	1.03	0.05	0.07	0.23	0.59	0.10	0.034	0.0016	0.0054	0.0006	0.093	0.150	0.003	0.217	0.1504	888	710	Conforming steel
58	0.10	1.74	1.1	0.00670	0.0012	0.110	0.005	0.004	0.00032	0.066	0.076	0.0028	0.60	0.88	0.06	0.27	0.49	0.03	0.025	0.0020	0.0089	0.0001	0.032	0.199	0.005	0.108	0.1841	945	739	Conforming steel
59	0.29	1.23	0.5	0.01400	0.0008	0.060	0.008	0.003	0.00017	0.084	0.046	0.0022	0.16	0.58	0.54	0.39	0.88	0.03	0.000	0.0049	0.0074	0.0018	0.170	0.027	0.000	0.166	0.0433	932	753	Conforming steel
60	0.17	1.36	1.1	0.01470	0.0005	0.008	0.006	0.002	0.00099	0.036	0.060	0.0004	0.62	0.87	0.82	0.47	0.35	0.03	0.050	0.0028	0.0098	0.0006	0.199	0.069	0.005	0.062	0.1169	914	748	Conforming steel

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

[0097]

[Table 1-3]

Steel No.	Chemical composition (% by mass) *1																											Ac3 point (°C)	Ac1 point (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H	Nb	Ti	Ca	Ni	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb			
61	0.16	1.79	0.9	0.00160	0.0015	0.122	0.008	0.003	0.00050	0.044	0.067	0.0039	1.18	0.54	0.77	0.60	0.13	0.10	0.025	0.0057	0.0051	0.0011	0.175	0.019	0.001	0.185	0.0580	952	751	Conforming steel
62	0.18	1.99	1.4	0.00430	0.0004	0.083	0.007	0.003	0.00022	0.022	0.062	0.0020	1.82	0.39	0.50	0.46	0.30	0.06	0.029	0.0100	0.0066	0.0001	0.032	0.060	0.001	0.257	0.1268	930	733	Conforming steel
63	0.21	0.65	1.2	0.00570	0.0005	0.037	0.001	0.003	0.00033	0.079	0.079	0.0043	1.54	0.14	0.26	0.29	0.33	0.03	0.046	0.0028	0.0096	0.0020	0.015	0.161	0.001	0.223	0.2176	873	704	Conforming steel
64	0.30	0.92	1.5	0.01390	0.0010	0.022	0.003	0.002	0.00031	0.018	0.054	0.0010	1.11	0.88	0.28	0.25	0.93	0.08	0.036	0.0051	0.0031	0.0001	0.159	0.000	0.001	0.031	0.1103	866	713	Conforming steel
65	0.12	1.37	1.0	0.00120	0.0003	0.106	0.005	0.004	0.00086	0.053	0.093	0.0042	0.80	0.91	0.26	0.26	0.60	0.06	0.007	0.0001	0.0017	0.0018	0.052	0.059	0.004	0.010	0.1775	922	734	Conforming steel
66	0.27	0.78	0.5	0.01450	0.0013	0.104	0.005	0.003	0.00078	0.077	0.009	0.0046	0.03	0.58	0.27	0.59	0.19	0.10	0.026	0.0100	0.0030	0.0004	0.001	0.167	0.001	0.189	0.0231	937	739	Conforming steel
67	0.36	0.31	1.2	0.00750	0.0007	0.028	0.007	0.002	0.00091	0.023	0.061	0.0007	0.16	0.80	0.33	0.23	0.96	0.02	0.016	0.0034	0.0051	0.0001	0.035	0.036	0.001	0.285	0.0975	847	718	Conforming steel
68	0.30	0.88	1.0	0.00530	0.0013	0.020	0.008	0.003	0.00054	0.076	0.023	0.0005	1.86	0.26	0.47	0.27	0.48	0.06	0.043	0.0039	0.0001	0.0020	0.025	0.137	0.001	0.130	0.0692	871	713	Conforming steel
69	0.29	0.26	1.2	0.00550	0.0014	0.045	0.008	0.003	0.00075	0.064	0.061	0.0002	0.92	0.27	0.90	0.31	0.41	0.03	0.011	0.0058	0.0100	0.0018	0.087	0.148	0.005	0.247	0.2765	848	720	Conforming steel
70	0.27	0.18	1.0	0.00780	0.0005	0.133	0.006	0.001	0.00061	0.024	0.033	0.0008	1.79	0.65	0.09	0.20	0.64	0.06	0.020	0.0064	0.0006	0.0014	0.034	0.173	0.002	0.153	0.1689	851	689	Conforming steel
71	0.11	0.97	1.4	0.01220	0.0007	0.009	0.009	0.003	0.00079	0.053	0.017	0.0047	0.47	0.87	0.72	0.30	0.11	0.10	0.044	0.0031	0.0063	0.0010	0.048	0.142	0.002	0.285	0.1012	897	735	Conforming steel
72	0.36	1.04	1.2	0.00470	0.0006	0.101	0.001	0.002	0.00061	0.013	0.055	0.0028	1.87	0.90	0.73	0.33	0.23	0.03	0.001	0.0021	0.0071	0.0001	0.075	0.073	0.001	0.216	0.1384	856	719	Conforming steel
