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(54) STAINLESS STEEL PIPE AND MANUFACTURING METHOD THEREOF

(57) Provided are a stainless steel pipe and a method for manufacturing the steel pipe. The stainless steel pipe according to the present invention has a chemical composition containing, by mass%, C: 0.05% or less, Si: 1.0% or less, Mn: 0.10% to 2.0%, P: 0.05% or less, S: less than 0.005%, Cr: 16.0% (not inclusive) to 20.0%, Mo: 0.6% (not inclusive) to 1.4% (not inclusive), Ni: 3.0% to 5.0% (not inclusive), Al: 0.001% to 0.10%, N: 0.010% to 0.100%, O: 0.01% or less, Cu: 0.3% to 3.5%, and a balance of Fe and incidental impurities, in which predetermined relational expressions are satisfied by Cr, Ni, Mo, W, Cu, and C, a microstructure including, in terms of volume fraction, 45% or more of a tempered martensitic phase, 20% to 40% of a ferrite phase, and 5% to 25% of a retained austenite phase, a yield strength of 758 MPa or higher, and an absorbed energy at a temperature of -10°C vE_{-10} of 40 J or more.

Description

Technical Field

[0001] The present invention relates to a stainless steel pipe which can preferably be used for oil wells and gas wells for crude oil and natural gas (hereafter, simply referred to as "oil wells") and geothermal wells and to a method for manufacturing the stainless steel pipe.

Background Art

[0002] Nowadays, deep oil fields, oil fields and gas fields which are in a harsh corrosive environment containing carbon dioxide gas, hydrogen sulfide, and the like, that is, a so-called sour environment, and so forth, to which consideration has never been given, are being actively developed from the viewpoint of the exhaustion of energy resources which is anticipated in the near future. Such oil fields and gas fields are generally found very deep in the ground and in a harsh corrosive environment in which the atmosphere has a high temperature and contains CO_2, Cl^-, and H_2S. Therefore, a steel pipe for oil wells which is used in such an environment is required to have material properties including not only high strength but also excellent corrosion resistance.

[0003] To date, a 13Cr martensitic stainless steel pipe has generally been used as an oil well pipe used for drilling in oil fields and gas fields in an environment containing carbon dioxide gas (CO_2), chloride ions (Cl^-), and the like. However, nowadays, oil wells in a corrosive environment having a notably higher temperature (as high as 200°C) are being developed, and, in such an environment, there has been a case of insufficient corrosion resistance in the case of the 13Cr martensitic stainless steel pipe. Therefore, there is a demand for a steel pipe for oil wells which have excellent corrosion resistance and which can be used even in such an environment.

[0004] Against the background of growing awareness of renewable energy, also regarding geothermal wells for drilling steam for geothermal power generation, geothermal wells deeper than ever before are being developed.

[0005] Against such a background, nowadays, there is a need for using a steel pipe for oil wells in a deep oil-well environment having a temperature of about 250°C and containing CO_2 and Cl^- and in a deep geothermal-well environment having a temperature of about 250°C and containing CO_2 and sulfuric acid.

[0006] In response to such demands, for example, there are techniques according to Patent Literature 1 to Patent Literature 8. Patent Literature 1 describes a high-strength stainless steel pipe for oil wells having improved high corrosion resistance. In the technique according to Patent Literature 1, the high-strength stainless steel pipe for oil wells has a chemical composition containing, by mass%, C: 0.005% to 0.05%, Si: 0.05% to 0.5%, Mn: 0.2% to 1.8%, P: 0.03% or less, S: 0.005% or less, Cr: 15.5% to 18%, Ni: 1.5% to 5%, Mo: 1% to 3.5%, V: 0.02% to 0.2%, N: 0.01% to 0.15%, and O: 0.006% or less, in which Cr, Ni, Mo, Cu, and C satisfy a specified relational expression, and in which Cr, Mo, Si, C, Mn, Ni, Cu, and N satisfy a specified relational expression, and a microstructure including a martensitic phase as a base phase, in which the volume fraction of a ferrite phase is 10% to 60%, and in which, optionally, the volume fraction of an austenite phase is 30% or less. Patent Literature 1 states that, with this, it is possible to stably manufacture a stainless steel pipe for oil wells having sufficient corrosion resistance even in a harsh corrosive environment having a high temperature of up to 230°C and containing CO_2 and Cl^-, high strength represented by a yield strength of more than 654 MPa (95 ksi), and high toughness.

[0007] Patent Literature 2 describes a high-strength stainless steel pipe for oil wells having high toughness and improved corrosion resistance. In the technique according to Patent Literature 2, the steel pipe has a chemical composition containing, by mass%, C: 0.04% or less, Si: 0.50% or less, Mn: 0.20% to 1.80%, P: 0.03% or less, S: 0.005% or less, Cr: 15.5% to 17.5%, Ni: 2.5% to 5.5%, V: 0.20% or less, Mo: 1.5% to 3.5%, W: 0.50% to 3.0%, Al: 0.05% or less, N: 0.15% or less, and O: 0.006% or less, in which Cr, Mo, W, and C satisfy a specified relationship, in which Cr, Mo, W, Si, C, Mn, Cu, Ni, and N satisfy a specified relationship, and in which Mo and W satisfy a specified relationship, and a microstructure including a martensitic phase as a base phase, in which the volume fraction of a ferrite phase is 10% to 50%. Patent Literature 2 states that, with this, it is possible to stably manufacture a high-strength stainless steel pipe for oil wells having high strength represented by a yield strength of more than 654 MPa (95 ksi) and sufficient corrosion resistance even in a high-temperature harsh corrosive environment containing CO_2, Cl^-, and furthermore H_2S.

