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(54) **STEEL TUBE EXHIBITING EXCELLENT FATIGUE CHARACTERISTICS AGAINST HYDROGEN AND PRODUCTION METHOD THEREFOR, AND STEEL MATERIAL AND PRODUCTION METHOD THEREFOR**

(57) To provide a steel pipe with a good fatigue property in hydrogen in a high-pressure hydrogen gas environment, which is suitable for a steel structure used in a high-pressure hydrogen gas environment, such as a line pipe for 100% hydrogen gas or a natural gas containing hydrogen at a hydrogen partial pressure of 1 MPa or more (natural gas is a gas containing hydrocarbons, such as methane and ethane, as main components), a method

for producing the steel pipe, a steel material, and a method for producing the steel material.

The steel pipe with a good fatigue property in hydrogen has a specific chemical composition and a specific microstructure and has a crack growth rate da/dN of $1.0 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less at a stress intensity factor range of 20 MPa $\sqrt{\text{m}}$ in hydrogen of 1 MPa or more.

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Description

Technical Field

- 5 **[0001]** The present invention relates to a steel pipe with a good fatigue property in hydrogen, a method for producing the steel pipe, a steel material, and a method for producing the steel material.

Background Art

- 10 **[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
 15 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
 20 a hydrogen gas environment.

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

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

- 30 **[0005]** Patent Literature 2 discloses that a low-alloy high-strength steel adjusted to have a specific chemical composition is used in the tensile strength range of 900 to 950 MPa in the atmosphere to increase the reduction in area and elongation as compared with JIS G 3128 SHY685NS in a 45-MPa hydrogen atmosphere and improve high-pressure hydrogen environment embrittlement resistance characteristics.

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

- [0007]** Patent Literature 4 proposes a low-alloy steel for a high-pressure hydrogen gas environment. In the low-alloy steel described 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
 45 normalizing treatment in the production of a steel plate finely and densely disperses and precipitates an MC carbide (Mo, V) C and improves the hydrogen resistance, such as hydrogen embrittlement resistance, of the steel.

- [0009]** Patent Literature 6 proposes a steel material for high-pressure hydrogen storage. 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
 50 the bainite.

Citation List

Patent Literature

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[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

Summary of Invention

Technical Problem

[0012] With respect to the pressure in a line pipe, due to fluctuations during operation or periodical shutdown, stress is repeatedly applied to a structure like the line pipe. 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 based on 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 fatigue strength in hydrogen gas, that is, there is a problem in that it is difficult to achieve both the suppression of the occurrence of hydrogen-induced cracking in a sour environment and high fatigue strength in hydrogen gas, which more easily affects the service life

[0013] In view of the problems of the related art, it is an object of the present invention to provide a steel pipe with a good fatigue property in hydrogen in a high-pressure hydrogen gas environment, which is suitable for a steel structure used in a high-pressure hydrogen gas environment, such as a line pipe for 100% hydrogen gas or a natural gas containing hydrogen at a hydrogen partial pressure of 1 MPa or more (natural gas is a gas containing hydrocarbons, such as methane and ethane, as main components), a method for producing the steel pipe, a steel material, and a method for producing the steel material.

[0014] The phrase "a good fatigue property in hydrogen in a high-pressure hydrogen environment", as used herein, means that the crack growth rate da/dN at a stress intensity factor range of 20 MPa $\sqrt{m}$ is $1.0 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less, as determined by a fatigue test in accordance with ASTM E647 at a frequency of 1 Hz, a repetitive waveform of a sine wave, a control method of load control, and a stress ratio of $R = 0.1$, in both environments of hydrogen gas at room temperature ($20^\circ\text{C} \pm 10^\circ\text{C}$) and at a pressure of 1 MPa or more and a natural gas (the main components are hydrocarbons, such as methane and ethane) mixed atmosphere containing hydrogen at a hydrogen partial pressure of 1 MPa or more. 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 30 MPa or less as the entire gas.

[0015] When the crack growth rate da/dN in a hydrogen environment is $1.0 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less, it is possible to design a structural steel for hydrogen in a plate thickness range that is possible in the production process. Solution to Problem

[0016] From the above perspective, the present inventors have conducted extensive studies on the conditions to be satisfied by various steel materials in hydrogen gas and have found a novel steel pipe and a novel steel material with a good fatigue property in hydrogen.

[0017] The present invention has been further studied based on such new findings, and the gist of the present invention is as follows:

[1] A steel pipe with a good fatigue property in hydrogen, the steel pipe having a chemical composition comprising:

on a mass percent basis,
 C: 0.10% to 0.45%,
 Si: 0.01% to 2.0%,
 Mn: 0.3% to 2.0%,
 Al: 0.01% to 0.15%,
 N: 0.0005% to 0.008%,
 P: 0.015% or less,
 S: 0.0015% or less,
 O: 0.01% or less,
 H: 0.0010% or less,
 Cu: 0% to 2.5%,

Ni: 0% to 2.5%,
 Cr: 0% to 2.5%,
 Mo: 0% to 2.0%,
 Nb: 0% to 0.5%,
 5 V: 0% to 0.5%,
 Ti: 0% to 0.5%,
 W: 0% to 2.5%,
 B: 0% to 0.005%,
 Sn: 0% to 0.3%,
 10 Sb: 0% to 0.3%,
 Ca: 0% to 0.01%,
 Mg: 0% to 0.01%, and
 REM: 0% to 0.005%,
 the remainder being Fe and incidental impurities,
 15 wherein retained austenite constitutes 3% or less,
 the number of carbides with a diameter of 200 nm or more is 20 pieces/10 μm^2 or less, and
 a crack growth rate da/dN at a stress intensity factor range of 20 MPa $\sqrt{\text{m}}$ in hydrogen of 1 MPa or more is 1.0×10^{-6}
 m $\cdot$ cycle $^{-1}$ or less.

20 [2] A method for producing a steel pipe, the method comprising:

a casting step of casting a steel raw material with the chemical composition according to [1] at a casting speed of
 1.8 m/min or less;
 a heating step of heating at 1350°C or less;
 25 a hot rolling step of rolling the steel raw material heated in the heating step at a finish rolling temperature of 820°C
 or more to form a steel pipe shape;
 a cooling step of holding a steel pipe obtained in the hot rolling step at a temperature of an A_{c3} temperature or
 higher and 1000°C or less, and a cooling condition is the following Group A or Group B; and
 a tempering step of tempering the steel pipe obtained in the cooling step at 400°C or more and an A_{c1} temperature
 30 or lower for less than 60 minutes,
 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 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 at the quarter thickness position from the inner surface of the steel pipe, and
 35 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 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 at the quarter thickness position from the inner surface of the steel pipe.

40 [3] The method for producing a steel pipe according to [2], comprising, before the tempering step, a quenching step of
 reheating to an A_{c3} temperature or higher and 1000°C or less, and a cooling condition is the following Group A or
 Group B,

Group A:
 45 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 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 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 at the
 50 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 at the quarter thickness position from the inner surface of the steel pipe.

[4] The method for producing a steel pipe according to [2] or [3], wherein the casting speed is 1.0 m/min or less.

55 [5] A steel material with a good fatigue property in hydrogen, the steel material having a chemical composition
 comprising:

on a mass percent basis,
 C: 0.10% to 0.45%,

Si: 0.01% to 2.0%,
Mn: 0.3% to 2.0%,
Al: 0.01% to 0.15%,
N: 0.0005% to 0.008%,
5 P: 0.015% or less,
S: 0.0015% or less,
O: 0.01% or less,
H: 0.0010% or less,
10 Cu: 0% to 2.5%,
Ni: 0% to 2.5%,
Cr: 0% to 2.5%,
Mo: 0% to 2.0%,
Nb: 0% to 0.5%,
V: 0% to 0.50,
15 Ti: 0% to 0.5%,
W: 0% to 2.5%,
B: 0% to 0.005%,
Sn: 0% to 0.3%,
Sb: 0% to 0.3%,
20 Ca: 0% to 0.01%,
Mg: 0% to 0.01%, and
REM: 0% to 0.005%,
the remainder being Fe and incidental impurities,
wherein retained austenite constitutes 3% or less,
25 the number of carbides with a diameter of 200 nm or more is 20 pieces/10 μm^2 or less, and
a crack growth rate da/dN at a stress intensity factor range of 20 MPa $\sqrt{\text{m}}$ in hydrogen of 1 MPa or more is 1.0×10^{-6}
 $\text{m} \cdot \text{cycle}^{-1}$ or less.

[6] A method for producing a steel material, the method comprising:

30 a casting step of casting a steel raw material with the chemical composition according to [5] at a casting speed of
1.8 m/min or less;
a heating step of heating at 1350°C or less;
a hot rolling step of rolling the steel raw material heated in the heating step at a finish rolling temperature of 820°C
35 or more;
a cooling step of holding a steel material obtained in the hot rolling step at a temperature of an Ac_3 temperature or
higher and 1000°C or less, and a cooling condition is the following Group A or Group B; and
a tempering step of tempering the steel material obtained in the cooling step at 400°C or more and an Ac_1
40 temperature or lower for less than 60 minutes,
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 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 at the quarter thickness position from the surface of the steel material, and
Group B:
45 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 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 at the quarter thickness position from the surface of the steel material.

[7] The method for producing a steel material according to [6], comprising, before the tempering step, a quenching step
50 of reheating to an Ac_3 temperature or higher and 1000°C or less, and a cooling condition is the following Group A or
Group B,

Group A:
55 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 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 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 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 at the quarter thickness position from the surface of the steel material.

[8] The method for producing a steel material according to [6] or [7], wherein the casting speed is 1.0 m/min or less.

Advantageous Effects of Invention

[0018] The present invention can provide a steel pipe and a steel material with a very good fatigue property in a high-pressure hydrogen gas environment and is industrially very useful.

Description of Embodiments

[0019] Next, a method for implementing the present invention is more specifically described.

[0020] 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.

First Embodiment

[Chemical Composition]

[0021] The reasons for limiting the 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".

C: 0.10% to 0.45%

[0022] C is an element necessary to increase strength. The effect is insufficient at less than 0.10%. Thus, the C content is 0.10% or more. The C content is preferably 0.13% or more. The C content is more preferably 0.15% or more, still more preferably 0.18% or more. On the other hand, more than 0.45% may result in a quenching crack at the time of quenching, causes the formation of a coarse carbide, and results in a degradation of the fatigue property in hydrogen. Thus, the C content is 0.45% or less. The C content is preferably 0.43% or less. The C content is more preferably 0.40% or less, still more preferably 0.38% or less.

Si: 0.01% to 2.0%

[0023] Si is contained as a deoxidizer in steelmaking and as an element for ensuring hardenability, but the effects are insufficient at less than 0.01%, so that the Si content is 0.01% or more. The Si content is preferably 0.1% or more. The Si content is more preferably 0.15% or more. On the other hand, more than 2.0% results in an embrittled grain boundary, a decrease in the low-temperature toughness, and a degradation of the fatigue property in hydrogen. Thus, the Si content is 2.0% or less. The Si content is preferably 1.5% or less. The Si content is preferably 1.0% or less, more preferably 0.8% or less.