73	0.17	1.14	0.9	0.01270	0.0006	0.119	0.001	0.003	0.00049	0.024	0.071	0.0030	1.25	0.34	0.44	0.53	0.12	0.08	0.025	0.0084	0.0043	0.0004	0.100	0.137	0.000	0.142	0.2516	932	728	Conforming steel
74	0.31	1.33	0.7	0.01140	0.0003	0.048	0.008	0.003	0.00073	0.033	0.059	0.0021	1.68	0.69	0.53	0.21	0.61	0.01	0.009	0.0016	0.0064	0.0002	0.000	0.174	0.002	0.001	0.2973	892	731	Conforming steel
75	0.22	1.33	0.9	0.01240	0.0003	0.091	0.009	0.001	0.00065	0.074	0.006	0.0020	0.72	0.89	0.01	0.45	0.82	0.06	0.003	0.0014	0.0025	0.0016	0.200	0.127	0.002	0.151	0.0842	929	730	Conforming steel
76	0.38	1.37	1.2	0.00640	0.0015	0.075	0.003	0.003	0.00092	0.056	0.054	0.0027	1.10	0.31	0.40	0.28	0.43	0.09	0.034	0.0058	0.0034	0.0007	0.131	0.100	0.001	0.038	0.2063	900	730	Conforming steel
77	0.33	1.94	1.4	0.00870	0.0012	0.067	0.004	0.005	0.00064	0.029	0.015	0.0048	0.98	0.35	0.25	0.02	0.56	0.04	0.040	0.0039	0.0081	0.0016	0.076	0.000	0.003	0.007	0.1181	914	738	Conforming steel
78	0.23	1.77	1.2	0.01110	0.0014	0.086	0.008	0.001	0.00035	0.039	0.023	0.0014	1.04	0.73	0.36	0.18	0.33	0.09	0.019	0.0094	0.0049	0.0012	0.187	0.200	0.004	0.179	0.2380	927	739	Conforming steel
79	0.42	0.82	0.5	0.00140	0.0011	0.084	0.007	0.002	0.00056	0.087	0.034	0.0018	1.83	0.14	0.20	0.02	0.03	0.10	0.046	0.0003	0.0008	0.0011	0.084	0.092	0.003	0.063	0.1539	877	712	Conforming steel
80	0.35	1.49	0.5	0.01240	0.0011	0.066	0.006	0.002	0.00018	0.019	0.053	0.0039	0.43	0.02	0.81	0.10	0.59	0.08	0.001	0.0083	0.0083	0.0003	0.151	0.008	0.000	0.035	0.2454	937	761	Conforming steel
81	0.24	0.10	1.2	0.00100	0.0008	0.091	0.006	0.003	0.00082	0.062	0.058	0.0041	0.83	0.12	0.54	0.46	0.09	0.08	0.032	0.0050	0.0070	0.0009	0.126	0.170	0.005	0.163	0.2486	866	709	Conforming steel
82	0.30	0.89	1.0	0.01140	0.0008	0.131	0.008	0.004	0.00083	0.042	0.097	0.0020	0.88	0.96	0.07	0.60	0.56	0.01	0.001	0.0010	0.0095	0.0011	0.119	0.159	0.003	0.150	0.1043	897	718	Conforming steel
83	0.19	1.70	1.2	0.00960	0.0013	0.098	0.007	0.002	0.00062	0.005	0.012	0.0017	1.99	0.05	0.44	0.34	0.59	0.03	0.047	0.0079	0.0047	0.0010	0.029	0.033	0.002	0.000	0.1156	925	725	Conforming steel
84	0.40	0.62	0.5	0.00290	0.0006	0.126	0.004	0.002	0.00097	0.039	0.091	0.0019	0.56	0.94	0.48	0.12	0.63	0.09	0.025	0.0043	0.0017	0.0007	0.005	0.150	0.001	0.300	0.0016	877	733	Conforming steel
85	0.39	1.87	0.8	0.00770	0.0010	0.146	0.002	0.003	0.00067	0.013	0.052	0.0041	0.30	0.15	0.31	0.12	0.34	0.05	0.006	0.0023	0.0085	0.0001	0.194	0.171	0.005	0.168	0.1501	948	756	Conforming steel
86	0.37	1.02	0.5	0.01150	0.0008	0.078	0.006	0.003	0.00046	0.095	0.051	0.0009	1.79	0.89	0.51	0.19	0.75	0.03	0.002	0.0002	0.0009	0.0015	0.062	0.075	0.003	0.141	0.0001	877	725	Conforming steel
87	0.20	0.72	1.1	0.01120	0.0010	0.143	0.002	0.005	0.00029	0.047	0.094	0.0035	0.06	0.44	0.64	0.15	0.58	0.05	0.027	0.0086	0.0034	0.0013	0.004	0.040	0.004	0.292	0.3000	904	737	Conforming steel
94	0.12	0.13	1.1	0.00700	0.0010	0.025	0.004	0.003	0.00080	0.042																		878	710	Conforming steel
95	0.11	0.16	1.1	0.00960	0.0011	0.031	0.004	0.003	0.00080							0.16												888	711	Conforming steel
96	0.15	0.20	1.1	0.00800	0.0010	0.033	0.004	0.003	0.00080	0.039		0.0019	0.10															878	711	Conforming steel
97	0.20	0.15	1.1	0.00700	0.0011	0.031	0.004	0.003	0.00080							0.11												875	711	Conforming steel
98	0.17	0.17	1.1	0.00900	0.0010	0.042	0.004	0.003	0.00080	0.050								0.03										881	711	Conforming steel