[0008] Patent Literature 3 describes a high-strength stainless steel pipe having improved sulfide stress cracking resistance and high-temperature carbon dioxide corrosion resistance. In the technique according to Patent Literature 3, by forming a chemical composition containing, by mass%, C: 0.05% or less, Si: 1.0% or less, P: 0.05% or less, S: less than 0.002%, Cr: 16% (not inclusive) to 18%, Mo: 2% (not inclusive) to 3%, Cu: 1% to 3.5%, Ni: 3% to 5% (not inclusive), and Al: 0.001% to 0.1%, in which Mn and N satisfy a specified relationship under the condition in which Mn: 1% or less and N: 0.05% or less, the steel pipe having a microstructure including a martensitic phase as a base phase, in which the volume fraction of a ferrite phase is 10% to 40%, and in which the volume fraction of a retained austenite (γ) phase is 10% or less, is obtained. Patent Literature 3 states that, with this, it is possible to obtain a high-strength stainless steel pipe having high strength represented by a yield strength of 758 MPa (110 ksi) or higher and improved corrosion resistance, that is, sufficient corrosion resistance even in a carbon dioxide gas environment having a high temperature of 200°C and sufficient sulfide stress cracking resistance even when there is a decrease in the temperature of the environmental gas.

[0009] Patent Literature 4 describes a stainless steel pipe for oil wells. In the technique according to Patent Literature 4, the stainless steel pipe for oil wells has a chemical composition containing, by mass%, C: 0.05% or less, Si: 0.5% or less, Mn: 0.01% to 0.5%, P: 0.04% or less, S: 0.01% or less, Cr: 16.0% (not inclusive) to 18.0%, Ni: 4.0% (not inclusive) to 5.6%, Mo: 1.6% to 4.0%, Cu: 1.5% to 3.0%, Al: 0.001% to 0.10%, and N: 0.050% or less, in which Cr, Cu, Ni, and Mo satisfy a specified relationship, and in which (C + N), Mn, Ni, Cu, and (Cr + Mo) satisfy a specified relationship, a microstructure including a martensitic phase and, in terms of volume fraction, 10% to 40% of a ferrite phase, in which ferrite phase grains intersect at a ratio of more than 85% with virtual line segments having a length of 50 μm in the wall thickness direction from the surface of the steel pipe and arranged in a line at intervals of 10 μm in a range of 200 μm, and high strength represented by a 0.2%-proof stress of 758 MPa or higher. Patent Literature 4 states that, with this, it is possible to obtain a stainless steel pipe for oil wells having sufficient corrosion resistance in an environment having a high temperature of 150°C to 250°C and improved sulfide stress cracking resistance at room temperature.

[0010] Patent Literature 5 describes a high-strength stainless steel pipe for oil wells having high toughness and improved corrosion resistance. In the technique according to Patent Literature 5, the steel pipe has a chemical composition containing, by mass%, C: 0.04% or less, Si: 0.50% or less, Mn: 0.20% to 1.80%, P: 0.03% or less, S: 0.005% or less, Cr: 15.5% to 17.5%, Ni: 2.5% to 5.5%, V: 0.20% or less, Mo: 1.5% to 3.5%, W: 0.50% to 3.0%, Al: 0.05% or less, N: 0.15% or less, and O: 0.006% or less, in which Cr, Mo, W, and C satisfy a specified relationship, in which Cr, Mo, W, Si, C, Mn, Cu, Ni, and N satisfy a specified relationship, and in which Mo and W satisfy a specified relationship, and a microstructure, in which, in the largest crystal grain, the distance between two randomly selected points is 200 μm or less. Patent Literature 5 states that this steel pipe has high strength represented by a yield strength of more than 654 MPa (95 ksi), sufficient toughness, and sufficient corrosion resistance even in a high-temperature corrosive environment having a temperature of 170°C or higher and containing CO_2, Cl^-, and furthermore H_2S.

[0011] Patent Literature 6 describes a high-strength seamless martensitic stainless steel pipe for oil wells. In the technique according to Patent Literature 6, the seamless steel pipe has a chemical composition containing, by mass%, C: 0.01% or less, Si: 0.5% or less, Mn: 0.1% to 2.0%, P: 0.03% or less, S: 0.005% or less, Cr: 15.5% (not inclusive) to 17.5%, Ni: 2.5% to 5.5%, Mo: 1.8% to 3.5%, Cu: 0.3% to 3.5%, V: 0.20% or less, Al: 0.05% or less, and N: 0.06% or less and, preferably, a microstructure including, in terms of volume fraction, 15% or more of a ferrite phase, 25% or less of a retained austenite phase, and a balance of a tempered martensitic phase. Here, Patent Literature 6 states that the chemical composition may further contain W: 0.25% to 2.0% and/or Nb: 0.20% or less in addition to the constituents described above. Patent Literature 6 states that, with this, it is possible to stably manufacture a high-strength seamless martensitic stainless steel pipe for oil wells having satisfactory tensile properties, that is, high strength represented by a yield strength of 655 MPa or higher and 862 MPa or lower and a yield ratio of 0.90 or more, and sufficient corrosion resistance (carbon dioxide corrosion resistance and sulfide stress cracking resistance) even in a high-temperature harsh corrosive environment having a temperature of 170°C or higher and containing not only CO_2, Cl^-, and the like but also H_2S.

