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(72) Inventors:
• **YOSHIDA, Shinji**
Tokyo 100-8071 (JP)
• **ARAI, Yuji**
Tokyo 100-8071 (JP)
• **SOMA, Atsushi**
Tokyo 100-8071 (JP)
• **KAMITANI, Hiroki**
Tokyo 100-8071 (JP)

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(74) Representative: **Zimmermann & Partner**
Patentanwälte mbB
Postfach 330 920
80069 München (DE)

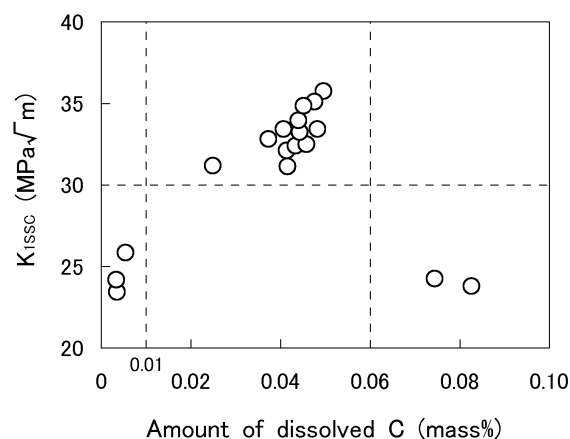
(71) Applicant: **Nippon Steel Corporation**
Tokyo 100-8071 (JP)

(54) **STEEL MATERIAL, AND STEEL MATERIAL MANUFACTURING METHOD**

(57) A steel material that has a yield strength in a range of 965 to 1069 MPa (140 ksi grade) and also have excellent SSC resistance are provided. The steel material according to the present disclosure contains a chemical composition consisting of, in mass%, C: more than 0.50 to 0.80%, Si: 0.05 to 1.00%, Mn: 0.05 to 1.00%, P: 0.025% or less, S: 0.0100% or less, Al: 0.005 to 0.100%, Cr: 0.20 to 1.50%, Mo: 0.25 to 1.50%, Ti: 0.002 to 0.050%,

B: 0.0001 to 0.0050%, N: 0.002 to 0.010% and O: 0.0100% or less, with the balance being Fe and impurities. The steel material contains an amount of dissolved C within a range of 0.010 to 0.060 mass%. The steel material also has a yield strength within a range of 965 to 1069 MPa, and a yield ratio of the steel material is 90% or more.

FIG. 1



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a steel material and a method for producing the steel material, and more particularly relates to a steel material suitable for use in a sour environment, and a method for producing the steel material.

BACKGROUND ART

10 **[0002]** Due to the deepening of oil wells and gas wells (hereunder, oil wells and gas wells are collectively referred to as "oil wells"), there is a demand to enhance the strength of oil-well steel pipes. Specifically, 80 ksi grade (yield strength is 80 to 95 ksi, that is, 551 to 655 MPa) and 95 ksi grade (yield strength is 95 to 110 ksi, that is, 655 to 758 MPa) oil-well steel pipes are being widely utilized, and recently requests are also starting to be made for 110 ksi grade (yield strength is 110 to 125 ksi, that is, 758 to 862 MPa), 125 ksi grade (yield strength is 125 ksi to 140 ksi, that is, 862 to 965 MPa) and 140 ksi grade (yield strength is 140 ksi to 155 ksi, that is, 965 to 1069 MPa) oil-well steel pipes.

15 **[0003]** Most deep wells are in a sour environment containing corrosive hydrogen sulfide. Oil-well steel pipes for use in such sour environments are required to have not only high strength, but to also have sulfide stress cracking resistance (hereunder, referred to as "SSC resistance").

20 **[0004]** Technology for enhancing the SSC resistance of steel materials as typified by oil-well steel pipes is disclosed in Japanese Patent Application Publication No. 62-253720 (Patent Literature 1), Japanese Patent Application Publication No. 59-232220 (Patent Literature 2), Japanese Patent Application Publication No. 6-322478 (Patent Literature 3), Japanese Patent Application Publication No. 8-311551 (Patent Literature 4), Japanese Patent Application Publication No. 2000-256783 (Patent Literature 5), Japanese Patent Application Publication No. 2000-297344 (Patent Literature 6), Japanese Patent Application Publication No. 2005-350754 (Patent Literature 7), National Publication of International Patent Application No. 2012-519238 (Patent Literature 8) and Japanese Patent Application Publication No. 2012-26030 (Patent Literature 9).

25 **[0005]** Patent Literature 1 proposes a method for improving the SSC resistance of steel for oil wells by reducing impurities such as Mn and P. Patent Literature 2 proposes a method for improving the SSC resistance of steel by performing quenching twice to refine the grains.

30 **[0006]** Patent Literature 3 proposes a method for improving the SSC resistance of a 125 ksi grade steel material by refining the steel microstructure by a heat treatment using induction heating. Patent Literature 4 proposes a method for improving the SSC resistance of steel pipes of 110 to 140 ksi grade by enhancing the hardenability of the steel by utilizing a direct quenching process and also increasing the tempering temperature.

35 **[0007]** Patent Literature 5 and Patent Literature 6 each propose a method for improving the SSC resistance of a steel for low-alloy oil country tubular goods of 110 to 140 ksi grade by controlling the shapes of carbides. Patent Literature 7 proposes a method for improving the SSC resistance of steel material of 125 ksi (862 MPa) grade or higher by controlling the dislocation density and the hydrogen diffusion coefficient to desired values. Patent Literature 8 proposes a method for improving the SSC resistance of steel of 125 ksi (862 MPa) grade by subjecting a low-alloy steel containing 0.3 to 0.5% of C to quenching multiple times. Patent Literature 9 proposes a method for controlling the shapes or number of carbides by employing a tempering process composed of a two-stage heat treatment. More specifically, in Patent Literature 9, a method is proposed that enhances the SSC resistance of 125 ksi (862 MPa) grade steel by suppressing the number density of large M_3C particles or M_2C particles.

CITATION LIST

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PATENT LITERATURE

[0008]

50 Patent Literature 1: Japanese Patent Application Publication No. 62-253720
 Patent Literature 2: Japanese Patent Application Publication No. 59-232220
 Patent Literature 3: Japanese Patent Application Publication No. 6-322478
 Patent Literature 4: Japanese Patent Application Publication No. 8-311551
 Patent Literature 5: Japanese Patent Application Publication No. 2000-256783
 55 Patent Literature 6: Japanese Patent Application Publication No. 2000-297344
 Patent Literature 7: Japanese Patent Application Publication No. 2005-350754
 Patent Literature 8: National Publication of International Patent Application No. 2012-519238
 Patent Literature 9: Japanese Patent Application Publication No. 2012-26030

[0009] However, even if the techniques disclosed in the aforementioned Patent Literatures 1 to 9 are applied, in the case of steel material (for example, oil-well steel pipes) having a yield strength of 140 ksi grade (965 to 1069 MPa), excellent SSC resistance cannot be stably obtained in some cases.

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0010] An objective of the present disclosure is to provide a steel material that has a yield strength within a range of 965 to 1069 MPa (140 to 155 ksi; 140 ksi grade) and that also has excellent SSC resistance.

SOLUTION TO PROBLEM

[0011] A steel material according to the present disclosure contains a chemical composition consisting of, in mass%, C: more than 0.50 to 0.80%, Si: 0.05 to 1.00%, Mn: 0.05 to 1.00%, P: 0.025% or less, S: 0.0100% or less, Al: 0.005 to 0.100%, Cr: 0.20 to 1.50%, Mo: 0.25 to 1.50%, Ti: 0.002 to 0.050%, B: 0.0001 to 0.0050%, N: 0.002 to 0.010%, O: 0.0100% or less, V: 0 to 0.30%, Nb: 0 to 0.100%, Ca: 0 to 0.0100%, Mg: 0 to 0.0100%, Zr: 0 to 0.0100%, Co: 0 to 0.50%, W: 0 to 0.50%, Ni: 0 to 0.50% and Cu: 0 to 0.50%, with the balance being Fe and impurities. The steel material according to the present disclosure also contains an amount of dissolved C within a range of 0.010 to 0.060 mass%. The steel material according to the present disclosure also has a yield strength within a range of 965 to 1069 MPa, and a yield ratio of the steel material is 90% or more.

[0012] A method for producing a steel material according to the present disclosure includes a preparation process, a quenching process and a tempering process. In the preparation process, an intermediate steel material containing the aforementioned chemical composition is prepared. In the quenching process, after the preparation process, the intermediate steel material that is at a temperature in a range of 800 to 1000°C is cooled at a cooling rate of 50°C/min or more. In the tempering process, the intermediate steel material after the quenching is held for 10 to 90 minutes at a temperature in a range of 660°C to an A_{c1} point, and thereafter is cooled from 600°C to 200°C at an average cooling rate of 5 to 300°C/sec.

ADVANTAGEOUS EFFECTS OF INVENTION

[0013] The steel material according to the present disclosure has a yield strength within a range of 965 to 1069 MPa (140 ksi grade), and also has excellent SSC resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

[FIG. 1] FIG. 1 is a view illustrating the relation between the amount of dissolved C and a fracture toughness value K_{ISCC} .

[FIG. 2A] FIG. 2A shows a side view and a cross-sectional view of a DCB test specimen that is used in a DCB test in the examples.

[FIG. 2B] FIG. 2B is a perspective view of a wedge that is used in the DCB test in the examples.

DESCRIPTION OF EMBODIMENTS

[0015] The present inventors conducted investigations and studies regarding a method for obtaining both a yield strength in a range of 965 to 1069 MPa (140 ksi grade) and SSC resistance in a steel material that it is assumed will be used in a sour environment, and obtained the following findings.

[0016] If the dislocation density in the steel material is increased, the yield strength of the steel material will increase. However, there is a possibility that dislocations will occlude hydrogen. Therefore, if the dislocation density of the steel material increases, there is a possibility that the amount of hydrogen that the steel material occludes will also increase. If the hydrogen concentration in the steel material increases as a result of increasing the dislocation density, even if high strength is obtained, the SSC resistance of the steel material will decrease. Accordingly, at first glance it seems that, in order to obtain both a high strength of 140 ksi grade (965 to 1069 MPa) and SSC resistance, utilizing the dislocation density to enhance the strength is not preferable.

[0017] However, the present inventors discovered that by adjusting the amount of dissolved C in a steel material, excellent SSC resistance can also be obtained while at the same time raising the yield strength to 140 ksi grade (965

to 1069 MPa) by utilizing the dislocation density. Although the reason is not certain, it is considered that the reason may be as follows.

[0018] Dislocations include mobile dislocations and sessile dislocations, and it is considered that dissolved C in a steel material immobilizes mobile dislocations to thereby form sessile dislocations. When mobile dislocations are immobilized by dissolved C, the disappearance of dislocations can be inhibited, and thus a decrease in the dislocation density can be suppressed. In this case, the yield strength of the steel material can be maintained.

[0019] In addition, it is considered that the sessile dislocations that are formed by dissolved C reduce the amount of hydrogen that is occluded in the steel material more than mobile dislocations. Therefore, it is considered that by increasing the density of sessile dislocations that are formed by dissolved C, the amount of hydrogen that is occluded in the steel material is reduced. As a result, the SSC resistance of the steel material can be increased. It is considered that because of this mechanism, excellent SSC resistance is obtained even when the steel material has high strength of 140 ksi grade.