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

[0098]

[Table 2-1]

Steel No.	Chemical composition (% by mass) [*1]																												Ac3 point (°C)	Ac1 point (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H	Nb	Ti	Ca	Ni	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb			
88	0.12	1.49	1.2	0.00160	0.0003	0.037	0.008	0.003	0.00083	0.040	0.010	0.0010	0.11	0.10	0.03	0.10	-	0.03	-	0.0001	-	0.0013	-	-	-	-	-	936	738	Conforming steel
89	0.10	1.73	1.2	0.01480	0.0005	0.060	0.003	0.001	0.00069	0.050	0.010	0.0010	0.01	0.12	0.03	0.10	-	0.03	-	-	-	0.0013	-	-	-	-	-	961	745	Conforming steel
90	0.45	1.97	1.0	0.01290	0.0011	0.146	0.008	0.001	0.03200	0.050	0.010	0.0010	0.13	0.10	0.03	0.10	-	0.03	-	-	-	0.0013	-	-	-	-	-	948	751	Comparative steel

[*1] The remainder is composed of Fe and incidental impurities "-": no intended addition

Underline: outside the scope of the present invention.

[0099]

[Table 2-2]

Steel No.	Chemical composition (% by mass) *1																											Ac3 point (°C)	Ac1 point (°C)	Notes
	C	Si	Mn	P	S	Al	O	N	H	Nb	Ti	Ca	Ni	Cu	Cr	Mo	W	V	Zr	REM	Mg	B	Hf	Ta	Re	Sn	Sb			
91	0.13	0.25	1.3	0.0016	0.0003	0.037	0.008	0.003	0.00083	0.040	0.010	0.0010	0.11	0.10	0.03	0.10	-	0.03	-	0.0001	-	0.0013	-	-	-	-	-	876	747	Conforming steel
92	0.12	0.40	1.2	0.0112	0.0005	0.062	0.005	0.002	0.00080	0.045	0.010	0.0010	0.01	0.12	0.03	0.11	-	0.02	-	-	-	0.0010	-	-	-	-	-	896	744	Conforming steel
93	0.12	0.25	1.0	0.0129	0.0011	0.146	0.008	0.001	0.04020	0.050	0.010	0.0010	0.13	0.10	0.03	0.10	-	0.02	-	-	-	0.0013	-	-	-	-	-	904	740	Comparative steel

*1 The remainder is composed of Fe and incidental impurities

Underline: outside the scope of the present invention.