[0012] Patent Literature 7 describes a stainless steel pipe for oil wells. In the technique according to Patent Literature 7, the stainless steel pipe has a chemical composition containing, by mass%, C: 0.05% or less, Si: 1.0% or less, Mn: 0.01% to 1.0%, P: 0.05% or less, S: less than 0.002%, Cr: 16% to 18%, Mo: 1.8% to 3%, Cu: 1.0% to 3.5%, Ni: 3.0% to 5.5%, Co: 0.01% to 1.0%, Al: 0.001% to 0.1%, O: 0.05% or less, and N: 0.05% or less, in which Cr, Ni, Mo, and Cu satisfy a specified relationship, and, preferably, a microstructure including, in terms of volume fraction, 10% to 60% (not inclusive) of a ferrite phase, 10% or less of a retained austenite phase, and 40% or more of a martensitic phase. Patent Literature 7 states that, with this, it is possible to stably obtain a stainless steel pipe for oil wells having high strength represented by a yield strength of 758 MPa or higher and sufficient high-temperature corrosion resistance.

[0013] Patent Literature 8 describes a stainless steel material. In the technique according to Patent Literature 8, the stainless steel material has a chemical composition containing, by mass%, C: 0.040% or less, Si: 0.05% to 1.0%, Mn: 0.010% to 0.30%, Cr: 18.0% (not inclusive) to 21.0%, Cu: 1.5% to 4.0%, Ni: 3.0% to 6.0%, sol.Al: 0.001% to 0.100%, Mo: 0% to 0.60%, W: 0% to 2.0%, Co: 0% to 0.30%, Ti: 0% to 0.10%, V: 0% to 0.15%, Zr: 0% to 0.10%, Nb: 0% to 0.10%, Ca: 0% to 0.010%, Mg: 0% to 0.010%, REM: 0% to 0.05%, B: 0% to 0.005%, and a balance of Fe and impurities, in which, regarding the impurities described above, that is, regarding the contents of P, S, O, and N, P: 0.050% or less, S: less than 0.0020%, O: 0.020% or less, and N: 0.020% or less, in which C, N, Si, Mn, Ni, Cr, Cu, and Mo satisfy a specified relationship, and a microstructure including, in terms of volume fraction, 20.0% to 60.0% of a ferrite phase, 1.0% to 10.0% of an austenite phase, and a balance of a martensitic phase. Patent Literature 8 states that, with this, it is possible to obtain a stainless steel material and a stainless steel pipe having high strength as heat-treated and satisfactory strong acid resistance and carbon dioxide corrosion resistance in a high-temperature environment.

Citation List

Patent Literature

[0014]

PTL 1: Japanese Unexamined Patent Application Publication No. 2005-336595
PTL 2: Japanese Unexamined Patent Application Publication No. 2008-81793
PTL 3: International Publication No. 2010/050519
PTL 4: International Publication No. 2010/134498
PTL 5: Japanese Unexamined Patent Application Publication No. 2010-209402
PTL 6: Japanese Unexamined Patent Application Publication No. 2012-149317
PTL 7: International Publication No. 2013/146046
PTL 8: Japanese Unexamined Patent Application Publication No. 2019-73789

Summary of Invention

Technical Problem

[0015] However, in the harsh environments described above (that is, a deep oil-well environment having a temperature of about 250°C and containing CO_2 and Cl^- and a deep geothermal-well environment having a temperature of about 250°C and containing CO_2 and sulfuric acid), it is not possible to achieve the desired corrosion resistance (carbon dioxide corrosion resistance and sulfide stress cracking resistance) with the techniques according to Patent Literature 1 to Patent Literature 8. In addition, in consideration of a case of usage in cold regions, there is also a demand for satisfactory high strength and low-temperature toughness.

[0016] An object of the present invention is to solve the related art problems described above and to thereby provide a stainless steel pipe having high strength represented by a yield strength of 758 MPa or higher, excellent low-temperature toughness, and excellent corrosion resistance and a method for manufacturing the steel pipe.

[0017] Here, the expression "excellent corrosion resistance" in the present invention denotes a case of excellent carbon dioxide corrosion resistance and sulfide stress cracking resistance.

[0018] The expression "excellent carbon dioxide corrosion resistance" in the present invention denotes a case where, when a corrosion test is performed by immersing a test specimen in a testing solution, that is, a 25 mass% NaCl aqueous solution (having a temperature of 250°C in a CO_2 gas environment under a pressure of 30 atm), which is contained in an autoclave, for an immersion time of 336 hours, the corrosion rate is 0.125 mm/y or lower and no pitting corrosion is found in the test specimen after the corrosion test, and, when a corrosion test is performed by immersing a test specimen in a testing solution, that is, a 0.01 mol/L H_2SO_4 aqueous solution (having a temperature of 250°C in a CO_2 gas environment under a pressure of 30 atm), for an immersion time of 336 hours, the corrosion rate is 0.125 mm/y or lower and no pitting corrosion is found in the test specimen after the corrosion test.