[0020] As described above, the present inventors considered that by appropriately adjusting the amount of dissolved C in a steel material, the SSC resistance of the steel material can be increased while maintaining a yield strength of 140 ksi grade. Therefore, using a steel material containing chemical composition consisting of, in mass%, C: more than 0.50 to 0.80%, Si: 0.05 to 1.00%, Mn: 0.05 to 1.00%, P: 0.025% or less, S: 0.0100% or less, Al: 0.005 to 0.100%, Cr: 0.20 to 1.50%, Mo: 0.25 to 1.50%, Ti: 0.002 to 0.050%, B: 0.0001 to 0.0050%, N: 0.002 to 0.010%, O: 0.0100% or less, V: 0 to 0.30%, Nb: 0 to 0.100%, Ca: 0 to 0.0100%, Mg: 0 to 0.0100%, Zr: 0 to 0.0100%, Co: 0 to 0.50%, W: 0 to 0.50%, Ni: 0 to 0.50% and Cu: 0 to 0.50%, with the balance being Fe and impurities, the present inventors investigated the relation between the amount of dissolved C, the yield strength, and a fracture toughness value K_{ISCC} that is an index of SSC resistance.

[Relation between amount of dissolved C and SSC resistance]

[0021] FIG. 1 is a view illustrating the relation between the amount of dissolved C and a fracture toughness value K_{ISCC} for respective test numbers of the examples. FIG. 1 was obtained by the following method. FIG. 1 was created using the amount of dissolved C (mass%) and the fracture toughness value K_{ISCC} (MPa \sqrt{m}) obtained with respect to steel materials for which, among the steel materials of the examples that are described later, conditions other than the amount of dissolved C satisfied the range of the present embodiment.

[0022] The yield strength YS of each of the steel materials shown in FIG. 1 was within the range of 965 to 1069 MPa (140 ksi grade). Adjustment of the yield strength YS was performed by adjusting the tempering temperature. Further, with respect to the SSC resistance, if the fracture toughness value K_{ISCC} that is an index of SSC resistance was 30.0 MPa \sqrt{m} or more, it was determined that the SSC resistance was good.

[0023] Referring to FIG. 1, in a steel material in which the conditions of the aforementioned chemical composition are satisfied, when the amount of dissolved C was 0.010 mass% or more, the fracture toughness value K_{ISCC} became 30.0 MPa \sqrt{m} or more, indicating excellent SSC resistance. On the other hand, in a steel material in which the conditions of the aforementioned chemical composition are satisfied, when the amount of dissolved C was more than 0.060 mass%, the fracture toughness value K_{ISCC} was less than 30.0 MPa \sqrt{m} . In other words, it was clarified that when the amount of dissolved C is too high, conversely, the SSC resistance decreases.

[0024] The reason the SSC resistance decreases when the amount of dissolved C is too high as described above has not been clarified. However, with respect to the range of the chemical composition and yield strength YS of the present embodiment, excellent SSC resistance can be obtained if the amount of dissolved C is made 0.060 mass% or less.

[0025] Therefore, by adjusting the chemical composition and tempering conditions to obtain a yield strength YS within a range of 965 to 1069 MPa (140 ksi grade) and also making the amount of dissolved C 0.010 to 0.060 mass%, the fracture toughness value K_{ISCC} becomes 30.0 MPa \sqrt{m} or more and excellent SSC resistance can be obtained.

[0026] Accordingly, in the present embodiment, the amount of dissolved C of the steel material is set within the range of 0.010 to 0.060 mass%.

[0027] Note that, in order to appropriately control the amount of dissolved C and inhibit the occurrence of mobile dislocations, the microstructure of the steel is made a microstructure that is principally composed of tempered martensite and tempered bainite. The term "principally composed of tempered martensite and tempered bainite" means that the total volume ratio of tempered martensite and tempered bainite is 90% or more. When the microstructure of the steel is principally composed of tempered martensite and tempered bainite, in the steel material according to the present embodiment, the yield strength YS is in a range of 965 to 1069 MPa (140 ksi grade), and a yield ratio YR (ratio of the yield strength YS to the tensile strength TS; in other words, yield ratio YR (%) = yield strength YS/tensile strength TS) is 90% or more.

[0028] A steel material according to the present embodiment that was completed based on the above findings contains a chemical composition consisting of, in mass%, C: more than 0.50 to 0.80%, Si: 0.05 to 1.00%, Mn: 0.05 to 1.00%, P: 0.025% or less, S: 0.0100% or less, Al: 0.005 to 0.100%, Cr: 0.20 to 1.50%, Mo: 0.25 to 1.50%, Ti: 0.002 to 0.050%, B: 0.0001 to 0.0050%, N: 0.002 to 0.010%, O: 0.0100% or less, V: 0 to 0.30%, Nb: 0 to 0.100%, Ca: 0 to 0.0100%, Mg: 0

to 0.0100%, Zr: 0 to 0.0100%, Co: 0 to 0.50%, W: 0 to 0.50%, Ni: 0 to 0.50% and Cu: 0 to 0.50%, with the balance being Fe and impurities. The steel material according to the present embodiment further contains an amount of dissolved C within a range of 0.010 to 0.060 mass%. Further, in the steel material according to the present embodiment, the yield strength is within a range of 965 to 1069 MPa, and the yield ratio is 90% or more.

[0029] In the present description, although not particularly limited, the steel material is, for example, a steel pipe or a steel plate.

[0030] The aforementioned chemical composition may contain one or more types of element selected from the group consisting of V: 0.01 to 0.30% and Nb: 0.002 to 0.100%.

[0031] The aforementioned chemical composition may contain one or more types of element selected from the group consisting of Ca: 0.0001 to 0.0100%, Mg: 0.0001 to 0.0100% and Zr: 0.0001 to 0.0100%.

[0032] The aforementioned chemical composition may contain one or more types of element selected from the group consisting of Co: 0.02 to 0.50% and W: 0.02 to 0.50%.

[0033] The aforementioned chemical composition may contain one or more types of element selected from the group consisting of Ni: 0.02 to 0.50% and Cu: 0.01 to 0.50%.

[0034] The aforementioned steel material may be an oil-well steel pipe.

[0035] In the present description, the oil-well steel pipe may be a steel pipe that is used for a line pipe or may be a steel pipe used for oil country tubular goods (OCTG). The oil-well steel pipe may be a seamless steel pipe, or may be a welded steel pipe. The oil country tubular goods are, for example, steel pipes that are used as casing pipes or tubing pipes.

[0036] Preferably, an oil-well steel pipe according to the present embodiment is a seamless steel pipe. If the oil-well steel pipe according to the present embodiment is a seamless steel pipe, even if the wall thickness is 15 mm or more, the oil-well steel pipe will have a yield strength within a range of 965 to 1069 MPa (140 ksi grade) and will also have excellent SSC resistance.

[0037] The term "excellent SSC resistance" mentioned above means, specifically, that a value of Kissc (MPa√m) is 30.0 MPa√m or more in a DCB test performed in accordance with "Method D" described in NACE TM0177-2005 using an autoclave in which a solution obtained by mixing a degassed 5% saline solution and 4g/L of sodium acetate and adjusting to pH 3.5 using hydrochloric acid, and a gaseous mixture consisting of 10% H₂S gas and 90% CO₂ gas at a total pressure of 1 atm were sealed.

[0038] Further, the term "amount of dissolved C" mentioned above means the difference between the amount of C (mass%) in carbides in the steel material and the C content of the chemical composition of the steel material. The amount of C in carbides in the steel material is determined by Formula (1) to Formula (5) using an Fe concentration <Fe>_a, a Cr concentration <Cr>_a, an Mn concentration <Mn>_a, a Mo concentration <Mo>_a, a V concentration <V>_a and an Nb concentration <Nb>_a in carbides (cementite and MC-type carbides) obtained as residue when extraction residue analysis is performed on the steel material, and an Fe concentration <Fe>_b, a Cr concentration <Cr>_b, an Mn concentration <Mn>_b and an Mo concentration <Mo>_b in cementite obtained by performing point analysis by EDS with respect to cementite identified by performing TEM observation of a replica film obtained by an extraction replica method.

$$\langle \text{Mo} \rangle_c = (\langle \text{Fe} \rangle_a + \langle \text{Cr} \rangle_a + \langle \text{Mn} \rangle_a) \times \langle \text{Mo} \rangle_b / (\langle \text{Fe} \rangle_b + \langle \text{Cr} \rangle_b + \langle \text{Mn} \rangle_b) \quad (1)$$

$$\langle \text{Mo} \rangle_d = \langle \text{Mo} \rangle_a - \langle \text{Mo} \rangle_c \quad (2)$$

$$\langle \text{C} \rangle_a = (\langle \text{Fe} \rangle_a / 55.85 + \langle \text{Cr} \rangle_a / 52 + \langle \text{Mn} \rangle_a / 53.94 + \langle \text{Mo} \rangle_c / 95.9) / 3 \times 12 \quad (3)$$

$$\langle \text{C} \rangle_b = (\langle \text{V} \rangle_a / 50.94 + \langle \text{Mo} \rangle_d / 95.9 + \langle \text{Nb} \rangle_a / 92.9) \times 12 \quad (4)$$

$$(\text{amount of dissolved C}) = \langle \text{C} \rangle - (\langle \text{C} \rangle_a + \langle \text{C} \rangle_b) \quad (5)$$

Note that, in the present description, the term "cementite" means carbides containing an Fe content of 50 mass% or more.

[0039] A method for producing a steel material according to the present embodiment includes a preparation process, a quenching process and a tempering process. In the preparation process, an intermediate steel material containing the aforementioned chemical composition is prepared. In the quenching process, after the preparation process, the intermediate steel material that is at a temperature in a range of 800 to 1000°C is cooled at a cooling rate of 50°C/min or

more. In the tempering process, the intermediate steel material after quenching is held at a temperature in a range of 660°C to the A_{c1} point for 10 to 90 minutes, and thereafter the intermediate steel material is cooled at an average cooling rate of 5 to 300°C/sec with respect to cooling from 600°C to 200°C.

[0040] In the present description, the term "intermediate steel material" refers to a hollow shell in a case where the end product is a steel pipe, and refers to a plate-shaped steel material in a case where the end product is a steel plate.

[0041] The preparation process of the aforementioned production method may include a starting material preparation process of preparing a starting material containing the aforementioned chemical composition, and a hot working process of subjecting the starting material to hot working to produce an intermediate steel material.

[0042] Hereunder, the steel material according to the present embodiment is described in detail. The symbol "%" in relation to an element means "mass percent" unless specifically stated otherwise.

[Chemical Composition]

[0043] The chemical composition of the steel material according to the present embodiment contains the following elements.

C: more than 0.50 to 0.80%

[0044] Carbon (C) enhances the hardenability and increases the strength of the steel material. C also promotes spheroidization of carbides during tempering in the production process, and increases the SSC resistance of the steel material. If the carbides are dispersed, the strength of the steel material increases further. These effects will not be obtained if the C content is too low. On the other hand, if the C content is too high, the toughness of the steel material will decrease and quench cracking is liable to occur. Therefore, the C content is within the range of more than 0.50 to 0.80%. A preferable lower limit of the C content is 0.51%. A preferable upper limit of the C content is 0.70%, and more preferably is 0.62%.

Si: 0.05 to 1.00%

[0045] Silicon (Si) deoxidizes the steel. If the Si content is too low, this effect is not obtained. On the other hand, if the Si content is too high, the SSC resistance of the steel material decreases. Therefore, the Si content is within the range of 0.05 to 1.00%. A preferable lower limit of the Si content is 0.15%, and more preferably is 0.20%. A preferable upper limit of the Si content is 0.85%, and more preferably is 0.50%.

Mn: 0.05 to 1.00%

[0046] Manganese (Mn) deoxidizes the steel material. Mn also enhances the hardenability. If the Mn content is too low, these effects are not obtained. On the other hand, if the Mn content is too high, Mn segregates at grain boundaries together with impurities such as P and S. In such a case, the SSC resistance of the steel material will decrease. Therefore, the Mn content is within a range of 0.05 to 1.00%. A preferable lower limit of the Mn content is 0.25%, and more preferably is 0.30%. A preferable upper limit of the Mn content is 0.90%, and more preferably is 0.80%.