"-": no intended addition

[0100]

[Table 3-1]

			Cooling step										
			A		B								
Steel pipe No.	Steel material No.	Steel No.	Average cooling rate of 800°C-550°C °C/s	Average cooling rate of 550°C-50°C °C/s	Average cooling rate of 800°C-300°C °C/s	Average cooling rate of 300°C-50°C °C/s	Residual r ratio (%)	B fraction (%)	M fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	Notes
1	1	1	48	8	-	-	0.0	93	-	689	358	0.91	Inventive example
2	2	2	48	7	-	-	0.8	99	-	603	283	0.97	Inventive example
3	3	3	19	9	-	-	0.4	93	-	633	323	0.92	Inventive example
4	4	4	10	5	-	-	0.3	70	-	622	334	0.82	Comparative example
5	5	5	30	5	-	-	1.1	93	-	594	315	0.97	Inventive example
6	6	6	48	6	-	-	0.2	95	-	593	314	0.90	Inventive example
7	7	7	40	8	-	-	1.6	98	-	615	283	0.92	Inventive example
8	8	8	15	25	-	-	5.0	92	-	622	334	0.85	Comparative example
9	9	9	30	7	-	-	0.2	97	-	533	267	0.97	Inventive example
10	10	10	40	9	-	-	0.6	95	-	613	307	0.95	Inventive example
11	11	11	35	6	-	-	2.3	93	-	657	309	0.95	Inventive example
12	12	12	5	7	-	-	1.7	60	-	676	338	0.75	Comparative example
13	13	13	30	8	-	-	2.4	93	-	666	320	0.93	Inventive example
14	14	14	40	7	-	-	2.2	97	-	580	290	0.99	Inventive example
15	15	15	48	9	-	-	0.1	95	-	679	312	0.95	Inventive example
16	16	16	48	6	-	-	1.9	92	-	630	302	0.91	Inventive example
17	17	17	45	8	-	-	2.0	92	-	640	288	0.93	Inventive example
18	18	18	48	7	-	-	2.5	92	-	608	322	0.90	Inventive example
19	19	19	45	8	-	-	1.5	90	-	656	321	0.92	Inventive example
20	20	20	48	7	-	-	0.5	93	-	550	297	0.96	Inventive example
21	21	21	48	9	-	-	1.1	95	-	581	302	0.90	Inventive example
22	22	22	45	8	-	-	0.6	98	-	557	262	0.99	Inventive example
23	23	23	48	7	-	-	1.0	93	-	582	274	0.91	Inventive example
24	24	24	48	9	-	-	2.3	96	-	573	281	0.94	Inventive example
25	25	25	35	8	-	-	3.0	95	-	676	338	1.00	Inventive example
26	26	26	45	7	-	-	2.9	96	-	602	325	0.98	Inventive example
27	27	27	48	8	-	-	0.1	95	-	561	286	0.93	Inventive example
28	28	28	48	7	-	-	2.1	92	-	592	320	0.90	Inventive example
29	29	29	48	9	-	-	0.8	95	-	604	290	1.00	Inventive example
30	30	30	48	7	-	-	1.8	92	-	666	340	0.95	Inventive example

Underline: outside the scope of the present invention.
γ: austenite, B: bainite, M: martensite

[0101]

[Table 3-2]

Steel pipe No.	Steel material No.	Steel No.	Cooling step				Residual r ratio (%)	B fraction (%)	M fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	Notes
			A		B								
			Average cooling rate of 800°C-550°C °C/s	Average cooling rate of 550°C-50°C °C/s	Average cooling rate of 800°C-300°C °C/s	Average cooling rate of 300°C-50°C °C/s							
31	31	31	35	9	-	-	1.2	91	-	644	341	0.91	Inventive example
32	32	32	45	8	-	-	2.8	92	-	547	301	0.99	Inventive example
33	33	33	48	7	-	-	1.6	97	-	692	374	0.99	Inventive example
34	34	34	45	9	-	-	2.8	94	-	632	322	0.91	Inventive example
35	35	35	48	6	-	-	2.5	95	-	694	354	0.96	Inventive example
36	36	36	48	9	-	-	1.8	92	-	535	262	1.00	Inventive example
37	37	37	35	8	-	-	0.9	95	-	523	262	0.95	Inventive example
38	38	38	45	7	-	-	1.7	96	-	584	292	0.99	Inventive example
39	39	39	48	8	-	-	2.3	90	-	548	279	0.99	Inventive example
40	40	40	45	7	-	-	1.5	93	-	602	313	0.94	Inventive example
41	41	41	48	9	-	-	1.4	96	-	629	296	0.93	Inventive example
42	42	42	48	7	-	-	2.4	91	-	625	281	0.94	Inventive example
43	43	43	35	8	-	-	1.0	91	-	587	288	0.96	Inventive example
44	44	44	45	7	-	-	0.9	96	-	671	349	0.95	Inventive example
45	45	45	48	9	-	-	1.7	98	-	587	311	0.98	Inventive example
46	46	46	48	9	-	-	0.6	90	-	625	338	0.92	Inventive example
47	47	47	48	6	-	-	1.3	93	-	624	300	0.90	Inventive example
48	48	48	35	8	-	-	2.1	98	-	650	338	0.91	Inventive example
49	49	49	45	7	-	-	2.8	92	-	653	294	0.97	Inventive example
50	50	50	48	8	-	-	0.6	95	-	564	276	0.96	Inventive example
51	51	51	48	7	-	-	1.7	90	-	621	317	0.95	Inventive example
52	52	52	35	9	-	-	1.0	93	-	603	302	0.93	Inventive example
53	53	53	48	8	-	-	1.8	96	-	658	322	0.96	Inventive example
54	54	54	48	7	-	-	0.1	91	-	693	381	0.96	Inventive example
55	55	55	35	9	-	-	1.6	97	-	584	286	0.96	Inventive example
56	56	56	45	8	-	-	0.8	94	-	647	330	0.99	Inventive example
57	57	57	48	7	-	-	0.3	90	-	655	301	0.92	Inventive example
58	58	58	48	9	-	-	0.1	94	-	608	322	0.92	Inventive example
59	59	59	48	9	-	-	3.0	90	-	544	277	0.97	Inventive example
60	60	60	35	8	-	-	1.2	96	-	584	280	0.99	Inventive example