[0019] In addition, the expression "excellent sulfide stress cracking resistance" in the present invention denotes a case of low sulfide stress cracking sensitivity in a sulfide stress cracking test (SSC test), in which the cracking sensitivity of a test specimen is evaluated under stress in a corrosive environment containing H_2S. Specifically, when the test is performed by immersing the test specimen in an aqueous solution, which has been prepared by adding acetic acid and sodium acetate to a testing solution, that is, a 5 mass% NaCl aqueous solution (having a temperature of 25°C in an atmosphere containing CO_2 gas corresponding to a pressure of 0.95 atm and H_2S corresponding to a pressure of 0.05 atm) so that the pH is 3.5, under a loading stress equal to 90% of its yield stress for an immersion time of 720 hours, no cracking is found in the test specimen after the test has been performed.

[0020] In addition, the expression "excellent low-temperature toughness (high toughness)" in the present invention denotes a case of an absorbed energy vE_{-10} of 40 J or more when a Charpy impact test is performed in accordance with the prescription in JIS Z 2242 (2018) at a testing temperature of -10°C. It is preferable that the absorbed energy vE_{-10} described above be 250 J or less.

[0021] Here, it is possible to perform the tests described above by using the methods described in EXAMPLES below.

Solution to Problem

[0022] To achieve the object described above, the present inventors diligently conducted investigations regarding factors having effects on corrosion resistance (carbon dioxide corrosion resistance and sulfide stress cracking resistance) by using seamless steel pipes having chemical compositions of stainless steel, a yield strength of 758 MPa or more, and high toughness as stainless steel pipes.

[0023] To achieve excellent carbon dioxide corrosion resistance in the case of a high-strength material having a yield strength of 758 MPa or more and high toughness, it is necessary that a protective dense corrosion product be formed on the surface of a steel material. It was found that, for such a purpose, it is necessary that the contents of Cr, Mo, W, Cu, Ni, and C be adjusted to satisfy relational expression (1) in the chemical composition of the stainless steel material.

$$Cr + 0.65 \times Ni + 0.6 \times (Mo + 0.5 \times W) + 0.55 \times Cu - 20 \times C \geq 21.7 \quad \cdots (1)$$

[0024] In addition, to achieve excellent sulfide stress cracking resistance in addition to the property described above, inhibiting pitting corrosion, which becomes the starting point at which cracking occurs, is effective. Therefore, it is necessary that the contents of C, Cr, and Mo be adjusted to satisfy relational expression (2) in the chemical composition of the stainless steel material.

$$Cr + 3.3 \times (Mo + 0.5 \times W) - 17 \times C \geq 21.0 \quad \cdots (2)$$

[0025] Here, in both relational expressions, each of Cr, Mo, W, Cu, Ni, and C denotes the content (mass%) of the corresponding element and is assigned a value of zero when the corresponding element is not added.

[0026] The present invention has been completed on the basis of the knowledge described above and additional investigations. That is, the subjective matter of the present invention is as follows.

[1] A stainless steel pipe having

a chemical composition containing, by mass%,

C: 0.05% or less,
Si: 1.0% or less,
Mn: 0.10% to 2.0%,
P: 0.05% or less,
S: less than 0.005%,
Cr: 16.0% (not inclusive) to 20.0%,
Mo: 0.6% (not inclusive) to 1.4% (not inclusive),
Ni: 3.0% to 5.0% (not inclusive),
Al: 0.001% to 0.10%,
N: 0.010% to 0.100%,
O: 0.01% or less,
Cu: 0.3% to 3.5%, and
a balance of Fe and incidental impurities, in which relational expression (1) and relational expression (2) are satisfied,

a microstructure including, in terms of volume fraction, 45% or more of a tempered martensitic phase, 20% to 40% of a ferrite phase, and 5% to 25% of a retained austenite phase,
a yield strength of 758 MPa or higher, and
an absorbed energy at a temperature of -10°C vE_{-10} of 40 J or more.

$$Cr + 0.65 \times Ni + 0.6 \times (Mo + 0.5 \times W) + 0.55 \times Cu - 20 \times C \geq 21.7 \quad \cdots (1)$$

$$Cr + 3.3 \times (Mo + 0.5 \times W) - 17 \times C \geq 21.0 \quad \cdots (2)$$

Here, in both relational expressions, each of Cr, Ni, Mo, W, Cu, and C denotes the content (mass%) of the corresponding element and is assigned a value of zero when the corresponding element is not added.