P: 0.025% or less

[0047] Phosphorous (P) is an impurity. In other words, the P content is more than 0%. P segregates at the grain boundaries and decreases the SSC resistance of the steel material. Therefore, the P content is 0.025% or less. A preferable upper limit of the P content is 0.020%, and more preferably is 0.015%. Preferably, the P content is as low as possible. However, if the P content is excessively reduced, the production cost increases significantly. Therefore, when taking industrial production into consideration, a preferable lower limit of the P content is 0.0001%, more preferably is 0.0003%, and further preferably is 0.001%.

S: 0.0100% or less

[0048] Sulfur (S) is an impurity. In other words, the S content is more than 0%. S segregates at the grain boundaries and decreases the SSC resistance of the steel material. Therefore, the S content is 0.0100% or less. A preferable upper limit of the S content is 0.0050%, and more preferably is 0.0030%. Preferably, the S content is as low as possible. However, if the S content is excessively reduced, the production cost increases significantly. Therefore, when taking industrial production into consideration, a preferable lower limit of the S content is 0.0001%, more preferably is 0.0002%, and further preferably is 0.0003%.

Al: 0.005 to 0.100%

[0049] Aluminum (Al) deoxidizes the steel material. If the Al content is too low, this effect is not obtained and the SSC resistance of the steel material decreases. On the other hand, if the Al content is too high, coarse oxide-based inclusions are formed and the SSC resistance of the steel material decreases. Therefore, the Al content is within a range of 0.005 to 0.100%. A preferable lower limit of the Al content is 0.015%, and more preferably is 0.020%. A preferable upper limit of the Al content is 0.080%, and more preferably is 0.060%. In the present description, the "Al" content means "acid-soluble Al", that is, the content of "sol. Al".

Cr: 0.20 to 1.50%

[0050] Chromium (Cr) enhances the hardenability of the steel material. Cr also increases temper softening resistance of the steel material and enables high-temperature tempering. As a result, the SSC resistance of the steel material increases. If the Cr content is too low, aforementioned effects are not obtained. On the other hand, if the Cr content is too high, the toughness and SSC resistance of the steel material decreases. Therefore, the Cr content is within a range of 0.20 to 1.50%. A preferable lower limit of the Cr content is 0.25%, and more preferably is 0.30%. A preferable upper limit of the Cr content is 1.30%.

Mo: 0.25 to 1.50%

[0051] Molybdenum (Mo) enhances the hardenability of the steel material. Mo also forms fine carbides and increases the temper softening resistance of the steel material. As a result, Mo increases the SSC resistance of the steel material by high temperature tempering. If the Mo content is too low, these effects are not obtained. On the other hand, if the Mo content is too high, the aforementioned effects are saturated. Therefore, the Mo content is within a range of 0.25 to 1.50%. A preferable lower limit of the Mo content is 0.50%, and more preferably is 0.65%. A preferable upper limit of the Mo content is 1.20%, and more preferably is 1.00%.

Ti: 0.002 to 0.050%

[0052] Titanium (Ti) forms nitrides, and refines crystal grains by the pinning effect. As a result, the strength of the steel material increases. If the Ti content is too low, this effect is not obtained. On the other hand, if the Ti content is too high, Ti nitrides coarsen and the SSC resistance of the steel material decreases. Therefore, the Ti content is within a range of 0.002 to 0.050%. A preferable lower limit of the Ti content is 0.003%, and more preferably is 0.005%. A preferable upper limit of the Ti content is 0.030%, and more preferably is 0.020%.

B: 0.0001 to 0.0050%

[0053] Boron (B) dissolves in the steel, enhances the hardenability of the steel material and increases the steel material strength. This effect is not obtained if the B content is too low. On the other hand, if the B content is too high, coarse nitrides form and the SSC resistance of the steel material decreases. Therefore, the B content is within a range of 0.0001 to 0.0050%. A preferable lower limit of the B content is 0.0003%, and more preferably is 0.0007%. A preferable upper limit of the B content is 0.0035%, and more preferably is 0.0025%.

N: 0.002 to 0.010%

[0054] Nitrogen (N) is unavoidably contained. N combines with Ti to form fine nitrides and thereby refines the grains. On the other hand, if the N content is too high, N will form coarse nitrides and the SSC resistance of the steel material will decrease. Therefore, the N content is within the range of 0.002 to 0.010%. A preferable upper limit of the N content is 0.005%, and more preferably is 0.004%.

O: 0.0100% or less

[0055] Oxygen (O) is an impurity. In other words, the O content is more than 0%. O forms coarse oxides and reduces the corrosion resistance of the steel material. Therefore, the O content is 0.0100% or less. A preferable upper limit of the O content is 0.0030%, and more preferably is 0.0020%. Preferably, the O content is as low as possible. However, if the O content is excessively reduced, the production cost increases significantly. Therefore, when taking industrial production into consideration, a preferable lower limit of the O content is 0.0001%, more preferably is 0.0002%, and further preferably is 0.0003%.

[0056] The balance of the chemical composition of the steel material according to the present embodiment is Fe and impurities. Here, the term "impurities" refers to elements which, during industrial production of the steel material, are mixed in from ore or scrap that is used as a raw material of the steel material, or from the production environment or the like, and which are allowed within a range that does not adversely affect the steel material according to the present embodiment.

[Regarding optional elements]

[0057] The chemical composition of the steel material described above may further contain one or more types of element selected from the group consisting of V and Nb in lieu of a part of Fe. Each of these elements is an optional element, and increases the SSC resistance of the steel material.

V: 0 to 0.30%

[0058] Vanadium (V) is an optional element, and need not be contained. In other words, the V content may be 0%. If contained, V combines with C or N to form carbides, nitrides or carbo-nitrides and the like (hereinafter, referred to as "carbo-nitrides and the like"). These carbo-nitrides and the like refine the substructure of the steel material by the pinning effect, and improve the SSC resistance of the steel. V also forms fine carbides during tempering. The fine carbides increase the temper softening resistance of the steel material, and increase the strength of the steel material. In addition, because V also forms spherical MC-type carbides, V suppresses the formation of acicular M₂C-type carbides and thereby increases the SSC resistance of the steel material. If even a small amount of V is contained, aforementioned effects are obtained to a certain extent. However, if the V content is too high, the toughness of the steel material decreases. Therefore, the V content is within the range of 0 to 0.30%. A preferable lower limit of the V content is more than 0%, more preferably is 0.01%, and further preferably is 0.02%. A preferable upper limit of the V content is 0.20%, more preferably is 0.15%, and further preferably is 0.12%.

Nb: 0 to 0.100%

[0059] Niobium (Nb) is an optional element, and need not be contained. In other words, the Nb content may be 0%. If contained, Nb forms carbo-nitrides and the like. These carbo-nitrides and the like refine the substructure of the steel material by the pinning effect, and increase the SSC resistance of the steel material. In addition, because Nb also forms spherical MC-type carbides, Nb suppresses the formation of acicular M₂C-type carbides and thereby increases the SSC resistance of the steel material. If even a small amount of Nb is contained, aforementioned effects are obtained to a certain extent. However, if the Nb content is too high, carbo-nitrides and the like are excessively formed and the SSC resistance of the steel material decreases. Therefore, the Nb content is within the range of 0 to 0.100%. A preferable lower limit of the Nb content is more than 0%, more preferably is 0.002%, further preferably is 0.003%, and further preferably is 0.007%. A preferable upper limit of the Nb content is 0.025%, and more preferably is 0.020%.

[0060] A total of the contents of the aforementioned V and Nb is preferably 0.30% or less, and further preferably is 0.20% or less.

[0061] The chemical composition of the steel material described above may further contain one or more types of element selected from the group consisting of Ca, Mg and Zr in lieu of a part of Fe. Each of these elements is an optional element, and increases the SSC resistance of the steel material.

Ca: 0 to 0.0100%

[0062] Calcium (Ca) is an optional element, and need not be contained. In other words, the Ca content may be 0%. If contained, Ca refines sulfides in the steel material and increases the SSC resistance of the steel material. If even a small amount of Ca is contained, aforementioned effect is obtained to a certain extent. However, if the Ca content is too high, oxides in the steel material coarsen and the SSC resistance of the steel material decreases. Therefore, the Ca content is within the range of 0 to 0.0100%. A preferable lower limit of the Ca content is more than 0%, more preferably is 0.0001%, further preferably is 0.0003%, and further preferably is 0.0006%. A preferable upper limit of the Ca content is 0.0025%, and more preferably is 0.0020%.

Mg: 0 to 0.0100%

[0063] Magnesium (Mg) is an optional element, and need not be contained. In other words, the Mg content may be 0%. If contained, Mg renders S in the steel material harmless by forming sulfides, and increases the SSC resistance of the steel material. If even a small amount of Mg is contained, aforementioned effect is obtained to a certain extent.

However, if the Mg content is too high, oxides in the steel material coarsen and decrease the SSC resistance of the steel material. Therefore, the Mg content is within the range of 0 to 0.0100%. A preferable lower limit of the Mg content is more than 0%, more preferably is 0.0001%, further preferably is 0.0003%, and further preferably is 0.0006%, and even further preferably is 0.0010%. A preferable upper limit of the Mg content is 0.0025%, and more preferably is 0.0020%.

Zr: 0 to 0.0100%

[0064] Zirconium (Zr) is an optional element, and need not be contained. In other words, the Zr content may be 0%. If contained, Zr refines sulfides in the steel material and increases the SSC resistance of the steel material. If even a small amount of Zr is contained, aforementioned effect is obtained to a certain extent. However, if the Zr content is too high, oxides in the steel material coarsen. Therefore, the Zr content is within the range of 0 to 0.0100%. A preferable lower limit of the Zr content is more than 0%, more preferably is 0.0001%, further preferably is 0.0003%, and further preferably is 0.0006%. A preferable upper limit of the Zr content is 0.0025%, and more preferably is 0.0020%.

[0065] In a case where two or more types of element selected from the aforementioned group containing Ca, Mg and Zr are contained in combination, the total of the contents of these elements is preferably 0.0100% or less, and more preferably is 0.0050% or less.

[0066] The chemical composition of the steel material described above may further contain one or more types of element selected from the group consisting of Co and W in lieu of a part of Fe. Each of these elements is an optional element that forms a protective corrosion coating in a hydrogen sulfide environment and suppresses hydrogen penetration. By this means, each of these elements increases the SSC resistance of the steel material.

Co: 0 to 0.50%

[0067] Cobalt (Co) is an optional element, and need not be contained. In other words, the Co content may be 0%. If contained, Co forms a protective corrosion coating in a hydrogen sulfide environment and suppresses hydrogen penetration. By this means, Co increases the SSC resistance of the steel material. If even a small amount of Co is contained, aforementioned effect is obtained to a certain extent. However, if the Co content is too high, the hardenability of the steel material will decrease, and the steel material strength will decrease. Therefore, the Co content is within the range of 0 to 0.50%. A preferable lower limit of the Co content is more than 0%, more preferably is 0.02%, and further preferably is 0.05%. A preferable upper limit of the Co content is 0.45%, and more preferably is 0.40%.

W: 0 to 0.50%

[0068] Tungsten (W) is an optional element, and need not be contained. In other words, the W content may be 0%. If contained, W forms a protective corrosion coating in a hydrogen sulfide environment and suppresses hydrogen penetration. By this means, W increases the SSC resistance of the steel material. If even a small amount of W is contained, aforementioned effect is obtained to a certain extent. However, if the W content is too high, coarse carbides form in the steel material and the SSC resistance of the steel material decreases. Therefore, the W content is within the range of 0 to 0.50%. A preferable lower limit of the W content is more than 0%, more preferably is 0.02%, and further preferably is 0.05%. A preferable upper limit of the W content is 0.45%, and more preferably is 0.40%.

[0069] The chemical composition of the steel material described above may further contain one or more types of element selected from the group consisting of Ni and Cu in lieu of a part of Fe. Each of these elements is an optional element, and increases the hardenability of the steel.