Underline: outside the scope of the present invention.
γ: austenite, B: bainite, M: martensite

[0102]

[Table 3-3]

			Cooling step										
			A		B								
Steel pipe No.	Steel material No.	Steel No.	Average cooling rate of 800°C-550°C °C/s	Average cooling rate of 550°C-50°C °C/s	Average cooling rate of 800°C-300°C °C/s	Average cooling rate of 300°C-50°C °C/s	Residual r ratio (%)	B fraction (%)	M fraction (%)	TS (MPa)	Fatigue limit stress in hydrogen (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	Notes
61	61	61	45	7	-	-	2.4	95	-	644	303	0.92	Inventive example
62	62	62	48	9	-	-	1.3	98	-	598	299	0.97	Inventive example
63	63	63	40	8	-	-	1.8	92	-	556	278	0.96	Inventive example
64	64	64	48	7	-	-	2.2	91	-	628	333	0.99	Inventive example
65	65	65	30	9	-	-	2.3	96	-	524	278	0.93	Inventive example
66	66	66	35	6	-	-	0.8	97	-	582	308	0.93	Inventive example
67	67	67	45	8	-	-	0.5	97	-	651	326	0.90	Inventive example
68	68	68	48	7	-	-	0.7	98	-	635	324	0.93	Inventive example
69	69	69	40	8	-	-	0.3	94	-	557	279	0.95	Inventive example
70	70	70	48	7	-	-	1.1	92	-	578	312	0.95	Inventive example
71	71	71	30	9	-	-	1.5	98	-	582	303	0.94	Inventive example
72	72	72	48	8	-	-	1.5	98	-	654	314	0.98	Inventive example
73	73	73	40	7	-	-	2.2	90	-	673	330	0.93	Inventive example
74	74	74	48	9	-	-	2.7	92	-	650	351	0.94	Inventive example
75	75	75	48	9	-	-	2.4	93	-	549	296	1.00	Inventive example
76	76	76	40	8	-	-	1.9	92	-	536	273	0.97	Inventive example
77	77	77	48	7	-	-	0.8	97	-	676	345	0.96	Inventive example
78	78	78	30	9	-	-	0.1	90	-	549	247	1.00	Inventive example
79	79	79	48	8	-	-	2.3	92	-	543	244	0.90	Inventive example
80	80	80	40	7	-	-	2.3	95	-	559	268	0.99	Inventive example
81	81	81	48	9	-	-	0.9	98	-	648	337	0.90	Inventive example
82	82	82	48	9	-	-	0.9	91	-	523	235	0.94	Inventive example
83	83	83	40	6	-	-	2.3	95	-	650	358	0.96	Inventive example
84	84	84	30	8	-	-	2.9	92	-	622	292	0.93	Inventive example
85	85	85	30	7	-	-	2.3	91	-	617	296	0.91	Inventive example
86	86	86	48	9	-	-	0.4	92	-	626	282	0.99	Inventive example
87	87	87	40	9	-	-	1.4	98	-	684	356	0.96	Inventive example
94	94	94	45	7	-	-	0.2	96	-	612	303	0.98	Inventive example
95	95	95	35	9	-	-	0.3	98	-	623	308	0.97	Inventive example
96	96	96	38	8	-	-	0.4	97	-	628	320	0.96	Inventive example
97	97	97	39	9	-	-	0.5	96	-	654	324	0.97	Inventive example
98	98	98	42	9	-	-	0.0	98	-	606	311	0.98	Inventive example