Mn: 0.3% to 2.0%

[0024] Mn is contained as an element for ensuring hardenability, but the effect is insufficient at less than 0.3%, so that the Mn content is 0.3% or more. The Mn content is preferably 0.4% or more. The Mn content is more preferably 0.5% or more. The Mn content is still more preferably 0.6% or more. On the other hand, more than 2.0% results in a decrease in grain boundary strength and low-temperature toughness. Furthermore, a high Mn content may result in an increase in austenite stability, an amount of retained austenite exceeding a specified amount, and an increase in the amount of hydrogen in the steel. Furthermore, the hardness of a surface layer portion or a center segregation zone increases during cooling (accelerated cooling or quenching) after hot rolling, and the fatigue property in hydrogen deteriorates. Thus, the Mn content is 2.0% or less. The Mn content is preferably 1.5% or less, more preferably 1.3% or less. The Mn content is most preferably 1.0% or less.

Al: 0.01% to 0.15%

[0025] Al is contained as a deoxidizer and at the same time has an effect of pinning an austenite grain as a fine precipitate of an Al nitride during heating and suppressing coarsening of grains, but the effects are insufficient at less than 0.01%. Thus, the Al content is 0.01% or more. The Al content is preferably 0.02% or more. The Al content is more preferably 0.03% or more. On the other hand, a content of more than 0.15% results in a steel with lower cleanliness and toughness and a

degradation of the fatigue property in hydrogen. Thus, the Al content is 0.15% or less. The Al content is preferably 0.13% or less. The Al content is more preferably 0.10% or less, still more preferably 0.08% or less.

N: 0.0005% to 0.008%

[0026] N is contained because N forms a fine precipitate by forming a nitride with Nb, Ti, Al, or the like and has an effect of pinning an austenite grain during heating, thereby suppressing coarsening of the grain and improving low-temperature toughness. The effect of refining the microstructure is insufficient at a content of less than 0.0005%, so that the N content is 0.0005% or more. The N content is preferably 0.001% or more. The N content is more preferably 0.0025% or more. On the other hand, a content of more than 0.008% results in an increase in the amount of solute N, a base material and a weld heat-affected zone with lower toughness, and a degradation of the fatigue property in hydrogen. Thus, the N content is 0.008% or less. The N content is preferably 0.007% or less. The N content is more preferably 0.006% or less, still more preferably 0.005% or less.

P: 0.015% or less

[0027] An impurity element P is likely to segregate at a grain boundary, and more than 0.015% results in lower bonding strength between adjacent crystal grains, a decrease in the low-temperature toughness, and a degradation of the fatigue property in hydrogen. Thus, the P content is 0.015% or less. The P content is preferably 0.013% or less, more preferably 0.010% or less. The lower limit is preferably, but not limited to, 0.001% or more due to an increase in cost.

S: 0.0015% or less

[0028] An impurity element S is likely to segregate at a grain boundary and form a non-metallic inclusion MnS. More than 0.0015% results in lower bonding strength between adjacent crystal grains, an increase in the amount of inclusion, a decrease in the low-temperature toughness, and a degradation of the fatigue property in hydrogen. Thus, the S content is 0.0015% or less. The S content is preferably 0.0013% or less. The S content is more preferably 0.0010% or less, still more preferably 0.0008% or less. The lower limit is preferably, but not limited to, 0.0001% or more due to an increase in cost.

O: 0.01% or less

[0029] O forms an oxide with Al or the like and affects the workability of the material, and a lower O content is better. A content of more than 0.01% results in an increase in the amount of inclusion and lower workability. Further, as the amount of inclusion increases, the fatigue property in hydrogen deteriorates. Thus, the O content is 0.01% or less. The O content is preferably 0.009% or less. The O content is more preferably 0.008% or less. The lower limit is preferably, but not limited to, 0.0001% or more due to an increase in cost. The O content is more preferably 0.002% or more.

H: 0.0010% or less

[0030] 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 increases the crack growth rate, and it is therefore important to decrease the amount of hydrogen in the steel material. The effects do not cause a problem at 0.0010% or less, and the H content is therefore 0.0010% or less, preferably 0.0005% or less, more preferably 0.0002% or less. On the other hand, less than 0.00001% causes an increase in cost, so that 0.00001% or more is preferred. The H content is preferably 0.0001% 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.

[0031] In the present invention, the remainder of the chemical composition is preferably a steel composition composed of Fe and incidental impurities but, depending on the desired characteristics, it is preferable to further appropriately contain one or two or more of Cu: 0% to 2.5%, Ni: 0% to 2.5%, Cr: 0% to 2.5%, Mo: 0% to 2.0%, Nb: 0% to 0.5%, V: 0% to 0.5%, Ti: 0% to 0.5%, W: 0% to 2.5%, B: 0% to 0.005%, Sn: 0% to 0.3%, Sb: 0% to 0.3%, Ca: 0% to 0.01%, Mg: 0% to 0.01%, and REM: 0% to 0.005% individually or simultaneously.

Cu: 0% to 2.5%

[0032] Cu has an effect of improving the hardenability. Thus, when Cu is contained, the Cu content may be 0% or more, but the above effect is difficult to ensure at less than 0.05%, so that the Cu content is preferably 0.05% or more. On the other hand, more than 2.5% is likely to cause hot cracking during heating of a steel billet. Thus, when Cu is contained, the Cu content is 2.5% or less. The Cu content is preferably 2.3% or less. The Cu content is more preferably 2.0% or less, still more

preferably 1.8% or less.

Ni: 0% to 2.5%

[0033] Ni has an effect of improving the hardenability similarly to Cu and further has an effect of improving the toughness. Thus, when Ni is contained, the Ni content may be 0% or more, but the above effect is difficult to ensure at less than 0.05%, so that the Ni content is preferably 0.05% or more. On the other hand, more than 2.5% results in low economic efficiency. Thus, when Ni is contained, the Ni content is 2.5% or less. The Ni content is preferably 2.3% or less, more preferably 2.0% or less, preferably 1.8% or less.

Cr: 0% to 2.5%

[0034] Cr is contained as an element for ensuring hardenability, and when Cr is contained, the Cr content may be 0% or more, but the above effect is difficult to ensure at less than 0.1%, so that the Cr content is preferably 0.1% or more. On the other hand, a content of more than 2.5% results in lower toughness and low economic efficiency. Thus, when Cr is contained, the Cr content is 2.5% or less. The Cr content is preferably 2.3% or less. The Cr content is more preferably 2.0% or less, still more preferably 1.8% or less, most preferably 1.5% or less.

Mo: 0% to 2.0%

[0035] Mo has an effect of improving the hardenability, and when Mo is contained, the Mo content may be 0% or more, but the above effect is difficult to ensure at less than 0.05%, so that the Mo content is preferably 0.05% or more. On the other hand, a content of more than 2.0% results in low economic efficiency. Thus, when Mo is contained, the Mo content is 2.0% or less. The Mo content is preferably 1.8% or less. The Mo content is more preferably 1.5% or less, still more preferably 1.2% or less.

Nb: 0% to 0.5%

[0036] Nb has an effect of improving the hardenability, pins an austenite grain as a fine precipitate of a Nb-based carbide/nitride/carbonitride during heating, and suppresses coarsening of the grain. Thus, when Nb is contained, the Nb content may be 0% or more, but the above effect is difficult to ensure at less than 0.005%, so that the Nb content is preferably 0.005% or more. The Nb content is more preferably 0.01% or more. On the other hand, a content of more than 0.5% may result in precipitation of a coarse Nb carbonitride and lower toughness. Thus, when Nb is contained, the Nb content is 0.5% or less. The Nb content is preferably 0.4% or less. The Nb content is preferably 0.3% or less, and the Nb content is preferably 0.2% or less.

V: 0% to 0.5%

[0037] V has an effect of improving the hardenability, pins an austenite grain as a fine precipitate of a V carbide during heating, and suppresses coarsening of the grain. Thus, when V is contained, the V content may be 0% or more, but the above effect is difficult to ensure at less than 0.005%, so that the V content is preferably 0.005% or more. On the other hand, a content of more than 0.5% may result in precipitation of a coarse V carbonitride and lower toughness. Thus, when V is contained, the V content is 0.5% or less. The V content is preferably 0.4% or less. The V content is more preferably 0.3% or less, still more preferably 0.2% or less.

Ti: 0% to 0.5%

[0038] Ti has an effect of improving the hardenability and has an effect of pinning an austenite grain as a fine precipitate of a Ti-based carbide/nitride/carbonitride during heating and suppressing the growth of the grain. Thus, when Ti is contained, the Ti content may be 0% or more, but the above effect is difficult to ensure at less than 0.005%, so that the Ti content is preferably 0.005% or more. The Ti content is preferably 0.01% or more. On the other hand, a content of more than 0.5% tends to result in the formation of a coarse angular nitride and results in lower toughness. Thus, when Ti is contained, the Ti content is 0.5% or less. The Ti content is preferably 0.4% or less. The Ti content is more preferably 0.3% or less, still more preferably 0.2% or less.

W: 0% to 2.5%

[0039] W has an effect of improving the hardenability, and when W is contained, the W content may be 0% or more, but

the above effect is difficult to ensure at less than 0.05%, so that the W content is preferably 0.05% or more. On the other hand, more than 2.5% results in low economic efficiency. Thus, when W is contained, the W content is 2.5% or less. The W content is preferably 2.3% or less. The W content is more preferably 2.0% or less, still more preferably 1.8% or less.

5 B: 0% to 0.005%

[0040] B is an element for ensuring hardenability, and when B is contained, the B content may be 0% or more, but the above effect is difficult to ensure at less than 0.0005%, so that the B content is preferably 0.0005% or more. On the other hand, more than 0.005% results in lower toughness. Thus, when B is contained, the B content is 0.005% or less. The B content is preferably 0.004% or less. The B content is more preferably 0.003% or less, still more preferably 0.002% or less.

Sn: 0% to 0.3%

[0041] Sn has an effect of increasing the corrosion resistance of a steel pipe. Thus, when Sn is contained, the Sn content may be 0% or more, but the above effect is difficult to ensure at less than 0.005%, so that the Sn content is preferably 0.005% or more. The Sn content is more preferably 0.01% or more. On the other hand, a content of more than 0.3% results in a decrease in high-temperature ductility and an increase in the possibility of cracking during casting. Thus, when Sn is contained, the Sn content is 0.3% or less. The Sn content is preferably 0.25% or less. The Sn content is more preferably 0.2% or less, still more preferably 0.15% or less.

Sb: 0% to 0.3%

[0042] Sb has an effect of increasing the corrosion resistance of a steel pipe. Thus, when Sb is contained, the Sb content may be 0% or more, but the above effect is difficult to ensure at less than 0.005%, so that the Sb content is preferably 0.005% or more. The Sb content is more preferably 0.01% or more. On the other hand, a content of more than 0.3% results in a decrease in high-temperature ductility and a decrease in hot rollability. Thus, when Sb is contained, the Sb content is 0.3% or less. The Sb content is preferably 0.25% or less. The Sb content is more preferably 0.2% or less, still more preferably 0.15% or less.

30 Ca: 0% to 0.01%

[0043] Ca forms CaS and has an effect of controlling the form of a sulfide inclusion to CaS, which is a spherical inclusion less likely to be ductile by rolling, instead of MnS, which is an inclusion likely to be ductile by rolling. Thus, when Ca is contained, the Ca content may be 0% or more, but the above effect is difficult to ensure at less than 0.0005%, so that the Ca content is preferably 0.0005% or more. The Ca content is more preferably 0.001% or more. On the other hand, a content of more than 0.01% results in lower cleanliness and a degradation of the material property, such as toughness. Thus, when Ca is contained, the Ca content is 0.01% or less. The Ca content is preferably 0.005% or less. The Ca content is more preferably 0.003% or less, still more preferably 0.002% or less.