Ni: 0 to 0.50%

[0070] Nickel (Ni) is an optional element, and need not be contained. In other words, the Ni content may be 0%. If contained, Ni enhances the hardenability of the steel material and increases the steel material strength. If even a small amount of Ni is contained, aforementioned effect is obtained to a certain extent. However, if the Ni content is too high, the Ni will promote local corrosion, and the SSC resistance of the steel material will decrease. Therefore, the Ni content is within the range of 0 to 0.50%. A preferable lower limit of the Ni content is more than 0%, more preferably is 0.02%, and further preferably is 0.05%. A preferable upper limit of the Ni content is 0.35%, and more preferably is 0.25%.

Cu: 0 to 0.50%

[0071] Copper (Cu) is an optional element, and need not be contained. In other words, the Cu content may be 0%. If contained, Cu enhances the hardenability of the steel material and increases the steel material strength. If even a small amount of Cu is contained, aforementioned effect is obtained to a certain extent. However, if the Cu content is too high,

the hardenability of the steel material will be too high, and the SSC resistance of the steel material will decrease. Therefore, the Cu content is within the range of 0 to 0.50%. A preferable lower limit of the Cu content is more than 0%, more preferably is 0.01%, further preferably is 0.02%, and further preferably is 0.05%. A preferable upper limit of the Cu content is 0.35%, and more preferably is 0.25%.

[Amount of dissolved C]

[0072] The steel material according to the present embodiment contains an amount of dissolved C which is within the range of 0.010 to 0.060 mass%. If the amount of dissolved C is less than 0.010 mass%, the immobilization of dislocations in the steel material will be insufficient and excellent SSC resistance of the steel material will not be obtained. On the other hand, if the amount of dissolved C is more than 0.060 mass%, conversely, the SSC resistance of the steel material will decrease. Therefore, the amount of dissolved C is within the range of 0.010 to 0.060 mass%. A preferable lower limit of the amount of dissolved C is 0.020 mass% and more preferably is 0.030 mass%

[0073] An amount of dissolved C within the aforementioned range is obtained by, for example, controlling the holding time for tempering and controlling the cooling rate in the tempering process. The reason is as described hereinafter.

[0074] The amount of dissolved C is highest immediately after quenching. Immediately after quenching, C is dissolved except for a small amount thereof that precipitated as carbides during quenching. In the tempering process thereafter, some of the C precipitates as carbides as a result of being held for tempering. As a result, the amount of dissolved C decreases toward the thermal equilibrium concentration with respect to the tempering temperature. If the holding time for tempering is too short, this effect will not be obtained and the amount of dissolved C will be too high. On the other hand, if the holding time for tempering is too long, the amount of dissolved C will approach the aforementioned thermal equilibrium concentration, and will hardly change. Therefore, in the present embodiment the holding time for tempering is set within the range of 10 to 90 minutes.

[0075] If the cooling rate for cooling after tempering is slow, dissolved C will reprecipitate while the temperature is decreasing. In the conventional methods for producing steel material, because cooling after tempering has been performed by allowing the steel material to cool, the cooling rate has been slow. Consequently, the amount of dissolved C has been almost 0 mass%. Therefore, in the present embodiment, the cooling rate after tempering is raised, and a dissolved C amount in the range of 0.010 to 0.060 mass% is obtained.

[0076] The cooling method is, for example, a method that performs forced cooling of the steel material continuously from the tempering temperature to thereby continuously decrease the surface temperature of the steel material. Examples of this kind of continuous cooling treatment include a method that cools the steel material by immersion in a water bath, and a method that cools the steel material in an accelerated manner by shower water cooling, mist cooling or forced air cooling.

[0077] The cooling rate after tempering is measured at a region that is most slowly cooled within a cross-section of the steel material that is tempered (for example, in the case of forcedly cooling both surfaces, the cooling rate is measured at the center portion of the steel material thickness). Specifically, in a case where the steel material is a steel plate, the cooling rate after tempering can be measured by inserting a sheath-type thermocouple into the center portion of the thickness of the steel plate and measuring the temperature. In a case where the steel material is a steel pipe, the cooling rate after tempering can be measured by inserting a sheath-type thermocouple into the center portion of the wall thickness of the steel pipe and measuring the temperature. Further, in a case of forcedly cooling only a surface on one side of the steel material, the surface temperature on the non-forcedly cooled side of the steel material can be measured by means of a non-contact type infrared thermometer.

[0078] The temperature region from 600°C to 200°C is a temperature region in which diffusion of C is comparatively fast. Therefore, in the present embodiment, the average cooling rate in the temperature region from 600°C to 200°C is made 5°C/sec or more.

[0079] On the other hand, if the cooling rate after tempering is too fast, very little of the C that had dissolved after being held during tempering precipitates. As a result, in some cases the amount of dissolved C is excessive. In this case, the SSC resistance of the steel material decreases. Therefore, in the present embodiment, the cooling rate after tempering is made 300°C/sec or less.

[0080] In this case, the amount of dissolved C can be made to fall within the range of 0.010 to 0.060 mass%. However, the amount of dissolved C in the steel material may be adjusted to within a range of 0.010 to 0.060 mass% by another method.

[Method for calculating amount of dissolved C]

[0081] The term "amount of dissolved C" means the difference between the amount of C (mass%) in carbides in the steel material and the C content of the chemical composition of the steel material. The amount of C in carbides in the steel material is determined by Formula (1) to Formula (5) using an Fe concentration $\langle \text{Fe} \rangle_a$, a Cr concentration $\langle \text{Cr} \rangle_a$,

an Mn concentration $\langle \text{Mn} \rangle_a$, an Mo concentration $\langle \text{Mo} \rangle_a$, a V concentration $\langle \text{V} \rangle_a$ and an Nb concentration $\langle \text{Nb} \rangle_a$ in carbides (cementite and MC-type carbides) obtained as residue when extraction residue analysis is performed on the steel material, and an Fe concentration $\langle \text{Fe} \rangle_b$, a Cr concentration $\langle \text{Cr} \rangle_b$, an Mn concentration $\langle \text{Mn} \rangle_b$ and an Mo concentration $\langle \text{Mo} \rangle_b$ in cementite obtained by performing point analysis by EDS with respect to cementite identified by performing TEM observation of a replica film obtained by an extraction replica method.

$$\langle \text{Mo} \rangle_c = (\langle \text{Fe} \rangle_a + \langle \text{Cr} \rangle_a + \langle \text{Mn} \rangle_a) \times \langle \text{Mo} \rangle_b / (\langle \text{Fe} \rangle_b + \langle \text{Cr} \rangle_b + \langle \text{Mn} \rangle_b) \quad (1)$$

$$\langle \text{Mo} \rangle_d = \langle \text{Mo} \rangle_a - \langle \text{Mo} \rangle_c \quad (2)$$

$$\langle \text{C} \rangle_a = (\langle \text{Fe} \rangle_a / 55.85 + \langle \text{Cr} \rangle_a / 52 + \langle \text{Mn} \rangle_a / 53.94 + \langle \text{Mo} \rangle_c / 95.9) / 3 \times 12 \quad (3)$$

$$\langle \text{C} \rangle_b = (\langle \text{V} \rangle_a / 50.94 + \langle \text{Mo} \rangle_d / 95.9 + \langle \text{Nb} \rangle_a / 92.9) \times 12 \quad (4)$$

$$(\text{amount of dissolved C}) = \langle \text{C} \rangle - (\langle \text{C} \rangle_a + \langle \text{C} \rangle_b) \quad (5)$$

Note that, in the present description, the term "cementite" means carbides containing an Fe content of 50 mass% or more. Hereunder, the method for calculating the amount of dissolved C is described in detail.

[Determination of C content of steel material]

[0082] In a case where the steel material is a plate material, an analysis sample having the shape of a machined chip is taken from a center portion of the thickness, and in a case where the steel material is a pipe material, an analysis sample having the shape of a machined chip is taken from a center portion of the wall thickness. The C content (mass%) is analyzed by an oxygen-stream combustion-infrared absorption method. The resulting value was taken to be the C content ($\langle \text{C} \rangle$) of the steel material.

[Calculation of C amount that precipitates as carbides (precipitated C amount)]

[0083] The precipitated C amount is calculated by the following procedures 1 to 4. Specifically, in procedure 1 an extraction residue analysis is performed. In procedure 2, an extraction replica method using a transmission electron microscope (hereunder, referred to as "TEM"), and an element concentration analysis (hereunder, referred to as "EDS analysis") of elements in cementite is performed by energy dispersive X-ray spectrometry (hereunder, referred to as "EDS"). In procedure 3, the Mo content is adjusted. In procedure 4, the precipitated C amount is calculated.

[Procedure 1. Determination of residual amounts of Fe, Cr, Mn, Mo, V and Nb by extraction residue analysis]

[0084] In procedure 1, carbides in the steel material are captured as residue, and the contents of Fe, Cr, Mn, Mo, V and Nb in the residue are determined. Here, the term "carbides" is a generic term for cementite (M_3C -type carbides) and MC-type carbides. The specific procedure is as follows. In a case where the steel material is a plate material, a cylindrical test specimen having a diameter of 6 mm and a length of 50 mm is extracted from a center portion of the thickness. In a case where the steel material is a steel pipe, a cylindrical test specimen having a diameter of 6 mm and a length of 50 mm is extracted from a center portion of the wall thickness of the steel pipe in a manner so that the center of the wall thickness becomes the center of the cross-section. The surface of the extracted test specimen is polished to remove about 50 μm by preliminary electropolishing to obtain a newly formed surface. The electropolished test specimen is subjected to electrolysis in an electrolyte solution of 10% acetylacetone + 1% tetra-ammonium + methanol. The electrolyte solution after electrolysis is passed through a 0.2- μm filter to capture residue. The obtained residue is subjected to acid decomposition, and the concentrations of Fe, Cr, Mn, Mo, V and Nb are determined in units of mass percent by ICP (inductively coupled plasma) optical emission spectrometry. The concentrations are defined as $\langle \text{Fe} \rangle_a$, $\langle \text{Cr} \rangle_a$, $\langle \text{Mn} \rangle_a$, $\langle \text{Mo} \rangle_a$, $\langle \text{V} \rangle_a$ and $\langle \text{Nb} \rangle_a$, respectively.

[Procedure 2. Determination of content of Fe, Cr, Mn and Mo in cementite by extraction replica method and EDS]

[0085] In procedure 2, the content of each of Fe, Cr, Mn and Mo in cementite is determined. The specific procedure is as follows. A micro test specimen is cut out from a center portion of the thickness in a case where the steel material is a plate material, and is cut out from a center portion of the wall thickness in a case where the steel material is a steel pipe, and the surface of the micro test specimen is finished by mirror polishing. The test specimen is immersed for 10 minutes in a 3% nital etching reagent to etch the surface. The surface thereof is covered with a carbon deposited film. The test specimen whose surface is covered with the deposited film is immersed in a 5% nital etching reagent, and held therein for 20 minutes to cause the deposited film to peel off. The deposited film that peeled off is cleaned with ethanol, and thereafter is scooped up with a sheet mesh and dried. The deposited film (replica film) is observed using a TEM, and point analysis by EDS is performed with respect to 20 particles of cementite. The concentration of each of Fe, Cr, Mn and Mo is determined in units of mass percent when taking the total of the alloying elements excluding carbon in the cementite as 100%. The concentrations are determined for 20 particles of cementite, and the arithmetic average values for the respective elements are defined as $\langle \text{Fe} \rangle_b$, $\langle \text{Cr} \rangle_b$, $\langle \text{Mn} \rangle_b$ and $\langle \text{Mo} \rangle_b$.