Underline: outside the scope of the present invention.
γ: austenite, B: bainite, M: martensite

[0103]

[Table 4-1]

			Cooling step										
			A		B								
Steel pipe No.	Steel material No.	Steel No.	Average cooling rate of 800°C-550°C °C/s	Average cooling rate of 550°C-50°C °C/s	Average cooling rate of 800°C-300°C °C/s	Average cooling rate of 300°C-50°C °C/s	Residual r ratio (%)	B fraction (%)	M fraction (%)	TS (MPa)	Fatigue limit stress (in hydrogen) MPa	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	Notes
88	88	88	-	-	20	4	0.0	-	93	689	358	0.91	Inventive example
89	89	89	-	-	5	5	0.8	-	70	603	271	0.85	Comparative example
90	90	90	-	-	30	15	0.4	-	93	753	339	0.82	Comparative example

Underline: outside the scope of the present invention.
γ: austenite, B: bainite, M: martensite

[0104]

[Table 4-2]

			Cooling step										
			A		B								
Steel pipe No.	Steel material No.	Steel No.	Average cooling rate of 800°C-550°C °C/s	Average cooling rate of 550°C-50°C °C/s	Average cooling rate of 800°C-300°C °C/s	Average cooling rate of 300°C-50°C °C/s	Residual γ fraction (%)	B fraction (%)	M fraction (%)	TS (MPa)	Fatigue limit stress (in hydrogen) (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	Notes
91	91	91	-	-	22	5	0.0	-	95	689	324	0.94	Inventive example
92	92	92	-	-	5	4	2.1	-	70	580	261	0.85	Comparative example
93	93	93	-	-	30	20	0.2	-	90	670	302	0.82	Comparative example

Underline: outside the scope of the present invention.
γ: austenite, B: bainite, M: martensite

EXAMPLE 2

[0105]

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 steels Nos. 1, 14, 46, and 91 shown in Tables 1-1, 1-2, and 2-2 were used, up to the tempering step was performed under the same conditions as the steel pipes Nos. 1, 14, and 46 shown in Tables 3-1 and 3-2 and the steel pipe No. 91 shown in Table 4-1. The characteristics were evaluated while the dehydrogenation treatment conditions were changed. Table 5 shows the results. In Example 2, for the steel pipes and steel materials Nos. 1A, 14A, 46A, and 91A, the dehydrogenation treatment temperature T (ambient temperature) is 50°C, and the holding time tc after the temperature Tc at the middle of the sheet thickness reaches 50°C satisfies the formula (A). For the steel pipes and steel materials Nos. 14B, 46B, and 91B, the dehydrogenation treatment temperature T (ambient temperature) is 50°C, and the holding time tc satisfied the formula (A) at a dehydrogenation treatment temperature T of 50°C, but the holding time tc after the temperature Tc at the middle of the sheet thickness reaches 50°C does not satisfy the formula (A). For the steel pipes and steel materials Nos.

14C, 46C, and 91C, the dehydrogenation treatment temperature T (ambient temperature) is 50°C, but neither the holding time t at the ambient temperature nor the holding time tc after the temperature Tc at the middle of the sheet thickness reaches 50°C satisfy the formula (A).

[0106]

In Table 5, “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 tc at steel material center temperature Tc" means that the holding time tc after the temperature Tc at the middle of the sheet thickness reaches 50°C satisfies the formula (A), and “N” in "Holding time tc 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 tc after Tc reaches 50°C does not satisfy the formula (A).

[0107]

The fatigue test, the microstructure, the method for measuring the tensile strength, and the like are the same as those in Example 1.

[0108]

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 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, and 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. A steel pipe and a steel material of the same number had the same characteristics.