[2] The stainless steel pipe according to item [1], in which the chemical composition further contains, by mass%, one, two, or more selected from group A to group E below.

group A: one, two, or more selected from Ti: 0.3% or less, Nb: 0.5% or less, V: 0.5% or less, and Ta: 0.5% or less
group B: one, two, or all selected from B: 0.0050% or less, Ca: 0.0050% or less, and REM: 0.010% or less
group C: one or both selected from Mg: 0.010% or less and Zr: 0.2% or less
group D: one or both selected from Sn: 0.20% or less and Sb: 0.20% or less, and
group E: one or both selected from Co: 1.0% or less and W: 3.0% or less

[3] A method for manufacturing the stainless steel pipe according to item [1] or [2], the method including

heating a steel pipe material to a heating temperature of 1100°C to 1350°C and performing hot working on the heated material to obtain a seamless steel pipe having a predetermined shape,
performing a quenching treatment of reheating the seamless steel pipe after the hot working to a temperature of 850°C to 1150°C and cooling the heated steel pipe to a cooling stop temperature of 0°C (not inclusive) to 50°C in terms of surface temperature at a cooling rate equal to or higher than a cooling rate corresponding to natural cooling, and
performing a tempering treatment of heating the quenched steel pipe to a tempering temperature of 500°C to 650°C.

Advantageous Effects of Invention

[0027] According to the present invention, it is possible to provide a stainless steel pipe having high strength represented by a yield strength (YS) of 758 MPa or higher, satisfactory low-temperature toughness at a temperature of - 10°C, and excellent corrosion resistance even in a harsh corrosive environment having a high temperature of 250°C or higher and containing CO_2 and Cl^- and a method for manufacturing the steel pipe. In addition, the stainless steel pipe according to the present invention can preferably be used as a seamless stainless steel pipe for oil wells. Description of Embodiments

[0028] Hereafter, the present invention will be described in detail. Here, the present invention is not limited to the embodiments below.

[0029] First, the chemical composition of the stainless steel pipe according to the present invention and the reasons for the limitations on the chemical composition will be described. Hereafter, "mass%" is simply referred to as "%", unless otherwise noted.

C: 0.05% or less

[0030] C is an important element which increases the strength of martensitic stainless steel. In the present invention, to achieve the desired high strength, it is preferable that the C content be 0.003% or more. On the other hand, in the case where the C content is more than 0.05%, there is a deterioration in sulfide stress cracking resistance. Therefore, the C content is set to be 0.05% or less. It is preferable that the C content be 0.005% or more. It is preferable that the C content be 0.040% or less or more preferably 0.035% or less.

Si: 1.0% or less

[0031] Si is an element which functions as a deoxidizing agent, and, to obtain such an effect, it is preferable that the Si content be 0.005% or more. On the other hand, in the case where the Si content is more than 1.0%, there is a deterioration in the hot workability of an intermediate product (billet or the like) in the intermediate stage of a process for manufacturing a product. Therefore, the Si content is set to be 1.0% or less. It is preferable that the Si content be 0.1% or more or more preferably 0.25% or more. It is preferable that the Si content be 0.6% or less.

Mn: 0.10% to 2.0%

[0032] Mn is an element which increases the strength of martensitic stainless steel, and, to achieve the strength intended by the present invention, it is necessary that the Mn content be 0.10% or more. On the other hand, in the case where the Mn content is more than 2.0%, there is a deterioration in low-temperature toughness. Therefore, the Mn content is set to be 0.10% to 2.0%. It is preferable that the Mn content be 0.15% or more or more preferably 0.20% or more. It is preferable that the Mn content be 0.5% or less.

P: 0.05% or less

[0033] Since P is an element which causes a deterioration in corrosion resistance such as carbon dioxide corrosion resistance or sulfide stress cracking resistance, it is preferable the P content be as small as possible in the present invention. It is acceptable that the P content be 0.05% or less. Therefore, the P content is set to be 0.05% or less. It is preferable that the P content be 0.02% or less. Here, there is no particular limitation on the lower limit of the P content. However, since an excessive decrease in the P content causes an increase in manufacturing costs, it is preferable that the P content be 0.005% or more.

S: less than 0.005%

[0034] Since S is an element which disturbs the operation stability of a hot pipe making process by causing a significant deterioration in hot workability, it is preferable that the S content be as small as possible in the present invention. In the case where the S content is less than 0.005%, it is possible to manufacture a pipe by using the process described below. Therefore, the S content is set to be less than 0.005%. It is preferable that the S content be 0.0015% or less or more preferably 0.0010% or less. Here, there is no particular limitation on the lower limit of the S content. However, since an excessive decrease in the S content causes an increase in manufacturing costs, it is preferable that the S content be 0.0003% or more.

Cr: 16.0% (not inclusive) to 20.0%

[0035] Cr is an element which contributes to improving corrosion resistance by forming a protective film on the surface of a steel pipe. In the case where the Cr content is 16.0% or less, it is not possible to achieve the corrosion resistance intended by the present invention. Therefore, it is necessary that the Cr content be more than 16.0%. On the other hand, in the case where the Cr content is more than 20.0%, since there is an excessive increase in the fraction of a ferrite phase, it is not possible to achieve the strength intended by the present invention. Therefore, the Cr content is set to be 16.0% (not inclusive) to 20.0%. It is preferable that the Cr content be 17.0% or more. It is preferable that the Cr content be 19.0% or less.