[Procedure 3. Adjustment of Mo amount]

[0086] Next, the Mo concentration in the carbides is determined. In this case, Fe, Cr, Mn and Mo concentrate in cementite. On the other hand, V, Nb and Mo concentrate in MC-type carbides. In other words, Mo is caused to concentrate in both cementite and MC-type carbides by tempering. Therefore, the Mo amount is calculated separately for cementite and for MC-type carbides. Note that, in some cases a part of V also concentrates in cementite. However, the amount of V that concentrates in cementite is negligibly small in comparison to the amount of V that concentrates in MC-type carbides. Therefore, when determining the amount of dissolved C, V is regarded as concentrating only in MC-type carbides.

[0087] Specifically, the amount of Mo precipitating as cementite ($\langle \text{Mo} \rangle_c$) is calculated by Formula (1).

$$\langle \text{Mo} \rangle_c = (\langle \text{Fe} \rangle_a + \langle \text{Cr} \rangle_a + \langle \text{Mn} \rangle_a) \times \langle \text{Mo} \rangle_b / (\langle \text{Fe} \rangle_b + \langle \text{Cr} \rangle_b + \langle \text{Mn} \rangle_b) \quad (1)$$

[0088] On the other hand, the amount of Mo precipitating as MC-type carbides ($\langle \text{Mo} \rangle_d$) is calculated in units of mass percent by Formula (2).

$$\langle \text{Mo} \rangle_d = \langle \text{Mo} \rangle_a - \langle \text{Mo} \rangle_c \quad (2)$$

[Procedure 4. Calculation of precipitated C amount]

[0089] The precipitated C amount is calculated as the total of the C amount precipitating as cementite ($\langle \text{C} \rangle_a$) and the C amount precipitating as MC-type carbides ($\langle \text{C} \rangle_b$). $\langle \text{C} \rangle_a$ and $\langle \text{C} \rangle_b$ are calculated in units of mass percent by Formula (3) and Formula (4), respectively. Note that, Formula (3) is a formula that is derived from the fact that the structure of cementite is a M_3C type structure (M include Fe, Cr, Mn and Mo).

$$\langle \text{C} \rangle_a = (\langle \text{Fe} \rangle_a / 55.85 + \langle \text{Cr} \rangle_a / 52 + \langle \text{Mn} \rangle_a / 53.94 + \langle \text{Mo} \rangle_c / 95.9) / 3 \times 12 \quad (3)$$

$$\langle \text{C} \rangle_b = (\langle \text{V} \rangle_a / 50.94 + \langle \text{Mo} \rangle_d / 95.9 + \langle \text{Nb} \rangle_a / 92.9) \times 12 \quad (4)$$

[0090] Thus, the precipitated C amount is $\langle \text{C} \rangle_a + \langle \text{C} \rangle_b$.

[Calculation of amount of dissolved C]

[0091] The amount of dissolved C (hereunder, also referred to as " $\langle \text{C} \rangle_c$ ") is calculated in units of mass percent by Formula (5) as a difference between the C content ($\langle \text{C} \rangle$) and the precipitated C amount of the steel material.

$$\langle \text{C} \rangle_c = \langle \text{C} \rangle - (\langle \text{C} \rangle_a + \langle \text{C} \rangle_b) \quad (5)$$

[Micro structure]

[0092] The microstructure of the steel material according to the present embodiment is principally composed of tempered martensite and tempered bainite. More specifically, the volume ratio of tempered martensite and/or tempered bainite in the microstructure is 90% or more. In other words, the total of the volume ratios of tempered martensite and tempered bainite in the microstructure is 90% or more. The balance of the microstructure is, for example, retained austenite or the like. If the microstructure of the steel material containing the aforementioned chemical composition contains tempered martensite and tempered bainite in an amount equivalent to a total volume ratio of 90% or more, the yield strength will be within the range of 965 to 1069 MPa (140 ksi grade), and the yield ratio will be 90% or more.

[0093] In the present embodiment, if the yield strength YS is within the range of 965 to 1069 MPa (140 ksi grade) and the YR is 90% or more, it is assumed that the total of the volume ratios of tempered martensite and tempered bainite in the microstructure is 90% or more. Preferably, the microstructure is composed of only tempered martensite and/or tempered bainite.

[0094] Note that, the following method can be adopted in the case of determining the total of the volume ratios of tempered martensite and tempered bainite by observation. In a case where the steel material is a plate material, a small piece having an observation surface with dimensions of 10 mm in the rolling direction and 10 mm in the plate width direction is cut out from a center portion of the thickness. In a case where the steel material is a steel pipe, a small piece having an observation surface with dimensions of 10 mm in the pipe axis direction and 10 mm in the pipe circumferential direction is cut out from a center portion of the wall thickness. After polishing the observation surface to obtain a mirror surface, the small piece is immersed for about 10 seconds in a nital etching reagent, to reveal the microstructure by etching. The etched observation surface is observed by means of a secondary electron image obtained using a scanning electron microscope (SEM), and observation is performed for 10 visual fields. The area of each visual field is 400 μm^2 (magnification of $\times 5000$). In each visual field, tempered martensite and tempered bainite are identified based on the contrast. The total of the area fractions of tempered martensite and tempered bainite that are identified is determined. In the present embodiment, the arithmetic average value of the totals of the area fractions of tempered martensite and tempered bainite determined in all visual fields is taken as the volume ratio of tempered martensite and tempered bainite.

[Shape of steel material]

[0095] The shape of the steel material according to the present embodiment is not particularly limited. The steel material is, for example, a steel pipe or a steel plate. In a case where the steel material is an oil-well steel pipe, preferably the steel material is a seamless steel pipe. In this case, a preferable wall thickness is 9 to 60 mm. The steel material according to the present embodiment is, in particular, suitable for use as a heavy-wall oil-well steel pipe. More specifically, even if the steel material according to the present embodiment is an oil-well steel pipe having a thick wall of 15 mm or more or, furthermore, 20 mm or more, the steel material exhibits excellent strength and SSC resistance.

[Yield strength YS and yield ratio YR of steel material]

[0096] The yield strength YS of the steel material according to the present embodiment is within a range of 965 to 1069 MPa (140 ksi grade), and the yield ratio YR of the steel material is 90% or more. In the present description, the term "yield strength YS" means the stress when elongation of 0.65% is obtained in a tensile test. In short, the strength of the steel material according to the present embodiment is of 140 ksi grade. Even though the steel material according to the present embodiment has such high strength, the steel material also has excellent SSC resistance by satisfying the conditions regarding the chemical composition, amount of dissolved C and microstructure, which are described above.

[SSC resistance of steel material]

[0097] The SSC resistance of the steel material according to the present embodiment can be evaluated by a DCB test performed in accordance with "Method D" described in NACE TM0177-2005. The liquid solution used is obtained by mixing a degassed 5% saline solution and 4g/L of sodium acetate and adjusting to pH 3.5 using hydrochloric acid. The gas charged inside the autoclave is a gaseous mixture of 10% H_2S gas and 90% CO_2 gas at a total pressure of 1 atm. Thereafter, a DCB test specimen into which a wedge was driven is enclosed inside the vessel, and is held for three weeks at 24°C while agitating the liquid solution and also continuously blowing in the aforementioned gaseous mixture. The Kissc ($\text{MPa}\sqrt{\text{m}}$) value of the steel material according to the present embodiment determined under the foregoing conditions is 30.0 $\text{MPa}\sqrt{\text{m}}$ or more.

[Production method]

[0098] The method for producing a steel material according to the present embodiment includes a preparation process, a quenching process and a tempering process. The preparation process may include a starting material preparation process and a hot working process. In the present embodiment, a method for producing an oil-well steel pipe will be described as one example of a method for producing a steel material. The method for producing an oil-well steel pipe includes a process of preparing a hollow shell (preparation process), and a process of subjecting the hollow shell to quenching and tempering to obtain an oil-well steel pipe (quenching process and tempering process). Each of these processes is described in detail hereunder.

[Preparation process]

[0099] In the preparation process, an intermediate steel material containing the aforementioned chemical composition is prepared. The method for producing the intermediate steel material is not particularly limited as long as the intermediate steel material contains the aforementioned chemical composition. As used here, the term "intermediate steel material" refers to a plate-shaped steel material in a case where the end product is a steel plate, and refers to a hollow shell in a case where the end product is a steel pipe.

[0100] The preparation process may preferably include a process in which a starting material is prepared (starting material preparation process), and a process in which the starting material is subjected to hot working to produce an intermediate steel material (hot working process). Hereunder, a case in which the preparation process includes the starting material preparation process and the hot working process is described in detail.

[Starting material preparation process]

[0101] In the starting material preparation process, a starting material is produced using molten steel containing the aforementioned chemical composition. Specifically, a cast piece (a slab, bloom or billet) is produced by a continuous casting process using the molten steel. An ingot may also be produced by an ingot-making process using the molten steel. As necessary, the slab, bloom or ingot may be subjected to blooming to produce a billet. The starting material (a slab, bloom or billet) is produced by the above described process.

[Hot working process]

[0102] In the hot working process, the starting material that was prepared is subjected to hot working to produce an intermediate steel material. In a case where the steel material is a steel pipe, the intermediate steel material corresponds to a hollow shell. First, the billet is heated in a heating furnace. Although the heating temperature is not particularly limited, for example, the heating temperature is within a range of 1100 to 1300°C. The billet that is extracted from the heating furnace is subjected to hot working to produce a hollow shell (seamless steel pipe). For example, the Mannesmann process is performed as the hot working to produce the hollow shell. In this case, a round billet is piercing-rolled using a piercing machine. When performing piercing-rolling, although the piercing ratio is not particularly limited, the piercing ratio is, for example, within a range of 1.0 to 4.0. The round billet that underwent piercing-rolling is further hot-rolled to form a hollow shell using a mandrel mill, a reducer, a sizing mill or the like. The cumulative reduction of area in the hot working process is, for example, 20 to 70%.

[0103] A hollow shell may also be produced from the billet by another hot working method. For example, in the case of a heavy-wall steel material of a short length such as a coupling, a hollow shell may be produced by forging such as Ehrhardt process. A hollow shell is produced by the above process. Although not particularly limited, the wall thickness of the hollow shell is, for example, 9 to 60 mm.

[0104] The hollow shell produced by hot working may be air-cooled (as-rolled). The hollow shell produced by hot working may be subjected to direct quenching after hot rolling without being cooled to normal temperature, or may be subjected to quenching after undergoing supplementary heating (reheating) after hot rolling. However, in the case of performing direct quenching or quenching after supplementary heating, it is preferable to stop the cooling midway through the quenching process and conduct slow cooling for the purpose of suppressing quench cracking.

[0105] In a case where direct quenching is performed after hot rolling, or quenching is performed after supplementary heating after hot rolling, for the purpose of eliminating residual stress, a stress relief treatment (SR treatment) may be performed at a time that is after quenching and before the heat treatment of the next process.

[0106] As described above, an intermediate steel material is prepared in the preparation process. The intermediate steel material may be produced by the aforementioned preferable process, or may be an intermediate steel material that was produced by a third party, or an intermediate steel material that was produced in another factory other than the factory in which a quenching process and a tempering process that are described later are performed, or at a different

works. The quenching process is described in detail hereunder.

[Quenching process]

[0107] In the quenching process, the intermediate steel material (hollow shell) that was prepared is subjected to quenching. In the present description, the term "quenching" means rapidly cooling the intermediate steel material that is at a temperature not less than the A_3 point. A preferable quenching temperature is 800 to 1000°C. In a case where direct quenching is performed after hot working, the quenching temperature corresponds to the surface temperature of the intermediate steel material that is measured by a thermometer placed on the exit side of the apparatus that performs the final hot working. Further, in a case where quenching is performed after supplementary heating is performed after hot working, the quenching temperature corresponds to the temperature of the furnace that performs the supplementary heating.

[0108] The quenching method, for example, continuously cools the hollow shell from the quenching starting temperature, and continuously decreases the surface temperature of the hollow shell. The method of performing the continuous cooling treatment is not particularly limited. The method of performing the continuous cooling treatment is, for example, a method that cools the hollow shell by immersing the hollow shell in a water bath, or a method that cools the hollow shell in an accelerated manner by shower water cooling or mist cooling.