[0109]

[Table 5]

Steel pipe No.	Steel material No.	Dehydrogenation holding time t	Holding time tc at steel material center temperature TC	Residual r ratio (%)	B fraction (%)	M fraction (%)	TS (MPa)	Fatigue limit stress (in hydrogen) (MPa)	Fatigue limit stress in hydrogen/ fatigue limit stress in inert gas environment	Notes
1A	1	Y	Y	0.0	93	-	689	324	0.93	Inventive example
14A	14	Y	Y	2.2	97	-	568	273	0.99	Inventive example
14B	14	Y	N	2.2	98	-	580	278	0.96	Inventive example
14C	14	N	N	2.2	99	-	592	284	0.91	Inventive example
46A	46	Y	Y	0.6	90	-	620	340	1.00	Inventive example
46B	46	Y	N	0.6	90	-	625	338	0.95	Inventive example
46C	46	N	N	0.6	90	-	630	315	0.92	Inventive example
91A	91	Y	Y	0.0	-	95	665	319	0.97	Inventive example
91B	91	Y	N	0.0	-	96	689	331	0.95	Inventive example
91C	91	N	N	0.0	-	97	692	332	0.94	Inventive example

Steel material center temperature: Y indicates holding for time R or more after the temperature Tc at the middle of the sheet thickness reached the target temperature Tc of the dehydrogenation treatment temperature, N indicates not holding

γ: austenite, B: bainite, M: martensite

EXAMPLE 3

[0110]

Examples that have verified the advantages of the present invention are described below. In the following Examples, steel materials and steel pipes were produced under the following production conditions and were characterized. Steel pipes and steel materials with the same chemical composition as Nos. 14 and 46 shown in Tables 3-1 and 3-2 and No. 91 shown in Table 4-2 were subjected to up to the cooling step under predetermined conditions, were reheated after the cooling step (before the tempering step), were subjected to the quenching step under the conditions shown in Tables 6-1 and 6-2, and were characterized. The results are also shown in Tables 6-1 and 6-2. The steel pipes and steel materials Nos. 14E, 14F, 46E, and 46F shown in Table 6-1 were produced by subjecting the steel pipes and steel materials Nos. 14 and 46 shown in Tables 3-1 and 3-2 to the reheating step. The steel pipes and steel materials Nos. 91E and 91F shown in Table 6-2 were produced by subjecting the steel pipe and steel material No. 91 shown in Table 4-2 to the reheating step.

[0111]

The fatigue test, the microstructure, the method for measuring the tensile strength, and the like are the same as those in Example 1.

[0112]

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 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, and the tensile strength satisfied 520 MPa or more. A steel pipe and a steel material of the same number had the same characteristics.

[0113]

[Table 6-1]

Steel pipe No.	Steel material No.	Steel No.	Reheating step	Cooling step				Residual r ratio (%)	B fraction (%)	M fraction (%)	TS (MPa)	Fatigue limit stress (in hydrogen) (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	Notes
				A		B								
			Reheating temperature (°C)	Average cooling rate of 800°C-550°C (°C/s)	Average cooling rate of 550°C-50°C (°C/s)	Average cooling rate of 800°C-300°C (°C/s)	Average cooling rate of 300°C-50°C (°C/s)							
14-1	14-1	14	-	-	-	13	3	0.1	98	-	596	280	0.95	Inventive example
14-1E	14-1E	14	900					0.0	95	-	612	288	0.97	Inventive example
14-1F	14-1F	14	950					0.2	95	-	632	297	0.95	Inventive example
46	46	46	-	48	9	-	-	0.6	90	-	625	338	0.95	Inventive example
46E	46E	46	920					0.0	95	-	640	349	0.97	Inventive example
46F	46F	46	970					0.2	94	-	630	342	0.96	Inventive example

γ: austenite, B: bainite, M: martensite

[0114]

[Table 6-2]

Steel pipe No.	Steel material No.	Steel No.	Reheating temperature	Cooling step				γ fraction (%)	B fraction (%)	M fraction (%)	TS (MPa)	Fatigue limit stress (in hydrogen) (MPa)	Fatigue limit stress in hydrogen/fatigue limit stress in inert gas environment	Notes
				A	B									
				Average cooling rate of 800°C-550°C (°C/s)	Average cooling rate of 550°C-50°C (°C/s)	Average cooling rate of 800°C-300°C (°C/s)	Average cooling rate of 300°C-50°C (°C/s)							
91	91	91	-	-	-	22	5	0.0	-	95	689	324	0.94	Inventive example
91E	91E	91	900					0.2	-	95	697	335	0.96	Inventive example
91F	91F	91	950					0.2	-	92	670	322	0.95	Inventive example

γ: austenite, B: bainite, M: martensite

CLAIMS

[Claim 1]

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: 0.10% to 0.45%,

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%,

Ti: 0% to 0.1%,

Ca: 0% to 0.005%,

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%, bainite or martensite presents at a quarter thickness position from an inner surface of the steel pipe with an area fraction of the bainite of 90% or more or an area fraction of the martensite of 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.

[Claim 2]

The steel pipe 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%,

Ti: 0.005% to 0.1%,

Ca: 0.0001% to 0.005%,

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%.