40 Mg: 0% to 0.01%

[0044] Mg may be used as a pig iron desulfurization material. Thus, when Mg is contained, the Mg content may be 0% or more, but the above effect is difficult to ensure at less than 0.0005%, so that the Mg content is preferably 0.0005% or more. The Mg content is more preferably 0.001% or more. On the other hand, a content of more than 0.01% results in lower cleanliness. Thus, when Mg is contained, the Mg content is 0.01% or less. The Mg content is preferably 0.005% or less. The Mg content is more preferably 0.004% or less, still more preferably 0.003% or less.

REM: 0% to 0.005%

[0045] REM forms a sulfide as REM(O, S) in steel, thereby reducing the amount of solute S at a grain boundary and improving SR cracking resistance characteristics. Thus, when REM is contained, the REM content may be 0% or more, but the above effect is difficult to ensure at less than 0.0005%, so that the REM content is preferably 0.0005% or more. On the other hand, a content of more than 0.005% results in significant accumulation of a REM sulfide in a sedimental zone and a deterioration of the material property. Thus, when REM is contained, the REM content is 0.005% or less. The REM content is preferably 0.003% or less. The REM content is more preferably 0.001% or less. REM is an abbreviation of Rare Earth Metal and refers to a rare-earth metal.

[0046] In the chemical composition of a steel plate and a steel pipe, the remainder other than the above components (elements) is composed of Fe and an incidental impurity element.

[0047] A preferred metallic microstructure of a steel pipe according to the present invention is more specifically described.

Retained austenite: 3% or less

[0048] 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, 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%.

Number of carbide with diameter of 200 nm or more: 20 pieces/10 μm^2 or less

[0049] In a steel pipe according to the present invention, a number of coarsened carbides equal to or greater than a predetermined number adversely affect the fatigue property in hydrogen. Thus, the number of carbides with a diameter of 200 nm or more is 20 pieces/10 μm^2 or less, preferably 15 pieces/10 μm^2 or less, more preferably 10 pieces/10 μm^2 or less, still more preferably 5 pieces/10 μm^2 or less. The lower limit is preferably as small as possible and may be 0 pieces/10 μm^2 . The diameter refers to a value calculated from $2\sqrt{(A/2 \times B/2)}$ using a long side A and a short side B passing through the center. Carbides refer to, for example, intermetallic compounds including cementite, ϵ -carbide, χ -carbide, Fe_7C_3 , and the like.

[0050] Furthermore, carbides with a diameter of less than 200 nm uniformly dispersed in a grain at intervals of 100 nm or more contribute to an improvement in strength without adversely affecting the fatigue property in hydrogen, so that carbides with a diameter of less than 200 nm dispersed in a grain are preferably 10 pieces/10 μm^2 or more. As for the upper limit, the number of carbides with a diameter of less than 200 nm dispersed in a grain is preferably 100 pieces/10 μm^2 or less for the reason that coarsening proceeds when the number of precipitates is too large. The precipitation of carbides is affected by the conditions of a cooling step and a tempering step after hot rolling described later, and it is therefore important to control these conditions.

[0051] Crack growth rate da/dN at stress intensity factor of 20 MPa $\sqrt{\text{m}}$ in hydrogen with pressure of 1 MPa or more: $1.0 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less

[0052] The fatigue crack growth rate is an important parameter in the design of a steel pipe used for a line pipe or a gas container and is necessary to obtain a service life in which the safety of a destructive structural member is ensured. In a destructive structural member, it is difficult to eliminate cracks and crack initiation sites, and a crack occurs inevitably and propagates under repeated stress. The crack growth rate is low when the stress applied to a crack tip is small, and increases as the stress to the crack tip increases. In a hydrogen environment, hydrogen enters a steel pipe and makes a crack more likely to propagate. The degree of acceleration of the crack growth rate by hydrogen is greatly affected by the microstructure and precipitates of the material. In a crack growth test in hydrogen at 1 MPa or more, when the crack growth rate da/dN at a stress intensity factor range of 20 MPa $\sqrt{\text{m}}$ is $1.0 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less determined in a fatigue test in accordance with ASTM E647 at a frequency of 1 Hz, a repetitive waveform of a sine wave, a control method of load control, and a stress ratio of $R = 0.1$, the service life of a steel structure in a high-pressure hydrogen environment can also be sufficiently ensured. Thus, in a crack growth test in hydrogen at 1 MPa or more, the crack growth rate da/dN at a stress intensity factor of 20 MPa $\sqrt{\text{m}}$ is $1.0 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less. The crack growth rate da/dN at a stress intensity factor of 20 MPa $\sqrt{\text{m}}$ is preferably $0.9 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less, more preferably $0.8 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less, still more preferably $0.7 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or less. The closer the lower limit is to the result in the atmosphere, the better it is considered, and the crack growth rate da/dN at a stress intensity factor of 20 MPa $\sqrt{\text{m}}$ is preferably $0.05 \times 10^{-6} \text{ m} \cdot \text{cycle}^{-1}$ or more.

[0053] The plate thickness of a steel pipe is preferably, but not limited to, 5 mm or more. The plate thickness is preferably 30 mm or less.

[0054] A steel pipe according to the present invention may be a seamless steel pipe, an electric-resistance-welded pipe, a UOE steel pipe, or the like, and a method for producing a seamless steel pipe is more specifically described as an example.

[0055] A steel pipe with a good fatigue property in hydrogen gas according to the present invention has the chemical composition described above and satisfies the crack growth rate in hydrogen, and a method for producing the steel pipe is more specifically described below.

[0056] 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 and cooling (accelerated cooling) step of heating and rolling a cast material to form a steel pipe shape (including a case of conducting reheating and quenching before a tempering step)
- (3) A step of tempering a steel pipe produced in the above step

[0058] Each of the steps is described below. Unless otherwise specified, the temperature in the following description is the temperature at the center of the plate thickness of a steel raw material or a steel pipe. The average cooling rate means the temperature at a quarter thickness position from the inner surface of a steel pipe. The temperature at the center of the plate 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.

[Casting Step]

Casting speed: 1.8 m/min or less

[0059] 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, so that the casting speed is 1.8 m/min or less, preferably 1.5 m/min or less, more preferably 1.0 m/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.

Heating Step

[0060] 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 slab, a billet, or the like produced by an ordinary continuous casting method.

Heating temperature: 1350°C or less

[0061] 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, so that 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.

Rolling Step

[0062] The steel raw material heated in the heating step is rolled into a steel pipe shape under the following conditions. The rolling can be hot rolling including piercing rolling, such as an ordinary Mannesmann-plug mill process or Mannesmann-mandrel mill process.

Finish rolling temperature: 820°C or more

[0063] 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.

[Cooling Step (Accelerated Cooling step)]

[0064] In the cooling step, a steel material with the chemical composition described above is heated and held at a temperature of the A_{c3} temperature 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.

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

[0065] A heating temperature lower than the Ac_3 temperature in the cooling step results in ferrite remaining in the steel after cooling, a decrease in the strength of a steel pipe, and a degradation of the fatigue property in hydrogen. Thus, the heating temperature is the Ac_3 temperature or higher. The heating temperature is preferably the Ac_3 temperature + 30°C or more, more preferably the Ac_3 temperature + 50°C or more. However, the Ac_3 temperature + 30°C or more or the Ac_3 temperature + 50°C or more is not applied to a composition system in which the Ac_3 temperature + 30°C or the Ac_3 temperature + 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 temperature. 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 superheating again and cooling. When a steel plate is cooled by air cooling once, the steel plate may be heated again to a temperature of the Ac_3 temperature 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 temperature (°C) is calculated using the following formula.

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

- 25 [0066] In the formula, [M] denotes the element M content (% by mass).

Average Cooling Rate

[0067] 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

[0068] The predetermined carbide density cannot be achieved at an average cooling rate of less than 15°C/s from 800°C to 550°C at the quarter thickness position from the inner surface of a steel pipe. Furthermore, although the microstructure is not particularly limited, to achieve a predetermined fatigue property in hydrogen, bainite or martensite preferably constitutes 90% or more by area. At an average cooling rate of less than 15°C/s, it is difficult for bainite to constitute 90% or more by area, and the formation of martensite may be affected depending on the chemical composition. 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 air cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 550°C, and air cooling is preferred from 550°C to 50°C.

[0069] 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

[0070] At an average cooling rate of less than 10°C/s from 800°C to 300°C at the quarter thickness position from the inner surface of a steel pipe, the predetermined carbide density cannot be achieved, and the fatigue property deteriorates. Furthermore, at an average cooling rate of less than 10°C/s, it is difficult for martensite to constitute 90% or more by area, and the formation of bainite may be affected depending on the chemical composition. 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 air cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 300°C, and air cooling is preferred from 300°C to 50°C.

[Reheating and Quenching Step (Suitable Conditions)]

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

[0071] When the temperature at the center of the plate thickness is lower than the Ac_3 temperature, 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 the Ac_3 temperature or higher, preferably higher than the Ac_3 temperature. 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 temperature or higher can result in a decrease in the initial austenite grain size and a decrease in the crack growth rate in hydrogen.

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

[0072] 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

The predetermined carbide density cannot be achieved at an average cooling rate of less than 15°C/s from 800°C to 550°C at the quarter thickness position from the inner surface of a steel pipe. At an average cooling rate of less than 15°C/s, it is difficult for bainite to constitute 90% or more by area, and the formation of martensite may be affected depending on the chemical composition. 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 air cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 550°C, and air cooling is preferred from 550°C to 50°C.

[0073] 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

At an average cooling rate of less than 10°C/s from 800°C to 300°C at the quarter thickness position from the inner surface of a steel pipe, the predetermined carbide density cannot be achieved, and the fatigue property deteriorates. Furthermore, at an average cooling rate of less than 10°C/s, it is difficult for martensite to constitute 90% or more by area, and the formation of bainite may be affected depending on the chemical composition. 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 plate, a steel microstructure with the microstructure intended in the present invention is not formed, and the fatigue property in hydrogen deteriorates, so that 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 air cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 300°C, and air cooling is preferred from 300°C to 50°C.

Cooling stop temperature during quenching: 50°C or less

[0074] When the cooling stop temperature is more than 50°C, a desired carbide density cannot be achieved, 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.

Tempering Step

Tempering temperature: 400°C or more and Ac_1 temperature or lower

[0075] Heating at an average heating rate of 0.01°C/s or more and a tempering temperature of 400°C or more can result in a decrease in austenite, a decrease in hydrogen in the steel, and a predetermined carbide density. 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 temperature may result in an increase in austenite and hydrogen in the steel. Thus, the tempering temperature is the Ac_1 temperature or lower, preferably (Ac_1 temperature - 30) °C or lower. The upper limit of the average heating rate during tempering is preferably, but not limited to, 1°C/s or less. An excessively long tempering time results in coarsening of a carbide and adversely affects hydrogen embrittlement, so that the tempering time is less than 60 minutes. The tempering time is preferably 50 minutes or less. An excessively short tempering time results in no decrease in austenite and the amount of hydrogen in a steel material, so that the tempering time is preferably 10 minutes or more, more preferably 20 minutes or more.