Mo: 0.6% (not inclusive) to 1.4% (not inclusive)

[0036] Mo is an element which increases resistance to pitting corrosion caused by Cl^- or a low pH by stabilizing a protective film on the surface of a steel pipe, thereby improving sulfide stress cracking resistance. To obtain such an effect, it is necessary that the Mo content be more than 0.6%. On the other hand, in the case where the Mo content is 1.4% or more when the Cr content is more than 16.0%, since there is an increase in the fraction of a ferrite phase, there is a deterioration in low-temperature toughness. Therefore, the Mo content is set to be 0.6% (not inclusive) to 1.4% (not inclusive). It is preferable that the Mo content be 0.7% or more. It is preferable that the Mo content be 1.2% or less or more preferably 1.1% or less.

Ni: 3.0% to 5.0% (not inclusive)

[0037] Ni is an element which contributes to improving corrosion resistance by strengthening a protective film on the surface of a steel pipe. Such an effect becomes noticeable in the case where the Ni content is 3.0% or more. On the other hand, in the case where the Ni content is 5.0% or more, since there is a deterioration in the stability of a martensitic phase, there is a deterioration in strength. Therefore, the Ni content is set to be 3.0% to 5.0% (not inclusive). It is preferable that the Ni content be 3.5% or more. It is preferable that the Ni content be 4.5% or less.

Al: 0.001% to 0.10%

[0038] Al is an element which functions as a deoxidizing agent. To obtain such an effect, it is necessary that the Al content be 0.001% or more. On the other hand, in the case where the Al content is more than 0.10%, since there is a deterioration in cleanliness due to an increase in the amounts of oxides, there is a deterioration in low-temperature toughness. Therefore, the Al content is set to be 0.001% to 0.10%. It is preferable that the Al content be 0.01% or more or more preferably 0.02% or more. It is preferable that the Al content be 0.07% or less or more preferably 0.040% or less.

N: 0.010% to 0.100%

[0039] N is an element which improves pitting corrosion resistance. To obtain such an effect, the N content is set to be 0.010% or more. On the other hand, in the case where the N content is more than 0.100%, since nitrides are formed, there is a deterioration in low-temperature toughness. Therefore, the N content is set to be 0.010% to 0.100%. It is preferable that the N content be 0.02% or more. It is preferable that the N content be 0.06% or less.

O: 0.01% or less

[0040] Since O (oxygen) exists in the form of oxides in steel, O has negative effects on various properties. Therefore, in the present invention, it is preferable that the O content be as small as possible. In particular, in the case where the O content is more than 0.01%, there is a deterioration in hot workability, corrosion resistance, and low-temperature toughness. Therefore, the O content is set to be 0.01% or less. It is preferable that the O content be 0.0050% or less. It is preferable that the O content be 0.0010% or more or more preferably 0.0025% or more.

Cu: 0.3% to 3.5%

[0041] Cu is effective for inhibiting hydrogen entry into steel by strengthening a protective film on the surface of a steel pipe, thereby improving sulfide stress cracking resistance. To obtain such an effect, it is necessary that the Cu content be 0.3% or more. On the other hand, in the case where the Cu content is more than 3.5%, since CuS is precipitated at grain boundaries, there is a deterioration in hot workability. Therefore, the Cu content is set to be 0.3% to 3.5%. It is preferable that the Cu content be 0.5% or more, more preferably 1.0% or more, or even more preferably 1.5% or more. It is preferable that the Cu content be 3.0% or less.

[0042] In addition, in the present invention, the contents of Cr, Ni, Mo, W, Cu, and C are controlled to be within the ranges described above and adjusted so that relational expression (1) is satisfied.

$$\mathrm{Cr} + 0.65 \times \mathrm{Ni} + 0.6 \times (\mathrm{Mo} + 0.5 \times \mathrm{W}) + 0.55 \times \mathrm{Cu} - 20 \times \mathrm{C} \geq 21.7 \quad \cdots (1)$$

[0043] Here, in relational expression (1), each of Cr, Ni, Mo, W, Cu, and C denotes the content (mass%) of the corresponding element and is assigned a value of zero when the corresponding element is not added.

[0044] In the case where a value of the left-hand side of relational expression (1), that is, Cr + 0.65 × Ni + 0.6 × (Mo + 0.5 × W) + 0.55 × Cu - 20 × C, is less than 21.7, since a corrosion product formed on the surface of the steel pipe is not sufficiently strengthened, it is not possible to achieve the corrosion resistance intended by the present invention. Therefore, in the present invention, the contents of Cr, Ni, Mo, W, Cu, and C are adjusted so that the left-hand side value of relational expression (1) is 21.7 or more. Here, as described above, in the case where one of the elements involved in relational expression (1) is not added, the left-hand side value of relational expression (1) is calculated with the corresponding atomic symbol being assigned a value of 0 (zero). It is preferable that the left-hand side value of relational expression (1) be 22.0 or more.

[0045] Here, there is no particular limitation on the upper limit of the left-hand side value of relational expression (1). From the viewpoint of inhibiting an increase in cost and of inhibiting a deterioration in strength caused by an excessive amounts of alloy elements added, it is preferable that the left-hand side value of relational expression (1) be 26.0 or less or more preferably 24.0 or less.