[0109] If the cooling rate during quenching is too slow, the microstructure does not become one that is principally composed of martensite and bainite, and the mechanical property defined in the present embodiment is not obtained. Therefore, as described above, in the method for producing the steel material according to the present embodiment, the intermediate steel material is rapidly cooled during quenching. Specifically, in the quenching process, the average cooling rate when the surface temperature of the intermediate steel material (hollow shell) is within the range of 800 to 500°C during quenching is defined as a cooling rate during quenching $CR_{800-500}$. The cooling rate during quenching $CR_{800-500}$ is 50°C/min or higher. A preferable lower limit of the cooling rate during quenching $CR_{800-500}$ is 100°C/min, and more preferably is 250°C/min. Although an upper limit of the cooling rate during quenching $CR_{800-500}$ is not particularly defined, for example, the upper limit is 60000°C/min.

[0110] Preferably, quenching is performed after performing heating of the hollow shell in the austenite zone a plurality of times. In this case, the SSC resistance of the steel material increases because austenite grains are refined prior to quenching. Heating in the austenite zone may be repeated a plurality of times by performing quenching a plurality of times, or heating in the austenite zone may be repeated a plurality of times by performing normalizing and quenching. Hereunder, the tempering process will be described in detail.

[Tempering process]

[0111] Tempering is performed after performing the aforementioned quenching. The tempering temperature is appropriately adjusted in accordance with the chemical composition of the steel material and the yield strength YS, which is to be obtained. In other words, with respect to the hollow shell containing the chemical composition of the present embodiment, the tempering temperature is adjusted so as to adjust the yield strength YS of the steel material to within a range of 965 to 1069 MPa (140 ksi grade) and to make the YR of the steel material 90% or more.

[0112] A preferable tempering temperature is in a range from 660°C to the A_{c1} point. If the tempering temperature is 660°C or more, carbides are sufficiently spheroidized and the SSC resistance is further increased.

[0113] If the holding time for tempering (tempering time) is too short, the amount of dissolved C becomes excessive because precipitation of carbides does not proceed. Even if the tempering time is overlong, there will be almost no change in the amount of dissolved C. Therefore, in order to control the amount of dissolved C to be within an appropriate range, the tempering time is set within a range of 10 to 90 minutes. A preferable lower limit of the tempering time is 15 minutes. A preferable upper limit of the tempering time is 70 minutes, and more preferably is 60 minutes. Note that, in a case where the steel material is a steel pipe, in comparison to other shapes, temperature variations with respect to the steel pipe are liable to occur during holding for tempering. Therefore, in a case where the steel material is a steel pipe, the tempering time is preferably set within a range of 15 to 90 minutes. A person skilled in the art will be sufficiently capable of making the yield strength YS of the steel material containing the chemical composition of the present embodiment fall within the range of 965 to less than 1069 MPa by appropriately adjusting the aforementioned holding time at the aforementioned tempering temperature.

[Regarding rapid cooling after tempering]

[0114] Conventionally, cooling after tempering has not been controlled. However, if the cooling rate of the steel material after tempering (that is, after being held for the aforementioned holding time at the aforementioned tempering temperature) is slow, almost all of the C that had dissolved will reprecipitate while the temperature is decreasing. In other words, the

amount of dissolved C will be approximately 0 mass%. Therefore, in the present embodiment, the intermediate steel material (hollow shell) after tempering is rapidly cooled.

[0115] Specifically, in the tempering process, the average cooling rate when the surface temperature of the intermediate steel material (hollow shell) is within the range of 600 to 200°C after tempering is defined as a cooling rate after tempering $CR_{600-200}$. In the method for producing the steel material according to the present embodiment, the cooling rate after tempering $CR_{600-200}$ is 5°C/sec or higher. By this means, the amount of dissolved C according to the present embodiment is obtained. The temperature region from 600°C to 200°C is a temperature region in which diffusion of C is comparatively fast. On the other hand, if the cooling rate after tempering is too fast, in some cases very little of the C that had dissolved will precipitate, and the amount of dissolved C will be excessive. In such a case, the SSC resistance of the steel material decreases. Furthermore, in such a case, the low-temperature toughness of the steel material may decrease.

[0116] Therefore, the cooling rate after tempering $CR_{600-200}$ is within the range of 5 to 300°C/sec. A preferable lower limit of the cooling rate after tempering $CR_{600-200}$ is 10°C/sec, and more preferably is 15°C/sec. A preferable upper limit of the cooling rate after tempering $CR_{600-200}$ is 100°C/sec, and more preferably is 50°C/sec.

[0117] A method for cooling so that the cooling rate after tempering $CR_{600-200}$ is within the range of 5 to 300°C/sec is not particularly limited, and a well-known method can be used. The cooling method, for example, is a method that performs forced cooling of a hollow shell continuously from the tempering temperature to thereby continuously decrease the surface temperature of the hollow shell. Examples of this kind of continuous cooling treatment include a method that cools the hollow shell by immersion in a water bath, and a method that cools the hollow shell in an accelerated manner by shower water cooling, mist cooling or forced air cooling. Note that, the cooling rate after tempering $CR_{600-200}$ is measured at a region that is most slowly cooled within a cross-section of the intermediate steel material that is tempered (for example, in the case of forcedly cooling both surfaces, the cooling rate is measured at the center portion of the thickness of the intermediate steel material).

[0118] A method for producing a steel pipe has been described as one example of the aforementioned production method. However, the steel material according to the present embodiment may be a steel plate or another shape. An example of a method for producing a steel plate or a steel material of another shape also includes, for example, a preparation process, a quenching process and a tempering process, similarly to the production method described above. However, the aforementioned production method is one example, and the steel material according to the present embodiment may be produced by another production method.

EXAMPLES

[0119] Molten steels of a weight of 180 kg containing the chemical compositions shown in Table 1 were produced.

[Table 1]

TABLE 1

Test Number	Chemical Composition (Unit is mass%; balance is Fe and impurities)																				
	C	Si	Mn	P	S	Al	Cr	Mo	Ti	B	N	O	V	Nb	Ca	Mg	Zr	Co	W	Ni	Cu
1	0.51	0.31	0.42	0.008	0.0007	0.036	0.49	0.71	0.015	0.0013	0.005	0.0006	0.10	0.010	-	-	-	-	-	-	-
2	0.52	0.29	0.46	0.009	0.0005	0.055	0.48	0.70	0.015	0.0011	0.003	0.0008	-	-	-	-	-	-	-	-	-
3	0.53	0.31	0.46	0.009	0.0008	0.036	1.05	0.70	0.014	0.0013	0.002	0.0007	0.09	-	-	-	-	-	-	-	-
4	0.51	0.30	0.43	0.008	0.0007	0.043	1.04	0.69	0.016	0.0014	0.005	0.0011	-	0.011	-	-	-	-	-	-	-
5	0.53	0.31	0.44	0.009	0.0008	0.049	0.50	0.70	0.014	0.0014	0.003	0.0013	-	-	0.0019	-	-	-	-	-	-
6	0.55	0.29	0.45	0.011	0.0008	0.041	0.48	1.25	0.013	0.0015	0.002	0.0015	-	-	-	0.0015	-	-	-	-	-
7	0.58	0.23	0.41	0.012	0.0006	0.045	1.01	0.68	0.013	0.0014	0.005	0.0007	-	-	-	-	0.0018	-	-	-	-
8	0.60	0.27	0.43	0.010	0.0008	0.039	0.99	0.70	0.014	0.0012	0.004	0.0006	-	-	-	-	-	0.32	-	-	-
9	0.62	0.26	0.42	0.010	0.0011	0.041	0.53	0.72	0.007	0.0012	0.003	0.0010	-	-	-	-	-	-	0.31	-	-
10	0.61	0.26	0.44	0.011	0.0008	0.035	0.53	0.68	0.007	0.0013	0.004	0.0009	-	-	-	-	-	-	-	0.06	-
11	0.62	0.26	0.44	0.009	0.0008	0.049	0.65	0.70	0.006	0.0012	0.003	0.0008	-	-	-	-	-	-	-	-	0.24
12	0.67	0.26	0.44	0.010	0.0008	0.045	1.35	0.50	0.007	0.0013	0.003	0.0016	-	-	-	-	-	-	-	-	-
13	0.68	0.24	0.41	0.011	0.0006	0.038	0.49	0.70	0.011	0.0013	0.004	0.0015	-	-	-	-	-	-	-	-	-
14	0.51	0.26	0.43	0.012	0.0007	0.046	0.49	0.71	0.006	0.0005	0.003	0.0012	-	-	-	-	-	-	-	-	-
15	0.51	0.29	0.40	0.010	0.0005	0.047	1.10	0.71	0.015	0.0023	0.004	0.0011	-	-	-	-	-	-	-	-	-
16	0.52	0.29	0.43	0.011	0.0010	0.050	0.65	0.70	0.018	0.0021	0.005	0.0018	-	-	-	-	-	-	-	-	-
17	0.51	0.31	0.47	0.012	0.0006	0.049	1.00	0.69	0.019	0.0014	0.004	0.0014	-	-	-	-	-	-	-	-	-
18	0.55	0.29	0.40	0.009	0.0008	0.036	0.12	0.68	0.015	0.0014	0.004	0.0014	-	-	-	-	-	-	-	-	-
19	0.56	0.28	0.44	0.009	0.0008	0.046	1.30	0.19	0.007	0.0015	0.003	0.0011	0.10	-	-	-	-	-	-	-	-
20	0.54	0.28	1.20	0.010	0.0006	0.043	0.52	0.57	0.006	0.0012	0.005	0.0014	-	-	-	-	-	-	-	-	-
21	0.58	0.28	0.44	0.011	0.0007	0.033	0.51	0.88	0.027	0.0015	0.015	0.0015	-	-	-	-	-	-	-	-	-
22	0.62	1.50	0.44	0.010	0.0010	0.045	0.52	0.98	0.027	0.0015	0.003	0.0017	-	-	-	-	-	-	-	-	-
23	0.52	0.27	0.38	0.009	0.0008	0.041	0.50	0.66	0.008	0.0013	0.004	0.0014	-	-	-	-	-	-	-	-	-
24	0.60	0.22	0.45	0.011	0.0008	0.031	0.51	0.71	0.012	0.0012	0.003	0.0016	0.10	-	-	-	-	-	-	-	-
25	0.55	0.30	0.42	0.009	0.0010	0.049	0.67	0.71	0.011	0.0015	0.004	0.0009	-	-	-	-	-	-	-	-	-

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[0120] Ingots were produced using the aforementioned molten steels. The ingots were hot rolled to produce steel plates having a thickness of 20 mm.

[0121] After hot rolling, the steel plate of each test number was allowed to cool to bring the steel plate temperature to normal temperature (25°C).

[0122] After being allowed to cool, the steel plates of each test number were reheated to bring the steel plate temperature to the quenching temperature (920°C, which is in the austenite single-phase zone), and were held for 20 minutes. After being held, the steel plates were immersed in a water bath and quenched. At this time, the cooling rate during quenching ($CR_{800-500}$) was 400°C/min. With respect to Test Number 23, after holding at the quenching temperature, the steel plate was cooled by immersion in an oil bath. At this time, the average cooling rate from 800°C to 500°C was 40°C/min.

[0123] After quenching, the steel plates of each test number were subjected to tempering. In the tempering, the tempering temperature was adjusted so that the steel plates became 140 ksi grade as specified in the API standards (yield strength of 965 to 1069 MPa). After performing a heat treatment at the respective tempering temperatures, the steel plates were cooled. For the cooling, controlled cooling by mist water cooling from both sides of the steel plate was performed. Note that, a type K thermocouple of a sheath type was inserted into a center portion of the thickness of the steel plate in advance, and the temperature was measured with respect to tempering and the cooling thereafter. The tempering temperature (°C) and tempering time (min) and the cooling rate ($CR_{600-200}$) (°C/sec) after tempering are shown in Table 2. Note that, the A_{c1} point of the steel material in each of Test Number 1 to Test Number 25 was 750°C, and the tempering temperature was set so as to be lower than the A_{c1} point.