[0076] In the present invention, the Ac_1 temperature (°C) may be determined by any method, for example, by $Ac_1 = 723 - 14Mn + 22Si - 14.4Ni + 23.3Cr$. Each element symbol in the formula represents the element content (% by mass) of the steel and is 0 for an element not contained.

Dehydrogenation Treatment Step

[0077] 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 (for removing hydrogen from steel materials) 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 plate with high fatigue resistance in a high-pressure hydrogen gas environment can be produced. The holding time R (s) is preferably determined from the plate thickness or the wall thickness t (mm) of a steel material or a steel pipe and the hydrogen diffusion coefficient D ($mm^2 \cdot s^{-1}$) in the steel at room temperature using the following formula (A).

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

[0078] The hydrogen diffusion coefficient varies depending on a component contained and the metallic microstructure and a value within a range from, for example, 1×10^{-5} to $5 \times 10^{-3} mm^2/s$, more preferably $5 \times 10^{-4} mm^2/s$ or less may be adopted. 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 corresponding temperature) at the holding temperature for the value of D in the formula (A). 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 atmosphere in the dehydrogenation treatment step. The room temperature refers to $20^\circ C \pm 10^\circ C$.

[0079] In particular, heating, if conducted, takes time for the temperature T_c at the center of the plate thickness of a steel material or a steel pipe to reach the temperature of the atmosphere in the dehydrogenation treatment step (dehydrogenation treatment temperature T), so even if the holding time R (s) is satisfied at the ambient temperature, the dehydrogenation treatment may be insufficient if the dehydrogenation treatment temperature T (ambient temperature) has not been reached at the center of the plate thickness. Thus, it is preferable to hold for R (s) or more after the temperature T_c at the center of the plate thickness reaches the 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 center of the plate thickness, and 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 T_c at the center of the plate 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 center of the plate thickness of the steel material or the steel pipe can be appropriately controlled. The temperature T_c at the center of the plate thickness may be actually measured with a thermocouple or the like or may be predicted using a finite element method or the like.

[0080] Furthermore, the scale on the steel surface inhibits dehydrogenation and is therefore preferably removed before 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.

Second Embodiment

[0081] A steel material according to the present invention is more specifically described below. The chemical composition, metallic microstructure, and crack growth rate 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.

Rolling Step

[0082] A steel raw material heated in the heating step as described in the method for producing a steel pipe is hot-rolled using a hot-rolling mill under the following conditions.

Finish rolling temperature: 820°C or more

[0083] 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.

Cooling Step (Accelerated Cooling Step)

[0084] In the cooling step, a steel material with the chemical composition described above is hot-rolled, then heated, and held at a temperature of the Ac₃ temperature 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.

Heating temperature after hot rolling: Ac₃ temperature or higher and 1000°C or less

[0085] A heating temperature lower than the Ac₃ temperature in the cooling step results in ferrite remaining in the steel after cooling, a decrease in the strength of a steel material, and a degradation of the fatigue property. Thus, the heating temperature is the Ac₃ temperature or higher. The heating temperature is preferably the Ac₃ temperature + 30°C or more, more preferably the Ac₃ temperature + 50°C or more. However, the Ac₃ temperature + 30°C or more or the Ac₃ temperature + 50°C or more is not applied to a composition system in which the Ac₃ temperature + 30°C or the Ac₃ temperature + 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, more preferably 950°C or less, still 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 Ac₃ temperature. 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 superheating again and

cooling. When a steel material is cooled by air cooling once, the steel sheet may be heated again to a temperature of the Ac_3 temperature 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 temperature (°C) is calculated using the following formula.

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

[0086] In the formula, [M] denotes the element M content (% by mass).

Average Cooling Rate

[0087] 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 surface of a steel material

The predetermined carbide density cannot be achieved at an average cooling rate of less than 15°C/s from 800°C to 550°C at the quarter thickness position from the surface of a steel material. Furthermore, although the microstructure is not particularly limited, to achieve a predetermined fatigue property in hydrogen, bainite or martensite preferably constitutes 90% or more by area. At an average cooling rate of less than 15°C/s, it is difficult for bainite to constitute 90% or more by area, and the formation of martensite may be affected depending on the chemical composition. 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 air cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 550°C, and air cooling is preferred from 550°C to 50°C.

[0088] 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 surface of a steel material

[0089] At an average cooling rate of less than 10°C/s from 800°C to 300°C at the quarter thickness position from the surface of a steel material, the predetermined carbide density cannot be achieved, and the fatigue property deteriorates. Furthermore, at an average cooling rate of less than 10°C/s, it is difficult for martensite to constitute 90% or more by area, and the formation of bainite may be affected depending on the chemical composition. Thus, the average cooling rate at the quarter thickness position from the 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 plate, a steel microstructure with the microstructure intended in the present invention is not formed, and the fatigue property in hydrogen deteriorates, so that 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 air cooling, can be used alone or in combination, but water cooling or oil cooling is preferred from 800°C to 300°C, and air cooling is preferred from 300°C to 50°C.

[0090] In a case of steel sheet (thin plate), it is preferable to coil the steel sheet, although coiling is not necessary for a steel plate.

[0091] Steel materials with a good fatigue property in hydrogen gas according to the present invention have the above chemical composition and include various types, such as a sheet, a plate, and a steel pipe, with high fatigue crack growth resistance in hydrogen gas, or may be steel materials for a hydrogen pipeline formed into a predetermined shape.

[0092] Under the above conditions, a steel pipe and a steel material with a good fatigue property in hydrogen satisfying a predetermined crack growth rate in hydrogen can be produced.

EXAMPLE 1

[0093] Examples that have verified the advantages of the present invention are described below. The examples are preferred examples of the present invention, and the present invention is not limited to these examples. A production method and characterization of a seamless steel pipe for an actual steel structure were studied in the examples.

[0094] Billets with the chemical compositions shown in the steel pipes Nos. 1 to 29 (billets Nos. A to AC) and 40 to 87 (billets Nos. AN to CI) in Tables 1-1 and 1-2 were produced at a casting speed of 0.6 m/min and were heated to 1250°C and expanded to produce seamless steel pipes. The steel pipes were produced under the conditions that expansion was finished at 820°C or more. The steel pipes were heated and held at 950°C for steel pipes with a A_{c3} temperature of 950°C or less or at 1000°C for steel pipes with a A_{c3} temperature of more than 950°C, were then water-cooled under the conditions shown in Tables 2-1 and 2-2, and were then tempered. The metallic microstructure and mechanical properties were evaluated. Furthermore, slabs with the chemical compositions shown in steel materials Nos. 30 to 39 (slabs Nos. AD to AM) of Tables 1-1 and 1-2 were produced at a casting speed of 0.6 m/min, were heated to 1250°C, and were then rolled using a hot-rolling mill at 820°C or more. The steel materials were heated and held at 950°C for steel materials with a A_{c3} temperature of 950°C or less or at 1000°C for steel materials with a A_{c3} temperature of more than 950°C, were then water-cooled under the conditions shown in Tables 2-1 and 2-2, were then tempered, and were evaluated for the metallic microstructure and mechanical properties in the same manner as the steel pipes. After tempering, Nos. 2, 5, 14, 15, 43, and 63 to 69 were also subjected to dehydrogenation treatment. In the dehydrogenation treatment, the ambient temperature, that is, the dehydrogenation treatment temperature T, was kept at 50°C for 3 hours, followed by natural cooling. The evaluation method is described below. The tempering temperature was arbitrarily adjusted so that the materials had a tensile strength in the range of 520 to 700 MPa.

[0095] Furthermore, billets with the chemical compositions shown in the steel pipes Nos. 88 to 101 (billets Nos. AO1 to BB1) in Table 2-3 were produced at various casting speeds and were heated to 1250°C and expanded to produce seamless steel pipes. The chemical compositions of the billets Nos. AO1 to BB1 are the same as the chemical compositions of Nos. AO to BB shown in Table 1-2. The steel pipes were produced under the conditions that expansion was finished at 820°C or more. The steel pipes were heated and held at 950°C for steel pipes with a A_{c3} temperature of 950°C or less or at 1000°C for steel pipes with a A_{c3} temperature of more than 950°C, were then water-cooled under the conditions shown in Table 2-3, and were then tempered under the conditions shown in Table 2-3. The metallic microstructure and mechanical properties were evaluated. The evaluation method is described below. The tempering temperature was arbitrarily adjusted so that the materials had a tensile strength in the range of 520 MPa to 700 MPa. In the dehydrogenation treatment, the ambient temperature, that is, the dehydrogenation treatment temperature T, was kept at 50°C for 3 hours, followed by natural cooling.

[0096] The fatigue crack propagation characteristics were evaluated by a fatigue crack growth test. A compact tension (CT) test specimen (a test specimen close to a square with a notch at one end portion) according to ASTM E 647 was taken from each steel material so that the load direction was parallel to the rolling direction, and a fatigue test was performed at a frequency of 1 Hz, a repetitive waveform of a sine wave, and a stress ratio of $R = 0.1$. The length of a fatigue crack was measured by a compliance method using a clip gauge to determine the fatigue crack propagation rate in 5-MPa high-pressure hydrogen gas. It was performed at room temperature ($20^{\circ}\text{C} \pm 10^{\circ}\text{C}$). A test specimen taken from a steel material with plate thickness of 10 mm or less was ground from the surface by 0.5 mm resulting in test specimen thickness of 2 mm, 5 mm, 8 mm, or 9 mm, respectively, and for a test specimen taken from a steel material with plate thickness other than these, a test specimen with a thickness of 10 mm was taken from a position of $t/2$ (t : sheet thickness), and the front and back sides of a crack growth portion were mirror-polished. At this time, the fatigue crack growth rate (m/cycle) in a stress intensity factor range $\Delta K = 20$ ($\text{MPa} \cdot \text{m}^{1/2}$) as a stable growth region where the Paris law holds was evaluated as a measure of central tendency. Tables 2-1, 2-2, and 2-3 show the results.

[0097] Furthermore, a carbide measurement method for a steel material is described below. A test specimen was cut out from a cross section parallel to the thickness direction from the center position of the plate thickness of a steel material and was subjected to nital etching, and a carbide was observed by SEM. Ten fields were randomly selected and observed at an acceleration voltage of 15 kV and a magnification of 20000 times. Tables 2-1, 2-2, and 2-3 show the average value of the 10 fields as the number of carbides, with Y indicating that the number of carbides with a diameter of 200 nm or more is 20 pieces/10 μm^2 or less, and N indicating that the number of carbides with a diameter of 200 nm or more is more than 20 pieces/10 μm^2 . Furthermore, a method for measuring the amount of austenite in a steel material is described below.

[0098] A sample for metallic microstructure observation was taken from the center of the sheet width in the center in the longitudinal direction of each of the steel materials and the steel pipes thus produced, a cross section parallel to the longitudinal direction was buffed as an observation surface, the surface layer was then removed by chemical polishing using picric acid etching, and X-ray diffractometry was performed. More specifically, a $\text{Co-K}\alpha$ radiation source was used for an incident X-ray, and the area fraction of retained austenite was calculated from the intensity ratios of the (200), (211), and (220) planes of ferrite to the (200), (220), and (311) planes of austenite.