[0046] Moreover, in the present invention, the contents of Cr, Mo, W, and C are controlled to be within the ranges described above and adjusted so that relational expression (2) is satisfied.

$$\mathrm{Cr} + 3.3 \times (\mathrm{Mo} + 0.5 \times \mathrm{W}) - 17 \times \mathrm{C} \geq 21.0 \quad \cdots (2)$$

[0047] Here, in relational expression (2), each of Cr, Mo, W, and C denotes the content (mass%) of the corresponding element and is assigned a value of zero when the corresponding element is not added.

[0048] In the case where a value of the left-hand side of relational expression (2), that is, Cr + 3.3 × (Mo + 0.5 × W) - 17 × C, is less than 21.0, since a passivation film existing on the surface of the steel pipe is not sufficiently strengthened, pitting corrosion, which becomes the starting point at which cracking occurs, occurs, which results in the sulfide stress cracking resistance intended by the present invention not being achieved. Therefore, in the present invention, the contents of Cr, Mo, W, and C are adjusted so that the left-hand side value of relational expression (2) is 21.0 or more. It is preferable that the left-hand side value of relational expression (2) be 21.5 or more.

[0049] Here, there is no particular limitation on the upper limit of the left-hand side value of relational expression (2). From the viewpoint of such an effect becoming saturated, it is preferable that the left-hand side value of relational expression (2) be 28.0 or less or more preferably 25.0 or less.

[0050] In the present invention, the remainder of the chemical composition which differs from the constituents described above is Fe and incidental impurities.

[0051] In the present invention, the constituents described above are the basic constituents. As a result of the stainless steel pipe according to the present invention containing such basic constituents and satisfying relational expression (1) and relational expression (2) described above, it is possible to achieve the desired properties. In the present invention, the selective elements described below may be added as needed in addition to the basic constituents described above. Here, since the elements described below, that is, Ti, Nb, V, Ta, B, Ca, REM, Mg, Zr, Sn, Sb, Co, and W, may be added as needed, the content of each of these constituents may be 0%.

One, two, or more selected from Ti: 0.3% or less, Nb: 0.5% or less, V: 0.5% or less, and Ta: 0.5% or less

[0052] Ti, Nb, V, and Ta are elements which all increase strength, and one, two, or more of Ti, Nb, V, and Ta may be selectively added as needed. In addition to the effect described above, Ti, Nb, V, and Ta are effective for improving sulfide stress cracking resistance by trapping hydrogen when hydrogen generated by corrosion enters steel. In particular, since Ta is an element which has the same effect as Nb, some of Nb may be replaced with Ta. To obtain such effects, it is preferable that each of Ti: 0.01% or more, Nb: 0.01% or more, V: 0.01% or more, and Ta: 0.01% or more be added. On the other hand, in the case where one of Ti: more than 0.3%, Nb: more than 0.5%, V: more than 0.5%, and Ta: more than 0.5% is added, there is a deterioration in low-temperature toughness. Therefore, in the case where Ti, Nb, V, and Ta are added, it is preferable that each of Ti: 0.3% or less, Nb: 0.5% or less, V: 0.5% or less, and Ta: 0.5% or less be added.

[0053] It is more preferable that each of Ti: 0.02% or more, Nb: 0.02% or more, V: 0.03% or more, and Ta: 0.03% or more be added. It is more preferable that each of Ti: 0.2% or less, Nb: 0.3% or less, V: 0.2% or less, and Ta: 0.2% or less be added.

One, two, or all selected from B: 0.0050% or less, Ca: 0.0050% or less, and REM: 0.010% or less

B: 0.0050% or less

[0054] Since B is an element which improves hot workability by improving grain-boundary strength, B may be added as needed. To obtain such an effect, it is preferable that the B content be 0.0010% or more. On the other hand, in the case where the B content is more than 0.0050%, since nitrides are formed at grain boundaries, there is a deterioration in sulfide stress cracking resistance. Therefore, in the case where B is added, it is preferable that the B content be 0.0050% or less. It is more preferable that the B content be 0.0020% or more. It is more preferable that the B content be 0.0040% or less.

Ca: 0.0050% or less and REM: 0.010% or less

[0055] Since Ca and REM (rare earth metals) are elements both of which contribute to improving sulfide stress cracking resistance through the morphological control of sulfides, one or both of Ca and REM may be added as needed. To obtain such an effect, it is preferable that each of Ca: 0.0001% or more and REM: 0.001% or more be added. On the other hand, in the case where one of Ca: more than 0.0050% and REM: more than 0.010% is added, since such an effect becomes saturated, it is not possible to expect an increase in effect commensurate with an increase in content. Therefore, in the case where Ca and REM are added, it is preferable that each of Ca: 0.0050% or less and REM: 0.010% or less be added. It is more preferable that each of Ca: 0.0005% or more and REM: 0.005% or more be added. It is more preferable that each of Ca: 0.0040% or less and REM: 0.008% or less be added.

One or both selected from Mg: 0.010% or less and Zr: 0.2% or less

Mg: 0.010% or less and Zr: 0.2% or less

[0056] Since Mg and Zr are elements both of which improve corrosion resistance through the morphological control of inclusions, one or both of Mg and Zr may be selectively added as needed. To obtain such an effect, it is preferable that each of Mg: 0.002% or more and Zr: 0.01% or more be added. On the other hand, in the case where one of Mg: more than 0.010% and Zr: more than 0.2% is added, since such an effect becomes saturated, it is not possible to expect an increase in effect commensurate with an increase in content. Therefore, in the case where Mg and Zr are added, it is preferable that each of Mg: 0.010% or less and Zr: 0.2% or less be added. It is more preferable that each of Mg: 0.003% or more and Zr: 0.02% or more be added. It is more preferable that each of Mg: 0.005% or less and Zr: 0.1% or less be added.