[Table 2]

[0124]

TABLE 2

Test Number	Tempering Temperature (°C)	Tempering Time (min)	Cooling Rate After Tempering (°C/sec)	YS (MPa)	TS (MPa)	YR (%)	Dissolved C Amount (mass%)	K _{1SSC} (MPa√m)			
								1	2	3	Average Value
1	700	15	25	1025	1087	94	0.043	31.4	32.0	33.9	32.4
2	690	15	10	973	1050	93	0.041	35.1	32.3	32.9	33.4
3	690	30	10	1059	1148	92	0.041	30.6	31.5	31.4	31.2
4	690	40	5	1065	1153	92	0.025	30.9	31.6	31.1	31.2
5	680	40	10	983	1059	93	0.041	33.3	32.0	31.2	32.2
6	680	35	10	988	1068	93	0.046	33.2	32.6	31.7	32.5
7	680	35	35	993	1073	93	0.044	32.6	34.0	35.2	33.9
8	680	35	35	991	1071	93	0.044	33.9	32.7	33.2	33.3
9	680	60	35	980	1056	93	0.048	32.9	33.6	33.8	33.4
10	680	30	15	984	1060	93	0.050	34.8	36.3	36.2	35.8
11	680	30	10	989	1062	93	0.037	31.6	33.6	33.2	32.8
12	680	30	10	986	1060	93	0.045	34.4	34.2	35.9	34.8
13	680	60	25	974	1048	93	0.047	35.9	34.7	34.8	35.1
14	670	30	2	987	1065	93	0.005	24.7	26.3	26.7	25.9
15	670	40	2	980	1053	93	0.003	26.2	21.5	22.7	23.5
16	690	5	10	990	1084	91	0.083	22.7	23.7	25.1	23.8
17	670	10	600	992	1078	92	0.074	23.5	24.5	24.8	24.3
18	660	20	15	973	1042	93	0.048	25.8	20.6	23.0	23.1
19	690	20	25	1056	1137	93	0.044	21.0	21.4	23.7	22.0
20	690	30	5	976	1045	93	0.033	20.5	19.5	21.4	20.5
21	690	30	25	973	1044	93	0.052	25.1	25.8	27.2	26.0
22	690	30	15	974	1047	93	0.046	22.4	24.2	20.8	22.5

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(continued)

Test Number	Tempering Temperature (°C)	Tempering Time (min)	Cooling Rate After Tempering (°C/sec)	YS (MPa)	TS (MPa)	YR (%)	Dissolved C Amount (mass%)	K _{1SSC} (MPa√m)			
								1	2	3	Average Value
23	670	10	15	966	1094	88	0.043	24.3	21.2	21.0	22.2
24	690	30	2	1041	1124	93	0.003	24.1	25.1	23.4	24.2
25	600	30	10	1345	1465	92	0.046	10.1	5.3	4.2	6.5

[Evaluation results]

[YS and TS tests]

[0125] A tensile test was performed in accordance with ASTM E8. Round bar tensile test specimens having a diameter of 6.35 mm and a parallel portion length of 35 mm were prepared from the center parts of the thickness of the steel plates of each test number after the quenching and tempering described above. The axial direction of each of the tensile test specimens was parallel to the rolling direction of the steel plate. A tensile test was performed in the atmosphere at normal temperature (25°C) using each round bar test specimen, and the yield strength YS (MPa) and tensile strength TS (MPa) were obtained. Note that, in the present examples, the stress at the time of 0.65% elongation obtained in the tensile test defined as the YS for each test number. Further, the largest stress during uniform elongation was taken as the TS. A ratio between the YS and the TS was adopted as the yield ratio YR (%).

[Microstructure determination test]

[0126] With respect to the microstructures of the steel plates of each test number, apart from Test Number 23 and 25, because the YS was in a range of 965 to 1069 MPa (140 ksi grade) and the YR was 90% or more, it was determined that the total of the volume ratios of tempered martensite and tempered bainite was 90% or more. In the case of Test Number 23, it is considered that ferrite formed.

[Amount of dissolved C measurement test]

[0127] With respect to the steel plates of each test number, the amount of dissolved C (mass%) was measured and calculated by the measurement method described above. Note that, the TEM used was JEM-2010 manufactured by JEOL Ltd., the acceleration voltage was set to 200 kV, and for the EDS point analysis the irradiation current was 2.56 nA, and measurement was performed for 60 seconds at each point. The observation regions for the TEM observation were 8 μm \times 8 μm , and observation was performed with respect to an arbitrary 10 visual fields. The residual amounts of each element and the concentrations of each element in cementite that were used to calculate the amount of dissolved C were as listed in Table 3.

[Table 3]

[0128]

TABLE 3

Test Number	Residual Amount (mass%)						Concentration In Cementite (mass%)				Dissolved C Amount (mass%)
	Fe	Mn	Cr	Mo	V	Nb	Fe	Mn	Cr	Mo	
1	5.6	0.25	0.27	0.23	0.088	0.010	88.8	2.7	3.9	4.6	0.043
2	5.9	0.25	0.28	0.36	-	-	83.7	3.8	7.5	5.0	0.041
3	5.6	0.22	0.52	0.33	0.075	-	77.6	2.8	14.6	5.0	0.041
4	5.7	0.21	0.47	0.40	-	0.011	78.0	2.9	14.4	4.7	0.025
5	6.1	0.24	0.23	0.36	-	-	86.5	2.9	5.6	5.0	0.041
6	6.0	0.29	0.24	0.68	-	-	84.8	3.0	3.7	8.5	0.046
7	6.5	0.23	0.44	0.44	-	-	81.2	2.5	10.7	5.6	0.044
8	6.7	0.24	0.48	0.43	-	-	77.8	2.6	14.6	5.0	0.044
9	7.1	0.32	0.25	0.46	-	-	83.6	2.8	8.1	5.5	0.048
10	6.9	0.27	0.33	0.44	-	-	84.2	2.9	7.7	5.2	0.050
11	7.2	0.29	0.32	0.47	-	-	80.8	2.9	10.8	5.5	0.037
12	7.4	0.32	0.67	0.42	-	-	72.1	2.5	20.9	4.5	0.045
13	7.8	0.35	0.36	0.46	-	-	85.6	2.6	6.8	5.0	0.047

(continued)

Test Number	Residual Amount (mass%)						Concentration In Cementite (mass%)				Dissolved C Amount (mass%)
	Fe	Mn	Cr	Mo	V	Nb	Fe	Mn	Cr	Mo	
14	6.3	0.25	0.29	0.29	-	-	85.9	2.9	7.2	4.0	0.005
15	6.0	0.26	0.55	0.35	-	-	78.0	2.2	15.0	4.8	0.003
16	5.4	0.20	0.33	0.24	-	-	88.7	3.0	4.5	3.8	0.083
17	5.2	0.17	0.43	0.40	-	-	80.4	3.3	10.0	6.3	0.074
18	6.4	0.25	0.08	0.39	-	-	90.5	2.5	2.0	5.0	0.048
19	6.0	0.23	0.68	0.11	0.058	-	78.0	3.2	17.0	1.8	0.044
20	6.1	0.49	0.15	0.51	-	-	81.3	5.0	6.8	6.9	0.033
21	6.5	0.26	0.30	0.46	-	-	84.0	3.0	7.0	6.0	0.052
22	7.2	0.26	0.28	0.38	-	-	86.0	1.5	8.0	4.5	0.046
23	5.9	0.24	0.26	0.38	-	-	84.5	2.9	7.1	5.5	0.043
24	7.2	0.26	0.28	0.41	0.091	-	86.2	3.2	5.8	4.8	0.003
25	6.1	0.28	0.31	0.42	-	-	85.8	2.8	6.3	5.1	0.046

[DCB test]

[0129] With respect to the steel plates of each test number, a DCB test was conducted in accordance with "Method D" of NACE TM0177-2005, and the SSC resistance was evaluated. Specifically, three of the DCB test specimen illustrated in FIG. 2A were taken from a center portion of the thickness of each steel plate. The DCB test specimens were taken in a manner such that the longitudinal direction of each DCB test specimen was parallel with the rolling direction. A wedge illustrated in FIG. 2B was further prepared from each steel plate. A thickness t of the wedge was 3.10 mm.

[0130] The wedge was driven in between the arms of the DCB test specimen. Thereafter, the DCB test specimen into which the wedge was driven was enclosed in a vessel. A liquid solution obtained by mixing a degassed 5% saline solution and 4g/L of sodium acetate and adjusting to pH 3.5 with hydrochloric acid was poured into the vessel so that a gas portion remained in the vessel. Thereafter, a gaseous mixture consisting of 10% H_2S gas and 90% CO_2 gas was charged at a total pressure of 1 atm inside the autoclave to stir the liquid phase, and the gaseous mixture was saturated in the liquid solution.

[0131] After sealing the vessel that had undergone the above described process, the vessel was held for three weeks at 24°C while stirring the liquid solution and also continuously blowing in the aforementioned gaseous mixture. Thereafter, the DCB test specimens were taken out from inside the vessel.

[0132] A pin was inserted into a hole formed in the tip of the arms of each DCB test specimen that was taken out and a notch portion was opened with a tensile testing machine, and a wedge releasing stress P was measured. In addition, the notch in the DCB test specimen was released in liquid nitrogen, and a crack propagation length " a " with respect to crack propagation that occurred during immersion was measured. The crack propagation length " a " was measured visually using vernier calipers. A fracture toughness value K_{ISSC} (MPa \sqrt{m}) was determined using Formula (6) based on the obtained wedge releasing stress P and the crack propagation length " a ". For each steel, the fracture toughness value K_{ISSC} (MPa \sqrt{m}) of the three DCB test specimens was determined. For each steel, the arithmetic average of the three fracture toughness values was defined as the fracture toughness value K_{ISSC} (MPa \sqrt{m}) of the relevant steel.

$$K_{ISSC} = \frac{Pa \left(2\sqrt{3} + 2.38 \frac{h}{a} \right) \left(\frac{B}{B_n} \right)^{\frac{1}{\sqrt{3}}}}{Bh^{\frac{3}{2}}} \quad (6)$$

In Formula (6), h represents the height (mm) of each arm of the DCB test specimen, B represents the thickness (mm) of the DCB test specimen, and B_n represents the web thickness (mm) of the DCB test specimen. These are defined in "Method D" of NACE TM0177-96.

[0133] For each test number, the obtained fracture toughness values K_{1SSC} are shown in Table 2. If the fracture toughness value K_{1SSC} that was defined as described above was 30.0 MPa \sqrt{m} or more, it was determined that the SSC resistance was good. Note that, the clearance between the arms when the wedge is driven in prior to immersion in the test bath influences the K_{1SSC} value. Accordingly, actual measurement of the clearance between the arms was performed in advance using a micrometer, and it was also confirmed that the clearance was within the range in the API standards.

[Test results]

[0134] The test results are shown in Table 2.

[0135] Referring to Table 1 and Table 2, the chemical compositions of the steel plates of Test Numbers 1 to 13 were appropriate, the YS was in the range of 965 to 1069 MPa (140 ksi grade), and the YR was 90% or more. In addition, the amount of dissolved C was in the range of 0.010 to 0.060 mass%. As a result, the K_{1SSC} value was 30.0 MPa \sqrt{m} or more and excellent SSC resistance was exhibited.