Hydrogen Thermal Desorption Analysis

[0099] The amount of hydrogen remaining in the steel was measured by thermal desorption analysis method using a low-temperature programmed hydrogen analyzer <gas chromatograph type> (JTF-20AL). The thermal desorption analysis 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 plate 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 and 1-2, and the amount before being subjected to a high-pressure hydrogen fatigue test explained in aging described later.

[0100] Steel pipes are also subjected to the various tests in the same manner as the steel materials described above.

[0101] The examples of the present invention all satisfied the condition that the fatigue crack growth rate in hydrogen gas was 1.0×10^{-6} m/cycle or less.

[0102] The steel pipes Nos. 94 and 101, in which the casting speed in Table 2-3 was outside the scope of the present invention, included coarse inclusions, had a fatigue crack growth rate in hydrogen gas outside the scope of the present invention, and were comparative examples.

[Table 1-1]

Billet or slab No.	Steel material No.	Steel pipe No.	Chemical composition (% by mass) ¹⁾																					Ac3 temperature (°C)	Ac1 temperature (°C)	Notes		
			C	Si	Mn	Al	N	P	S	O	H	Cu	Ni	Cr	Mo	Nb	V	Ti	W	B	Sn	Sb	Ce				Mg	REM
A	-	1	0.275	0.720	0.42	0.080	0.0021	0.0067	0.0008	0.001	0.0004														914	733	Conforming steel	
B	-	2	0.100	0.650	1.26	0.030	0.0045	0.0052	0.0008	0.004	0.0001														898	720	Conforming steel	
C	-	3	0.450	0.360	1.19	0.120	0.0029	0.0088	0.0011	0.009	0.0008														863	714	Conforming steel	
D	-	4	0.350	1.005	1.30	0.030	0.0057	0.0070	0.0003	0.004	0.0005														888	727	Conforming steel	
E	-	5	0.360	0.010	1.98	0.080	0.0053	0.0069	0.0014	0.006	0.0001														827	696	Conforming steel	
F	-	6	0.140	2.000	1.00	0.140	0.0037	0.0128	0.0011	0.002	0.0009														978	753	Conforming steel	
G	-	7	0.300	1.020	1.15	0.130	0.0049	0.0124	0.0006	0.006	0.0007														912	729	Conforming steel	
H	-	8	0.110	0.860	0.30	0.120	0.0080	0.0135	0.0005	0.008	0.0004														950	738	Conforming steel	
I	-	9	0.220	1.830	2.00	0.140	0.0036	0.0070	0.0008	0.004	0.0005														928	735	Conforming steel	
J	-	10	0.200	1.930	1.70	0.130	0.0041	0.0076	0.0013	0.002	0.0005														943	742	Conforming steel	
K	-	11	0.450	1.860	1.79	0.020	0.0019	0.0150	0.0015	0.010	0.0004														906	739	Conforming steel	
L	-	12	0.400	0.260	1.09	0.060	0.0008	0.0046	0.0009	0.006	0.0006														858	713	Conforming steel	
M	-	13	0.200	1.540	1.32	0.110	0.0050	0.0142	0.0015	0.010	0.0009														940	738	Conforming steel	
N	-	14	0.420	0.920	1.26	0.080	0.0033	0.0120	0.0011	0.002	0.0004														887	726	Conforming steel	
O	-	15	0.120	0.690	0.51	0.010	0.0045	0.0043	0.0012	0.001	0.0001														917	731	Conforming steel	
P	-	16	0.430	0.690	0.97	0.150	0.0035	0.0016	0.0012	0.007	0.0004														884	725	Conforming steel	
Q	-	17	0.200	0.480	1.27	0.060	0.0025	0.0082	0.0015	0.006	0.0006														885	716	Conforming steel	
R	-	18	0.230	0.540	1.12	0.020	0.0066	0.0090	0.0002	0.010	0.0004														885	719	Conforming steel	
S	-	19	0.300	1.380	0.81	0.060	0.0043	0.0041	0.0007	0.007	0.0003														926	742	Conforming steel	
T	-	20	0.450	0.200	1.16	0.110	0.0005	0.0097	0.0005	0.005	0.0004														856	711	Conforming steel	
U	-	21	0.280	1.580	1.71	0.080	0.0080	0.0097	0.0015	0.005	0.0005														916	734	Conforming steel	
V	-	22	0.130	0.750	1.75	0.070	0.0077	0.0137	0.0012	0.004	0.0004	1.86	1.63	1.41	0.92	0.25	0.46	0.33	2.41		0.29	0.28	0.003	0.010		894	724	Conforming steel
W	-	23	0.130	1.730	0.69	0.010	0.0014	0.0107	0.0011	0.009	0.0008	0.02	2.04	2.40	0.45		0.34	0.26	2.43		0.28	0.28	0.004	0.010		954	778	Conforming steel
X	-	24	0.320	1.000	1.02	0.150	0.0051	0.0050	0.0012	0.004	0.0004	0.04	0.77	1.32	1.64	0.50	0.25	0.39	0.22		0.12	0.07	0.001	0.010		961	750	Conforming steel
Y	-	25	0.390	1.750	1.36	0.140	0.0064	0.0026	0.0014	0.004	0.0006	0.15	1.67	0.52	1.71	0.16	0.23	0.36	0.99		0.13	0.22	0.005	0.010		967	731	Conforming steel
Z	-	26	0.380	0.340	1.69	0.130	0.0041	0.0083	0.0005	0.008	0.0004	0.80	0.67	1.00	0.28	0.36	0.15	0.37	2.02		0.10	0.27		0.010		842	720	Conforming steel
AA	-	27	0.230	0.110	1.51	0.080	0.0011	0.0114	0.0011	0.003	0.0008	0.49	1.60	0.52	0.50	0.22	0.44	0.01	1.75		0.22	0.12	0.010		884	693	Conforming steel	
AB	-	28	0.420	1.580	1.25	0.040	0.0030	0.0005	0.0015	0.008	0.0004	0.04	1.25	1.93	0.29	0.41	0.42	0.05	1.08		0.17	0.14	0.010	0.010		917	767	Conforming steel
AC	-	29	0.400	0.250	1.83	0.030	0.0067	0.0096	0.0006	0.007	0.0005	2.50		1.92	0.64	0.14	0.05	0.14	1.78		0.15	0.17	0.008	0.010		790	748	Conforming steel
AD	30	-	0.360	1.290	0.48	0.070	0.0074	0.0114	0.0011	0.001	0.0004	1.47	2.50	0.97	0.36	0.04	0.23	0.49	2.35		0.18	0.12	0.002	0.010		889	731	Conforming steel
AE	31	-	0.330	1.200	1.53	0.080	0.0078	0.0015	0.0003	0.003	0.0004	0.78	2.12	0.45	1.23	0.36	0.43	0.25	2.02		0.14	0.25	0.003			924	708	Conforming steel
AF	32	-	0.300	1.070	0.69	0.080	0.0039	0.0116	0.0004	0.006	0.0004	2.33	1.79	1.51	0.71	0.41	0.10		0.13		0.01	0.11	0.008	0.010		865	746	Conforming steel
AG	33	-	0.440	1.830	0.74	0.090	0.0038	0.0003	0.0006	0.006	0.0004	1.96	2.48	0.30	1.81	0.02	0.50	0.50	1.58		0.11	0.13				963	724	Conforming steel
AH	34	-	0.350	1.180	1.69	0.030	0.0019	0.0088	0.0012	0.006	0.0004	1.25	0.38	1.32	1.95	0.25	0.09	0.34	0.76		0.16	0.11	0.007	0.010		911	751	Conforming steel
AI	35	-	0.220	0.120	1.75	0.120	0.0067	0.0008	0.0010	0.002	0.0004		1.99	1.75	0.98	0.10	0.43	0.49	2.30		0.27	0.14	0.009			879	713	Conforming steel
AJ	36	-	0.170	0.250	1.25	0.060	0.0015	0.0024	0.0013	0.003	0.0009	2.50	1.93	1.38	0.34	0.46	0.11	0.13	1.35		0.30	0.17	0.003			802	715	Conforming steel
AK	37	-	0.440	0.580	0.64	0.030	0.0013	0.0012	0.0014	0.003	0.0004	0.64	1.57	1.26	0.96	0.03	0.05	0.32	1.69		0.10	0.11	0.008			861	733	Conforming steel
AL	38	-	0.350	1.510	1.15	0.110	0.0049	0.0116	0.0002	0.002	0.0003	2.45	1.57	0.01	1.87	0.10	0.22	0.20	0.75		0.23	0.01	0.004			935	718	Conforming steel
AM	39	-	0.180	1.700	1.37	0.040	0.0028	0.0032	0.0011	0.003	0.0004	0.21	0.71	2.50	1.29	0.04	0.13	0.41	0.46		0.27	0.02	0.001	0.010		945	789	Conforming steel
AN	-	40	0.320	1.980	1.49	0.140	0.0011	0.0097	0.0009	0.003	0.0005	1.20	0.54	0.55	1.00		0.06	0.25	1.09		0.15	0.06	0.001			940	753	Conforming steel

¹⁾ The remainder is composed of Fe and incidental impurities
Underline: outside the scope of the present invention.

Blank: no intended addition.

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[Table 1-2]