[Claim 3]

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

a casting step of casting a steel raw material having the chemical composition according to Claim 1 or 2 at a casting speed of 1.8 m/min or less;

a heating step of heating the steel raw material at 1350°C or less;

a hot rolling step of rolling the steel raw material heated in the heating step with a finish rolling temperature of 820°C or more to form a steel pipe shape;

a cooling step of, after holding a steel pipe produced in the hot rolling step at a temperature of an Ac_3 point or higher and 1000°C or less, cooling the steel pipe wherein a cooling condition is the following Group A or Group B; and

a tempering step of tempering the steel pipe produced in the cooling step at 400°C or more and an Ac_1 point or lower,

Group A:

cooling the steel pipe to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C in terms of a temperatuer at a quarter thickness position from an inner surface of the steel pipe and at an average cooling rate of 15°C/s or less from 550°C to 50°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe, and

Group B:

cooling the steel pipe to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe and at an average cooling rate of 5°C/s or less from 300°C to 50°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe.

[Claim 4]

The method for producing a steel pipe for a line pipe according to Claim 3, comprising, before the tempering step, a quenching step of reheating the steel pipe to an Ac_3 point or higher and 1000°C or less, and cooling the steel pipe wherein a cooling condition is the following Group A or Group B,

Group A:

cooling the steel pipe to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe and at an average cooling rate of 15°C/s or less from 550°C to 50°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe, and

Group B:

cooling the steel pipe to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe and at an average cooling rate of 5°C/s or less from 300°C to 50°C in terms of a temperature at the quarter thickness position from the inner surface of the steel pipe.

[Claim 5]

The method for producing a steel pipe for a line pipe according to Claim 3 or 4, wherein the casting speed is 1.0 m/min or less.

[Claim 6]

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: 0.10% to 0.45%,

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%,

Ti: 0% to 0.1%,

Ca: 0% to 0.005%,

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%, bainite or martensite presents at a quarter thickness position of the steel material with an area fraction of the bainite of 90% or more or an area fraction of the martensite of 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.

[Claim 7]

The steel material for a line pipe with high hydrogen embrittlement resistance according to Claim 6, wherein the chemical composition contains, on a mass percent basis,

Nb: 0.001% to 0.10%,
Ti: 0.005% to 0.1%,
Ca: 0.0001% to 0.005%,
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%.

[Claim 8]

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

a casting step of casting a steel raw material having the chemical composition according to Claim 6 or 7 at a casting speed of 1.8 m/min or less;

a heating step of heating the steel raw material at 1350°C or less;

a hot rolling step of rolling the steel raw material heated in the heating step with a finish rolling temperature of 820°C or more;

a cooling step of, after holding a steel material produced in the hot rolling step at a temperature of an Ac_3 point or higher and 1000°C or less, cooling the steel material wherein a cooling condition is the following Group A or Group B; and

a tempering step of tempering the steel material produced in the cooling step at 400°C or more and an Ac_1 point or lower,

Group A:

cooling the steel material to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C in terms of a temperature at a quarter thickness position from a surface of the steel material and at an average cooling rate of 15°C/s or less from 550°C to 50°C in terms of a temperature at the quarter thickness position from the surface of the steel material, and

Group B:

cooling the steel material to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C in terms of a temperature at the quarter thickness position from the surface of the steel material and at an average cooling rate of 5°C/s or less from 300°C to 50°C in terms of a temperature at the quarter thickness position from the surface of the steel material.

[Claim 9]

The method for producing a steel material for a line pipe according to Claim 8, comprising, before the tempering step, a quenching step of reheating the steel material to an Ac_3 point or higher and 1000°C or less, and cooling *the* steel material wherein a cooling condition is the following Group A or Group B,

Group A:

cooling the steel material to 50°C or less at an average cooling rate of 15°C/s or more from 800°C to 550°C in terms of a temperature at the quarter thickness position from the surface of the steel material and at an average cooling rate of 15°C/s or less from 550°C to 50°C in terms of a temperature at the quarter thickness position from the surface of the steel material, and

Group B:

cooling the steel material to 50°C or less at an average cooling rate of 10°C/s or more from 800°C to 300°C in terms of a temperatre at the quarter thickness position from the surface of the steel material and at an average cooling rate of 5°C/s or less from 300°C to 50°C in terms of a temperature at the quarter thickness position from the surface of the steel material.

[Claim 10]

The method for producing a steel material for a line pipe according to Claim 8 or 9, wherein the casting speed is 1.0 m/min or less.