[0136] On the other hand, for the steel plates of Test Numbers 14 and 15, the cooling rate after tempering was too slow. Consequently, the amount of dissolved C was less than 0.010 mass%. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0137] For the steel plate of Test Number 16, the tempering time was too short. Consequently, the amount of dissolved C was more than 0.060 mass%. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0138] For the steel plate of Test Number 17, the cooling rate after tempering was too fast. Consequently, the amount of dissolved C was more than 0.060 mass%. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0139] In the steel plate of Test Number 18, the Cr content was too low. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0140] For the steel plate of Test Number 19, the Mo content was too low. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0141] In the steel plate of Test Number 20, the Mn content was too high. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0142] For the steel plate of Test Number 21, the N content was too high. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0143] For the steel plate of Test Number 22, the Si content was too high. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0144] For the steel plate of Test Number 23, the YR was less than 90%. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited. It is considered that the reason was that ferrite mixed into the microstructure because the cooling rate during quenching was slow.

[0145] For the steel plate of Test Number 24, the cooling rate after tempering was too slow. Consequently, the amount of dissolved C was less than 0.010 mass%. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0146] For the steel plate of Test Number 25, the tempering temperature was too low. Consequently, the YS was more than 1069 MPa. As a result, the fracture toughness value K_{1SSC} was less than 30.0 MPa \sqrt{m} and excellent SSC resistance was not exhibited.

[0147] An embodiment of the present invention has been described above. However, the embodiment described above is merely an example for implementing the present invention. Accordingly, the present invention is not limited to the above embodiment, and the above embodiment can be appropriately modified and performed within a range that does not deviate from the gist of the present invention.

INDUSTRIAL APPLICABILITY

[0148] The steel material according to the present invention is widely applicable to steel materials to be utilized in a sour environment, and preferably can be utilized as a steel material for oil wells that is utilized in an oil well environment, and further preferably can be utilized as oil-well steel pipes, such as casing, tubing and line pipes.

Claims

1. A steel material comprising:

a chemical composition consisting of, in mass%,
 C: more than 0.50 to 0.80%,
 Si: 0.05 to 1.00%,
 Mn: 0.05 to 1.00%,
 P: 0.025% or less,
 S: 0.0100% or less,
 Al: 0.005 to 0.100%,
 Cr: 0.20 to 1.50%,
 Mo: 0.25 to 1.50%,
 Ti: 0.002 to 0.050%,
 B: 0.0001 to 0.0050%,
 N: 0.002 to 0.010%,
 O: 0.0100% or less,
 V: 0 to 0.30%,
 Nb: 0 to 0.100%,
 Ca: 0 to 0.0100%,
 Mg: 0 to 0.0100%,
 Zr: 0 to 0.0100%,
 Co: 0 to 0.50%,
 W: 0 to 0.50%,
 Ni: 0 to 0.50%, and
 Cu: 0 to 0.50%
 with the balance being Fe and impurities,
 an amount of dissolved C within a range of 0.010 to 0.060 mass%,
 a yield strength within a range of 965 to 1069 MPa, and
 a yield ratio of 90% or more.

2. The steel material according to claim 1, wherein the chemical composition contains one or more types of element selected from the group consisting of:

V: 0.01 to 0.30%, and
 Nb: 0.002 to 0.100%.

3. The steel material according to claim 1 or claim 2, wherein the chemical composition contains one or more types of element selected from the group consisting of:

Ca: 0.0001 to 0.0100%,
 Mg: 0.0001 to 0.0100%, and
 Zr: 0.0001 to 0.0100%.

4. The steel material according to any one of claim 1 to claim 3, wherein the chemical composition contains one or more types of element selected from the group consisting of:

Co: 0.02 to 0.50%, and
 W: 0.02 to 0.50%.

5. The steel material according to any one of claim 1 to claim 4, wherein the chemical composition contains one or more types of element selected from the group consisting of:

Ni: 0.02 to 0.50%, and
 Cu: 0.01 to 0.50%.

6. The steel material according to any one of claim 1 to claim 5, wherein the steel material is an oil-well steel pipe.

7. A method for producing a steel material, comprising:

a preparation process of preparing an intermediate steel material containing a chemical composition according to any one of claim 1 to claim 5,

a quenching process of, after the preparation process, cooling the intermediate steel material that is at a temperature in a range of 800 to 1000°C at a cooling rate of 50°C/min; and

a tempering process of holding the intermediate steel material after quenching at a temperature in a range of 660°C to an A_{c1} point for 10 to 90 minutes, and thereafter cooling the intermediate steel material at an average cooling rate in a temperature region from 600°C to 200°C of 5 to 300°C/sec.

8. The method for producing a steel material according to claim 7, wherein the preparation process includes:

a starting material preparation process of preparing a starting material containing a chemical composition according to any one of claim 1 to claim 5, and

a hot working process of subjecting the starting material to hot working to produce an intermediate steel material.

FIG. 1

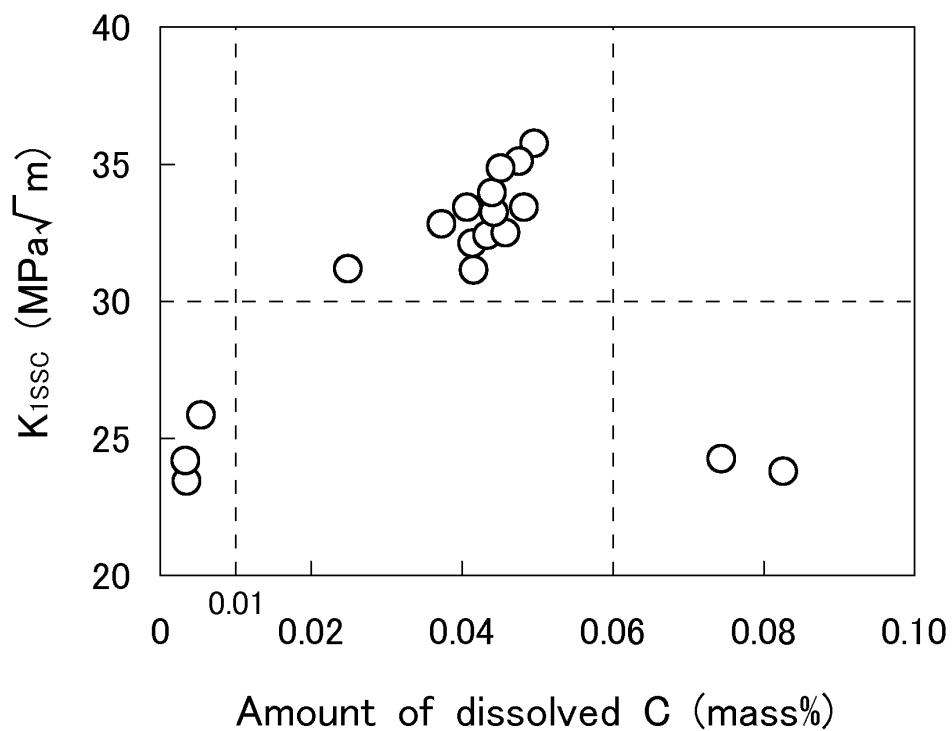


FIG. 2A

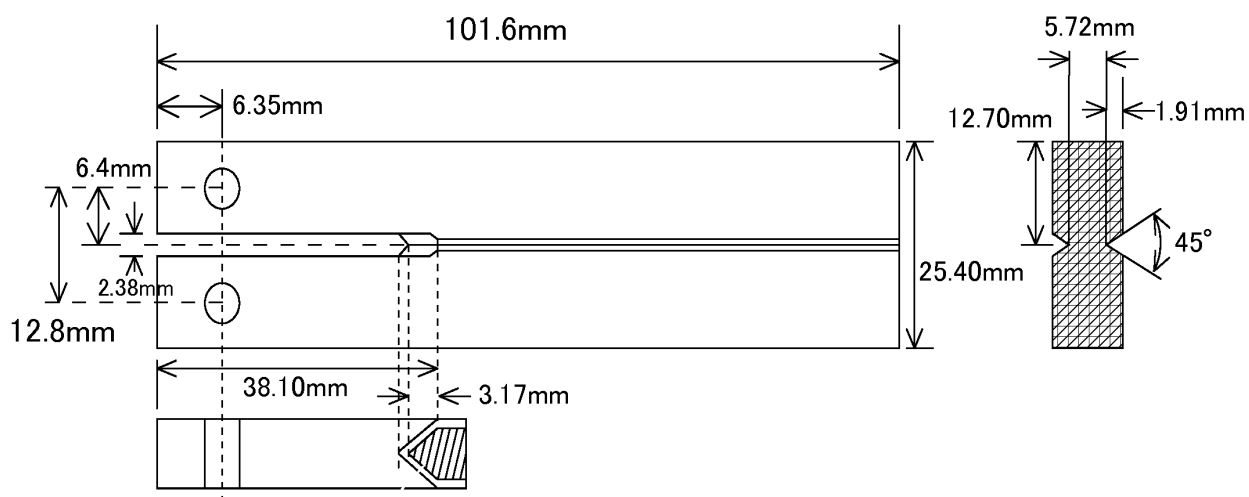
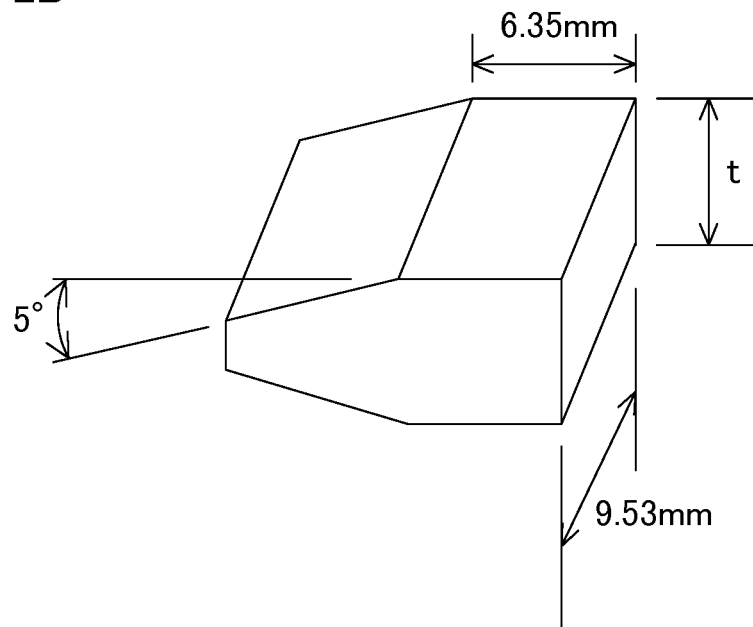


FIG. 2B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/001750

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C38/00 (2006.01) i, C22C38/54 (2006.01) i, C21D8/10 (2006.01) n,
C21D9/08 (2006.01) n

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)

Int.Cl. C22C38/00-38/60, C21D8/10, C21D9/08

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 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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	JP 2012-026030 A (JFE STEEL CORPORATION) 09 February 2012 (Family: none)	1-8
A	JP 08-073987 A (SUMITOMO METAL INDUSTRIES, LTD.) 19 March 1996 (Family: none)	1-8
A	JP 11-050148 A (SUMITOMO METAL INDUSTRIES, LTD.) 23 February 1999 (Family: none)	1-8

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

* Special categories of cited documents:

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search
10.04.2018

Date of mailing of the international search report
24.04.2018

Name and mailing address of the ISA/
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Tokyo 100-8915, Japan

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Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/001750

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 60-187664 A (NIPPON STEEL CORPORATION) 25 September 1985 & GB 2155950 A & DE 3507124 A1 & CA 1239568 A	1-8
A	JP 2000-297344 A (SUMITOMO METAL INDUSTRIES, LTD.) 24 October 2000 (Family: none)	1-8
A	JP 2000-204433 A (KOBE STEEL, LTD.) 25 July 2000 (Family: none)	1-8
A	JP 2007-191776 A (KOBE STEEL, LTD.) 02 August 2007 & US 2010/0224287 A1 & EP 1985721 A1	1-8

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REFERENCES CITED IN THE DESCRIPTION

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