Billet No.	Steel material No.	Steel pipe No.	Chemical composition (% by mass) ^{*)}																							Ac3 temperature (°C)	Ac1 temperature (°C)	Notes	
			C	Si	Mn	Al	N	P	S	O	H	Cu	Ni	Cr	Mo	Nb	V	Ti	W	B	Sn	Sb	Ca	Mg	REM				
AO	-	41	0.220	0.290	1.62	0.080	0.0050	0.0045	0.0011	0.0001	0.0003	1.42	0.40	0.58		0.47	0.16	0.03	0.31		0.11	0.19	0.003	0.010		839	714	Conforming steel	
AP	-	42	0.170	1.070	1.17	0.100	0.0017	0.0009	0.0012	0.0008	0.0004	2.50	1.90	1.74	2.00	0.25	0.22	0.01	1.61		0.20	0.19	0.003			904	743	Conforming steel	
AQ	-	43	0.190	1.020	1.02	0.060	0.0041	0.0129	0.0013	0.004	0.0004	1.93	0.63	1.74	1.85	0.30	0.34	0.50	1.25		0.17	0.23	0.005			947	763	Conforming steel	
AR	-	44	0.310	1.520	0.54	0.090	0.0069	0.0050	0.0006	0.002	0.0004	1.98	0.39	0.41	0.48	0.27	0.21	0.31			0.25	0.09	0.001	0.010		930	753	Conforming steel	
AS	-	45	0.200	0.540	0.71	0.070	0.0027	0.0094	0.0010	0.004	0.0004	1.31	1.18	0.12	0.48	0.36	0.34	0.49	2.50		0.26	0.21	0.009	0.010		911	711	Conforming steel	
AT	-	46	0.380	0.990	0.34	0.040	0.0008	0.0118	0.0009	0.005	0.0005	0.84	1.25	1.86	0.11	0.05	0.25	0.18	1.71		0.05	0.29	0.007			891	765	Conforming steel	
AU	-	47	0.320	1.360	0.34	0.090	0.0032	0.0150	0.0005	0.008	0.0004	1.93	2.27	1.82	0.84	0.11		0.50	0.51		0.02	0.11	0.008	0.010		883	753	Conforming steel	
AV	-	48	0.410	0.780	1.69	0.100	0.0066	0.0097	0.0012	0.009	0.0004	0.10	0.25	2.34	0.24	0.29	0.50	0.11	1.27		0.17	0.26	0.004	0.010		897	767	Conforming steel	
AW	-	49	0.120	1.990	0.74	0.060	0.0075	0.0019	0.0013	0.008	0.0007	0.64	0.50	0.96	0.05	0.03	0.33	0.21	2.26	0.0025	0.05	0.25	0.005	0.010		977	772	Conforming steel	
AX	-	50	0.310	0.360	1.38	0.020	0.0067	0.0056	0.0009	0.004	0.0004	0.96	1.21	0.50	1.42	0.46	0.45	0.45	1.30		0.23	0.16	0.008			908	706	Conforming steel	
AY	-	51	0.170	1.600	1.37	0.070	0.0011	0.0102	0.0005	0.006	0.0003	0.04	0.83	2.02		0.21	0.13	0.39	1.33	0.0050	0.28	0.22	0.009			915	774	Conforming steel	
AZ	-	52	0.250	1.240	0.63	0.060	0.0060	0.0129	0.0010	0.001	0.0006	1.20	1.13	1.63	1.44	0.41	0.11	0.16	1.06		0.04	0.13	0.005		0.0025	934	763	Conforming steel	
BA	-	53	0.100	0.860	0.82	0.050	0.0053	0.0138	0.0003	0.003	0.0004	0.82	0.62	0.33	1.67	0.43	0.40	0.07	1.18		0.19	0.16	0.009	0.010		993	729	Conforming steel	
BB	-	54	0.150	1.850	1.65	0.070	0.0076	0.0025	0.0008	0.002	0.0008	0.17	0.07	2.05	1.45	0.17	0.32	0.07	0.03		0.07	0.05	0.005		0.0050	989	787	Conforming steel	
BC	-	55	0.250	1.000	0.41	0.010	0.0045	0.0127	0.0014	0.004	0.0006	0.0004	0.71	1.65	0.04	1.15	0.01	0.28	0.14	2.43		0.30	0.04	0.006	0.005		953	716	Conforming steel
BD	-	56	0.120	1.130	1.20	0.120	0.0013	0.0123	0.0009	0.007	0.0008	1.85	0.23	0.81	1.99	0.41	0.15	0.03	1.86		0.09	0.07	0.002			962	747	Conforming steel	
BE	-	57	0.180	1.600	1.35	0.070	0.0043	0.0031	0.0006	0.006	0.0004	0.72	0.88	2.34	1.54	0.45	0.06	0.17	1.61		0.22	0.25	0.001	0.010		933	781	Conforming steel	
BF	-	58	0.370	1.500	0.84	0.120	0.0015	0.0025	0.0009	0.001	0.0004	1.35	0.12	1.98	0.90	0.05	0.39	0.36	2.00		0.15	0.27	0.005			946	769	Conforming steel	
BG	-	59	0.140	0.250	0.91	0.060	0.0059	0.0065	0.0011	0.007	0.0009	1.44	2.06	1.42	1.32	0.33	0.09	0.19	2.31			0.04	0.004			885	719	Conforming steel	
BH	-	60	0.290	1.420	1.83	0.030	0.0057	0.0148	0.0004	0.003	0.0004	0.66	1.20	1.06	1.17	0.18	0.29	0.18	1.21		0.30	0.10	0.009			926	736	Conforming steel	
BI	-	61	0.350	1.760	1.15	0.140	0.0011	0.0114	0.0008	0.001	0.0004	0.77	0.08	0.53	0.94	0.28	0.12	0.08	2.37		0.09	0.15	0.004			960	757	Conforming steel	
BJ	-	62	0.230	1.350	1.25	0.070	0.0024	0.0082	0.0004	0.009	0.0004	0.30	2.28	0.91	0.15	0.17	0.10	0.14	1.36		0.08		0.009	0.010		887	724	Conforming steel	
BK	-	63	0.170	1.530	1.96	0.070	0.0074	0.0081	0.0013	0.001	0.0001	0.91	0.36	0.46	1.00	0.46	0.15	0.44	2.37		0.28	0.30	0.010			933	735	Conforming steel	
BL	-	64	0.250	0.700	1.23	0.080	0.0010	0.0073	0.0010	0.001	0.0001	0.30	0.02	1.10	0.25											882	747	Conforming steel	
BM	-	65	0.250	0.700	1.23	0.080	0.0010	0.0073	0.0010	0.001	0.0001	0.30	0.02	1.10	0.25											882	747	Conforming steel	
BN	-	66	0.250	0.700	1.23	0.080	0.0010	0.0073	0.0010	0.001	0.0011	0.30	0.02	1.10	0.25											882	747	Comparative steel	
BO	-	67	0.250	0.700	1.23	0.080	0.0010	0.0073	0.0010	0.001	0.0012	0.30	0.02	1.10	0.25											882	747	Comparative steel	
BP	-	68	0.250	0.700	1.23	0.080	0.0010	0.0073	0.0010	0.001	0.0001	0.30	0.02	1.10	0.25											882	747	Conforming steel	
BQ	-	69	0.250	0.700	1.23	0.080	0.0010	0.0073	0.0010	0.001	0.0001	0.30	0.02	1.10	0.25											882	747	Conforming steel	
BR	-	70	<u>0.480</u>	0.170	0.99	0.090	0.0014	0.0104	0.0004	0.006	0.0005															857	713	Comparative steel	
BS	-	71	<u>0.480</u>	1.530	1.50	0.090	0.0074	0.0033	0.0005	0.007	0.0004	2.33	1.74	1.90	1.86	0.50	0.38	0.08	1.17		0.13	0.01	0.005	0.010		902	755	Comparative steel	
BT	-	72	0.190	2.100	1.00	0.130	0.0023	0.0138	0.0004	0.002	0.0004															980	755	Comparative steel	
BU	-	73	0.210	2.100	1.61	0.090	0.0062	0.0021	0.0007	0.006	0.0007	1.35	2.33	1.63	1.29	0.26	0.24	0.27	0.32		0.29	0.23	0.007			930	751	Comparative steel	
BV	-	74	0.160	0.900	2.10	0.040	0.0079	0.0070	0.0014	0.003	0.0004															880	713	Comparative steel	
BW	-	75	0.370	0.130	2.10	0.010	0.0014	0.0006	0.0011	0.004	0.0004	1.25	1.38	2.37	1.48	0.34	0.35	0.43	2.18		0.05	0.01	0.010			828	732	Comparative steel	
BX	-	76	0.380	1.610	1.36	<u>0.160</u>	0.0063	0.0052	0.0009	0.007	0.0003															922	739	Comparative steel	
BY	-	77	0.390	0.790	0.83	<u>0.160</u>	0.0062	0.0069	0.0013	0.010	0.0006	1.88	2.12	1.81	1.31	0.50	0.38	0.16	1.54		0.29	0.28	0.004			893	740	Comparative steel	
BZ	-	78	0.180	1.010	0.64	0.060	<u>0.0090</u>	0.0065	0.0007	0.005	0.0004															928	736	Comparative steel	
CA	-	79	0.520	0.410	1.53	0.130	0.0090	0.0117	0.0008	0.002	0.0004	2.36	1.63	0.48	0.75	0.40	0.24	0.33	0.11		0.17	0.13	0.008			838	701	Comparative steel	
CB	-	80	0.440	0.730	1.88	0.070	0.0020	<u>0.0160</u>	0.0006	0.009	0.0008															860	713	Comparative steel	
CC	-	81	0.240	0.430	0.95	0.130	0.0047	<u>0.0160</u>	0.0009	0.007	0.0004	1.94	1.66	1.19	1.31	0.23	0.06	0.28	0.41		0.05	0.13	0.002	0.010		868	720	Comparative steel	
CD	-	82	0.340	1.070	0.67	0.130	0.0016	0.0041	0.0016	0.005	0.0005															919	737	Comparative steel	
CE	-	83	0.380	0.090	0.48	0.070	0.0041	0.0043	0.0016	0.006	0.0006	2.32	0.62	1.09	1.74	0.03	0.21	0.09	2.33		0.15	0.21	0.006	0.010		880	735	Comparative steel	
CF	-	84	0.280	0.180	0.83	0.070	0.0050	0.0055	0.0005	0.015	0.0004															876	715	Comparative steel	
CG	-	85	0.100	1.700	1.84	0.070	0.0018	0.0035	0.0009	0.015	0.0007	1.94	0.80	1.45	1.14	0.18	0.25	0.47	2.38		0.27	0.19	0.002			925	757	Comparative steel	
CH	-	86	0.410	0.780	1.69	0.100	0.0066	0.0097	0.0013	0.004	0.0004	1.93	0.63	1.74	1.85	0.45	0.06	0.17	0.32							867	748	Conforming steel	
CI	-	87	0.330	1.200	1.53	0.080	0.0078	0.0015	0.0003	0.003	0.0004		1.26													879	757	Conforming steel	

^{*)} The remainder is composed of Fe and incidental impurities
Underline: outside the scope of the present invention.

Blank: no intended addition.

[Table 2-1]

Steel material No.	Steel pipe No.	Cooling step					Tempering step		Carbide	Amount of residual y (%)	Crack growth rate in hydrogen at ΔK=20 (MPa·m ^{1/2}) 10 ⁻⁶ m/cycle	Notes
		A		B		Cooling stop temperature (°C)	Temperature (°C)	Time (min)				
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)							
-	1	-	-	14	4	39	633	20	Y	0	0.788	Inventive example
-	2	15	5	-	-	32	620	30	Y	0	0.640	Inventive example
-	3	16	6	-	-	25	614	30	Y	0	0.455	Inventive example
-	4	16	4	-	-	26	627	30	Y	0	0.512	Inventive example
-	5	18	9	-	-	25	596	30	Y	2	0.213	Inventive example
-	6	19	5	-	-	25	653	30	Y	0	0.180	Inventive example
-	7	19	4	-	-	25	629	30	Y	0	0.106	Inventive example
-	8	20	5	-	-	33	638	30	Y	0	0.661	Inventive example
-	9	18	3	-	-	25	635	50	Y	2	0.211	Inventive example
-	10	19	4	-	-	25	642	30	Y	1	0.169	Inventive example
-	11	26	5	-	-	32	639	30	Y	1	0.637	Inventive example
-	12	19	6	-	-	25	613	30	Y	0	0.078	Inventive example

(continued)

Steel material No.	Steel pipe No.	Cooling step					Tempering step		Carbide	Amount of residual y (%)	Crack growth rate in hydrogen at ΔK=20 (MPa·m ^{1/2}) 10 ⁻⁶ m/cycle	Notes
		A		B		Cooling stop temperature (°C)	Temperature (°C)	Time (min)				
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)							
-	13	18	4	-	-	25	638	30	Y	0	0.188	Inventive example
-	14	19	5	-	-	25	626	30	Y	0	0.097	Inventive example
-	15	17	6	-	-	25	631	30	Y	0	0.385	Inventive example
-	16	16	8	-	-	25	625	30	Y	0	0.491	Inventive example
-	17	-	-	13	3	41	616	30	Y	0	0.815	Inventive example
-	18	18	4	-	-	25	619	30	Y	0	0.282	Inventive example
-	19	16	2	-	-	25	642	30	Y	0	0.444	Inventive example
-	20	16	3	-	-	28	611	30	Y	0	0.551	Inventive example
-	21	19	6	-	-	25	634	30	Y	1	0.128	Inventive example
-	22	17	8	-	-	25	624	30	Y	1	0.411	Inventive example
-	23	18	5	-	-	25	678	40	Y	0	0.280	Inventive example
-	24	17	4	-	-	25	650	30	Y	0	0.315	Inventive example

(continued)

Steel material No.	Steel pipe No.	Cooling step						Tempering step		Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa·m ^{1/2}) 10 ⁻⁶ m/cycle	Notes
		A		B		Cooling stop temperature (°C)							
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)		Temperature (°C)	Time (min)					
-	25	18	3	-	-	25	631	30	Y	0	0.249	Inventive example	
-	26	19	3	-	-	25	620	30	Y	1	0.125	Inventive example	
-	27	18	5	-	-	25	593	30	Y	1	0.310	Inventive example	
-	28	18	4	-	-	25	667	30	Y	0	0.210	Inventive example	
-	29	23	3	-	-	29	648	30	Y	2	0.585	Inventive example	
30	-	-	-	13	2	41	631	30	Y	0	0.813	Inventive example	
31	-	15	3	-	-	30	608	30	Y	1	0.597	Inventive example	
32	-	-	-	14	3	37	646	30	Y	0	0.743	Inventive example	
33	-	16	4	-	-	27	624	30	Y	0	0.548	Inventive example	
34	-	16	5	-	-	25	651	20	Y	1	0.476	Inventive example	
35	-	-	-	14	4	35	613	30	Y	1	0.694	Inventive example	
36	-	19	7	-	-	25	615	30	Y	0	0.146	Inventive example	

(continued)

Steel material No.	Steel pipe No.	Cooling step				Tempering step		Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa·m ^{1/2}) 10 ⁻⁶ m/cycle	Notes
		A		B		Temperature (°C)	Time (min)				
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)	Cooling stop temperature (°C)					
37	-	-	-	13	3	41	633	Y	0	0.826	Inventive example
38	-	16	5	-	-	25	618	Y	0	0.502	Inventive example
39	-	16	4	-	-	25	689	Y	0	0.483	Inventive example
-	40	-	-	14	3	38	653	Y	1	0.766	Inventive example
Underline: outside the scope of the present invention. γ : austenite											

[Table 2-2]

Steel material No.	Steel pipe No.	Cooling step						Tempering step		Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa m ^{1/2}) 10 ⁻⁶ m/cycle	Notes
		A		B		Cooling stop temperature (°C)							
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)		Temperature (°C)	Time (min)					
-	41	18	6	-	-	25	614	40	Y	1	0.286	Inventive example	
-	42	-	-	14	4	35	643	30	Y	0	0.695	Inventive example	
-	43	15	4	-	-	31	663	30	Y	0	0.620	Inventive example	
-	44	-	-	14	3	37	653	30	Y	0	0.741	Inventive example	
-	45	18	5	-	-	25	611	30	Y	0	0.252	Inventive example	
-	46	17	6	-	-	25	665	30	Y	0	0.421	Inventive example	
-	47	18	6	-	-	25	653	30	Y	0	0.273	Inventive example	
-	48	18	7	-	-	25	667	30	Y	1	0.299	Inventive example	
-	49	-	-	14	3	37	672	30	Y	0	0.731	Inventive example	
-	50	-	-	13	3	41	606	40	Y	0	0.825	Inventive example	
-	51	18	6	-	-	25	674	30	Y	0	0.308	Inventive example	
-	52	-	-	13	3	41	663	30	Y	0	0.829	Inventive example	

(continued)

Steel material No.	Steel pipe No.	Cooling step						Tempering step		Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa m ¹²) 10 ⁻⁶ m/cycle	Notes
		A		B		Cooling stop temperature (°C)							
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)		Temperature (°C)	Time (min)					
-	53	-	-	14	4	35	629	30	Y	0	0.703	Inventive example	
-	54	18	8	-	-	25	687	50	Y	1	0.267	Inventive example	
-	55	16	6	-	-	27	616	20	Y	0	0.542	Inventive example	
-	56	18	7	-	-	25	647	30	Y	0	0.267	Inventive example	
-	57	18	8	-	-	25	681	30	Y	0	0.272	Inventive example	
-	58	15	6	-	-	32	689	30	Y	0	0.647	Inventive example	
-	59	-	-	13	2	42	619	30	Y	0	0.842	Inventive example	
-	60	-	-	14	3	40	636	30	Y	3	0.791	Inventive example	
-	61	16	5	-	-	26	657	40	Y	0	0.524	Inventive example	
-	62	16	6	-	-	25	624	30	Y	0	0.450	Inventive example	
-	63	-	-	13	3	44	635	30	Y	2	0.880	Inventive example	
-	64	-	-	9	2	25	647	30	N	0	<u>1.123</u>	Comparative example	

(continued)

Steel material No.	Steel pipe No.	Cooling step					Tempering step		Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa m ¹²) 10 ⁻⁶ m/cycle	Notes
		A		B		Cooling stop temperature (°C)	Time (min)					
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)							
-	65	-	-	9	1	25	647	30	N	0	<u>1.046</u>	Comparative example
-	66	-	-	14	4	40	<u>757</u>	30	Y	4	<u>1.995</u>	Comparative example
-	67	17	<u>16</u>	-	-	33	737	30	Y	4	<u>1.642</u>	Comparative example
-	68	20	9	-	-	26	647	<u>80</u>	N	0	<u>1305</u>	Comparative example
-	69	-	-	12	3	25	647	<u>70</u>	N	0	<u>1.029</u>	Comparative example
-	70	16	6	-	-	48	613	30	N	0	<u>2.375</u>	Comparative example
-	71	18	7	-	-	37	655	30	N	0	<u>1834</u>	Comparative example
-	72	18	8	-	-	50	655	20	Y	0	<u>2513</u>	Comparative example
-	73	15	5	-	-	25	651	30	Y	1	<u>1.243</u>	Comparative example
-	74	-	-	13	3	46	613	30	Y	4	<u>2.316</u>	Comparative example
-	75	-	-	14	4	33	632	30	Y	4	<u>1.642</u>	Comparative example
-	76	16	5	-	-	41	639	40	Y	0	<u>2.047</u>	Comparative example

(continued)

Steel material No.	Steel pipe No.	Cooling step					Tempering step		Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa m ^{1/2}) 10 ⁻⁶ m/cycle	Notes
		A		B		Cooling stop temperature (°C)	Time (min)					
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)							
-	77	16	6	-	-	25	640	30	Y	0	<u>1206</u>	Comparative example
-	78	-	-	13	2	41	636	30	Y	0	<u>2.050</u>	Comparative example
-	79	-	-	14	3	37	601	40	Y	0	<u>1827</u>	Comparative example
-	80	18	5	-	-	42	613	30	Y	2	<u>2106</u>	Comparative example
-	81	-	-	13	2	28	620	30	Y	0	<u>1.395</u>	Comparative example
-	82	-	-	14	4	33	637	30	Y	0	<u>1.666</u>	Comparative example
-	83	18	6	-	-	30	635	30	Y	0	<u>1.492</u>	Comparative example
-	84	-	-	14	4	35	615	30	Y	0	<u>1735</u>	Comparative example
-	85	15	5	-	-	30	657	30	Y	2	<u>1.495</u>	Comparative example
-	86	22	5	-	-	<u>55</u>	620	30	<u>N</u>	1	<u>1.223</u>	Comparative example
-	87	-	-	15	3	43	630	30	Y	0	0.892	Inventive example
Underline: outside the scope of the present invention. γ : austenite												

[Table 2-3]

Billet No.	Steel pipe No.	Casting speed (m/min)	Cooling step						Tempering step		Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa·m ^{1/2}) ₁₀₋₆ m/cycle	Notes
			A		B		Cooling stop temperature (°C)							
			Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)		Time (min)						
			Temperature (°C)	Time (min)										
AO1	88	0.8	18	6	-	-	25	614	40	Y	1	0.255	Inventive ex-ample	
* AP1	89	1.2	-	-	14	4	35	643	30	Y	0	0.839	Inventive ex-ample	
	AQ1	1.5	15	4	-	-	31	663	30	Y	0	0.918	Inventive ex-ample	
AR1	91	1.5	-	-	14	3	37	653	30	Y	0	0.882	Inventive ex-ample	
AS1	92	1.8	18	5	-	-	25	611	30	Y	0	0.902	Inventive ex-ample	
AT1	93	1.8	17	6	-	-	25	665	30	Y	0	0.911	Inventive ex-ample	
AU1	94	<u>20</u>	18	6	-	-	25	653	30	Y	0	<u>1.190</u>	Comparative example	
AV1	95	0.8	18	7	-	-	25	667	30	Y	1	0.252	Inventive ex-ample	
AW1	96	1.2	-	-	14	3	37	672	30	Y	0	0.839	Inventive ex-ample	
AX1	97	1.5	-	-	13	3	41	606	40	Y	0	0.892	Inventive ex-ample	
AY1	98	1.5	18	6	-	-	25	674	30	Y	0	0.914	Inventive ex-ample	
AZ1	99	1.8	-	-	13	3	41	663	30	Y	0	0.958	Inventive ex-ample	

(continued)

Billet No.	Steel pipe No.	Casting speed (m/min)	Cooling step					Tempering step		Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa·m ^{1/2}) 10 ⁻⁶ m/cycle	Notes
			A		B		Cooling stop temperature (°C)	Temperature (°C)	Time (min)				
			Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 50°C (°C/s)	Average cooling rate from 800°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)							
BA1	100	1.8	-	-	14	4	35	629	30	Y	0	0.961	Inventive ex-ample
BB1	101	<u>2.0</u>	18	8	-	-	25	687	50	Y	1	<u>1.090</u>	Comparative example
Underline: outside the scope of the present invention. γ : austenite													

EXAMPLE 2

[0103] Examples in which the advantages of the present invention have been verified are described below. In the following Examples, steel pipes were produced under the following production conditions and were characterized. Steel pipes with the same chemical composition as the billets Nos. Q and BC shown in Tables 1-1 and 1-2 and AS1 shown in Table 2-3 were subjected to up to the cooling step under predetermined conditions, were reheated under the conditions shown in Table 3 after the cooling step (before the tempering step), were subjected to the quenching step, and were characterized. The steel pipes Nos. 17A to 17C shown in Table 3 were the steel pipes No. 17 shown in Tables 1-1 and 2-1 subjected to the reheating step. The steel pipes Nos. 55A to 55C were the steel pipes No. 55 shown in Tables 1-2 and 2-2 subjected to the reheating step, and the steel pipes Nos. 92A and 92B were the steel pipes No. 92 shown in Table 2-3 subjected to the reheating step. The examples of Example 2 all satisfied the condition that the crack growth rate da/dN in hydrogen gas was 1.0×10^{-6} m/cycle or less. Among them, the crack propagation characteristics were better when the reheating and quenching steps were performed under more suitable conditions.

[Table 3]

Billet No.	Steel pipe No.	Cooling step						Reheating step	Cooling step						Tempering step		Carbide	Amount of residual Y (%)	Crack growth rate in hydrogen at ΔK=20 (MPa·m ^{1/2}) 10 ⁻⁶ m/cycle	Notes
		A		B		Cooling stop temperature (°C)	A		B		Cooling stop temperature (°C)									
		Average cooling rate from 800°C to 550°C (°C/s)	Average cooling rate from 550°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)	Average cooling rate from 800°C to 550°C (°C/s)		Average cooling rate from 550°C to 300°C (°C/s)		Average cooling rate from 300°C to 50°C (°C/s)	Average cooling rate from 800°C to 550°C (°C/s)		Average cooling rate from 550°C to 300°C (°C/s)	Average cooling rate from 300°C to 50°C (°C/s)							
Q	17	-	-	13	3	41	-	-	-	-	-	-	616	30	0	0.815	Inventive example			
Q	17A	-	-	13	3	41	890	-	-	13	3	36	616	30	0	0.723	Inventive example			
Q	17B	-	-	13	3	41	950	-	-	13	3	38	616	30	0	0.756	Inventive example			
Q	17C	-	-	13	3	41	1000	-	-	13	3	49	616	30	0	0.978	Inventive example			
BC	55	16	6	-	-	27	-	-	-	-	-	-	616	20	0	0.542	Inventive example			
BC	55A	16	6	-	-	27	960	16	6	-	-	25	616	20	0	0.492	Inventive example			
BC	55B	16	6	-	-	27	980	16	6	-	-	25	616	20	0	0.508	Inventive example			
BC	55C	16	6	-	-	27	1000	16	6	-	-	35	616	20	0	0.695	Inventive example			
AS1	92	18	5	-	-	25	-	-	-	-	-	-	611	30	0	0.902	Inventive example			
AS1	92A	18	5	-	-	25	920	18	5	-	-	25	611	30	0	0.816	Inventive example			
AS1	92B	18	5	-	-	25	950	18	5	-	-	25	611	30	0	0.838	Inventive example			
γ: austenite																				

EXAMPLE 3

[0104] Examples in which the advantages of the present invention have been verified are described below. In the following Examples, steel pipes were produced under the following production conditions and were characterized. The billets Nos. N and AQ shown in Tables 1-1 and 1-2 and AX1 shown in Table 2-3 were used, up to the tempering step was performed under the same conditions as the steel pipes Nos. 14 and 43 shown in Tables 2-1 and 2-2 and the steel pipe No. 97 shown in Table 2-3, and the characteristics were evaluated while the dehydrogenation treatment conditions were changed. Table 4 shows the results. Although the dehydrogenation treatment of the steel pipes Nos. 14, 43, and 97 in Example 1 was performed at a dehydrogenation treatment temperature T (ambient temperature) of 50°C for a holding time of 3 hours, in the present example, the dehydrogenation treatment of the steel pipes Nos. 14D, 43D, and 97D was performed at a dehydrogenation treatment temperature T (ambient temperature) of 50°C so that the holding time t_c after the temperature T_c at the center of the plate thickness reached 50°C satisfied the formula (A). For the steel pipes Nos. 14E, 43E, and 97E, the dehydrogenation treatment temperature T (ambient temperature) was 50°C, and the holding time t_c satisfied the formula (A) at a dehydrogenation treatment temperature T of 50°C, but the holding time t_c after the temperature T_c at the center of the plate thickness reached 50°C did not satisfy the formula (A). For the steel pipes Nos. 14F and 97F, the dehydrogenation treatment temperature T (ambient temperature) was 50°C, but neither the holding time t at the ambient temperature nor the holding time t_c after the temperature T_c at the center of the plate thickness reached 50°C did not satisfy the formula (A).

[0105] In Table 4, "Dehydrogenation holding time t is Y" means that the dehydrogenation treatment temperature T (ambient temperature) is 50°C and the holding time t satisfies the formula (A), and "Dehydrogenation holding time t is N" means that the dehydrogenation treatment temperature T (ambient temperature) is 50°C, but the holding time t does not satisfy the formula (A). Furthermore, "Holding time t_c at center temperature of steel plate thickness T_c is Y" means that the holding time t_c after the temperature T_c at the center of the plate thickness reaches 50°C satisfies the formula (A), and "Holding time t_c at steel material center temperature T_c is N" means that the temperature T_c at the center of the plate thickness reaches 50°C, but the holding time t_c after T_c reaches 50°C does not satisfy the formula (A).

[0106] Investigation of the fatigue crack propagation characteristics was evaluated by the fatigue crack growth test described in Example 1.

[0107] The examples of the present invention all satisfied the condition that the crack growth rate da/dN in hydrogen gas was 1.0×10^{-6} m/cycle or less. Among them, a steel pipe subjected to the dehydrogenation treatment under more suitable conditions had better crack propagation characteristics.

[Table 4]

Billet No.	Steel pipe No.	Dehydrogenation holding time t	Holding time t_c at center temperature of steel plate thickness T_c	Carbide	Amount of residual γ (%)	Crack growth rate in hydrogen at $\Delta K=20$ (MPa $\cdot$ m $^{1/2}$) 10^{-6} m/cycle	Notes
N	14D	Y	Y	Y	0	0.087	Inventive example
N	14E	Y	N	Y	0	0.099	Inventive example
N	14F	N	N	Y	0	0.337	Inventive example
AQ	430	Y	Y	Y	0	0.543	Inventive example
AQ	43E	Y	N	Y	0	0.650	Inventive example
AX1	97D	Y	Y	Y	0	0.772	Inventive example
AX1	97E	Y	N	Y	0	0.888	Inventive example
AX1	97F	N	N	Y	0	0.913	Inventive example
γ : austenite							

Claims

1. A steel pipe with a good fatigue property in hydrogen, the steel pipe having a chemical composition comprising:

on a mass percent basis,

C: 0.10% to 0.45%,

Si: 0.01% to 2.0%,

Mn: 0.3% to 2.0%,

Al: 0.01% to 0.15%,

N: 0.0005% to 0.008%,

P: 0.015% or less,

S: 0.0015% or less,

O: 0.01% or less,

H: 0.0010% or less,

Cu: 0% to 2.5%,

Ni: 0% to 2.5%,

Cr: 0% to 2.5%,

Mo: 0% to 2.0%,

Nb: 0% to 0.5%,

V: 0% to 0.5%,

Ti: 0% to 0.5%,

W: 0% to 2.5%,

B: 0% to 0.005%,

Sn: 0% to 0.3%,

Sb: 0% to 0.3%,

Ca: 0% to 0.01%,

Mg: 0% to 0.01%, and

REM: 0% to 0.005%,

the remainder being Fe and incidental impurities,

wherein retained austenite constitutes 3% or less,

the number of carbides with a diameter of 200 nm or more is 20 pieces/10 μm^2 or less, and

a crack growth rate da/dN at a stress intensity factor range of 20 MPa $\sqrt{\text{m}}$ in hydrogen of 1 MPa or more is 1.0×10^{-6} m $\cdot$ cycle $^{-1}$ or less.

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

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

a heating step of heating at 1350°C or less;

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

a cooling step of holding a steel pipe obtained in the hot rolling step at a temperature of an A_{c3} temperature or higher and 1000°C or less, and a cooling condition is the following Group A or Group B; and

a tempering step of tempering the steel pipe obtained in the cooling step at 400°C or more and an A_{c1} temperature or lower for less than 60 minutes,

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 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 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 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 at the quarter thickness position from the inner surface of the steel pipe.

3. The method for producing a steel pipe according to Claim 2, comprising, before the tempering step, a quenching step of reheating to an A_{c3} temperature or higher and 1000°C or less, and 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 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 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 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 at the quarter thickness position from the inner surface of the steel pipe.

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4. The method for producing a steel pipe according to Claim 2 or 3, wherein the casting speed is 1.0 m/min or less.
5. A steel material with a good fatigue property in hydrogen, the steel material having a chemical composition comprising:

10 on a mass percent basis,

C: 0.10% to 0.45%,

Si: 0.01% to 2.0%,

Mn: 0.3% to 2.0%,

15 Al: 0.01% to 0.15%,

N: 0.0005% to 0.008%,

P: 0.015% or less,

S: 0.0015% or less,

O: 0.01% or less,

20 H: 0.0010% or less,

Cu: 0% to 2.5%,

Ni: 0% to 2.5%,

Cr: 0% to 2.5%,

Mo: 0% to 2.0%,

25 Nb: 0% to 0.5%,

V: 0% to 0.5%,

Ti: 0% to 0.5%,

W: 0% to 2.5%,

B: 0% to 0.005%,

30 Sn: 0% to 0.3%,

Sb: 0% to 0.3%,

Ca: 0% to 0.01%,

Mg: 0% to 0.01%, and

REM: 0% to 0.005%,

35 the remainder being Fe and incidental impurities,

wherein retained austenite constitutes 3% or less,

the number of carbides with a diameter of 200 nm or more is 20 pieces/10 μm^2 or less, and

a crack growth rate da/dN at a stress intensity factor range of 20 MPa $\sqrt{\text{m}}$ in hydrogen of 1 MPa or more is 1.0×10^{-6} m $\cdot$ cycle $^{-1}$ or less.

- 40
6. A method for producing a steel material, the method comprising:

a casting step of casting a steel raw material with the chemical composition according to Claim 5 at a casting speed of 1.8 m/min or less;

45 a heating step of heating at 1350°C or less;

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

a cooling step of holding a steel material obtained in the hot rolling step at a temperature of an A_{c3} temperature or higher and 1000°C or less, and a cooling condition is the following Group A or Group B; and

50 a tempering step of tempering the steel material obtained in the cooling step at 400°C or more and an A_{c1} temperature or lower for less than 60 minutes,

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 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

55 550°C to 50°C 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 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 at the quarter thickness position from the surface of the steel material.

7. The method for producing a steel material according to Claim 6, comprising, before the tempering step, a quenching step of reheating to an A_{c3} temperature or higher and 1000°C or less, and 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 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 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 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 at the quarter thickness position from the surface of the steel material.

8. The method for producing a steel material according to Claim 6 or 7, wherein the casting speed is 1.0 m/min or less.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

B21B 17/00(2006.01)i; **C21D 8/02**(2006.01)i; **C21D 8/10**(2006.01)i; **C21D 9/08**(2006.01)i; **C22C 38/00**(2006.01)i;
C22C 38/60(2006.01)i; **B22D 11/00**(2006.01)i

FI: C22C38/00 301Z; C22C38/00 301F; C22C38/60; C21D8/10 C; C21D8/02 C; C21D9/08 E; B22D11/00 A; B21B17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B21B17/00; C21D8/02; C21D8/10; C21D9/08; C22C38/00-38/60; B22D11/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2018/074109 A1 (JFE STEEL CORP.) 26 April 2018 (2018-04-26) entire text	1-8
A	WO 2013/191131 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 27 December 2013 (2013-12-27) entire text	1-8
A	JP 2008-56991 A (NIPPON STEEL CORP.) 13 March 2008 (2008-03-13) entire text	1-8
A	WO 2017/047099 A1 (JFE STEEL CORP.) 23 March 2017 (2017-03-23) entire text	1-8
A	WO 2020/137812 A1 (JFE STEEL CORP.) 02 July 2020 (2020-07-02) entire text	1-8
P, A	WO 2022/209896 A1 (JFE STEEL CORP.) 06 October 2022 (2022-10-06) entire text	1-8

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

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"P" document published prior to the international filing date but later than the priority date claimed	

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