One or both selected from Sn: 0.20% or less and Sb: 0.20% or less

Sn: 0.20% or less and Sb: 0.20% or less

[0057] Since Sn and Sb are elements both of which improve corrosion resistance by inhibiting active dissolution and by promoting passivation, one or both of Sn and Sb may be selectively added as needed. To obtain such an effect, it is preferable that each of Sn: 0.01% or more and Sb: 0.01% or more be added. On the other hand, in the case where one of Sn: more than 0.20% and Sb: more than 0.20% is added, since such an effect becomes saturated, it is not possible to expect an increase in effect commensurate with an increase in content. Therefore, in the case where Sn and Sb are added, it is preferable that each of Sn: 0.20% or less and Sb: 0.20% or less be added. It is more preferable that each of Sn: 0.02% or more and Sb: 0.02% or more be added. It is more preferable that each of Sn: 0.15% or less and Sb: 0.15% or less be added.

One or both selected from Co: 1.0% or less and W: 3.0% or less

Co: 1.0% or less

[0058] Since Co is an element which decreases the fraction of a retained austenite phase by increasing the Ms temperature, thereby improving strength and sulfide stress cracking resistance, Co may be selectively added. To obtain such effects, it is preferable that the Co content be 0.01% or more. On the other hand, in the case where the Co content is more than 1.0%, such effects become saturated. Therefore, in the case where Co is added, the Co content is set to be 1.0% or less. It is preferable that the Co content be 0.01% or more, more preferably 0.05% or more, or even more preferably 0.07% or more. It is preferable that the Co content be 0.15% or less or more preferably 0.09% or less.

W: 3.0% or less

[0059] Since W is an element which contributes to increasing the strength of steel and which can improve sulfide stress cracking resistance by stabilizing a protective film on the surface of a steel pipe, W may be added as needed. By adding W in combination with Mo, there is a particularly marked improvement in sulfide stress cracking resistance. To obtain such effects, it is preferable that the W content be 0.1% or more. On the other hand, in the case where the W content is more than 3.0%, since intermetallic compounds are formed, there is a deterioration in low-temperature toughness. Therefore, in the case where W is added, the W content is set to be 3.0% or less. It is preferable that the W content be 0.1% or more, more preferably 0.5% or more, or even more preferably 0.8% or more. It is preferable that the W content be 2.0% or less.

[0060] Hereafter, the microstructure of the stainless steel pipe according to the present invention and the reasons for the limitations on the microstructure will be described.

[0061] The stainless steel pipe according to the present invention has the chemical composition described above and a microstructure including, in terms of volume fraction, 45% or more of a tempered martensitic phase, 20% to 40% of a ferrite phase, and 5% to 25% of a retained austenite phase.

Tempered martensitic phase: 45% or more in terms of volume fraction

[0062] The microstructure of the stainless steel pipe according to the present invention is controlled to include a tempered martensitic phase as a main phase to achieve the desired strength. Here, the expression "main phase" denotes a phase constituting 45% or more in terms of volume fraction with respect to the entire steel pipe. It is preferable that the volume fraction of a tempered martensitic phase be 50% or more or more preferably 55% or more. It is preferable that the volume fraction of a tempered martensitic phase be 75% or less or more preferably 70% or less.

Ferrite phase: 20% to 40% in terms of volume fraction

[0063] In the present invention, a ferrite phase is precipitated as a second phase at least in an amount of 20% or more in terms of volume fraction with respect to the entire steel pipe. Consequently, since strain applied when hot rolling is performed is concentrated in a soft ferrite phase, it is possible to prevent flaws from occurring. In addition, by precipitating a ferrite phase in an amount of 20% or more in terms of volume fraction, since a ferrite phase functions as crack propagation resistance, it is possible to inhibit the propagation of sulfide stress cracking, which results in the corrosion resistance intended by the present invention being achieved. On the other hand, in the case where a soft ferrite phase is precipitated in a large amount of more than 40% in terms of volume fraction, there may be a case where it is not possible to achieve the desired strength. Therefore, the volume fraction of a ferrite phase is set to be 20% to 40%. It is preferable that the volume fraction of a ferrite phase be 23% or more or more preferably 26% or more. It is preferable that the volume fraction of a ferrite phase be 37% or less or more preferably 34% or less.

Retained austenite phase: 5% to 25% in terms of volume fraction

[0064] In the present invention, an austenite phase (retained austenite phase) is precipitated as a second phase in addition to a ferrite phase. As a result of the existence of a retained austenite phase, which is excellent in terms of ductility and low-temperature toughness, there is an improvement in the ductility and low-temperature toughness of the entire steel. To obtain such effects of improving ductility and low-temperature toughness while achieving the desired strength, a retained austenite phase is precipitated in an amount of 5% or more in terms of volume fraction with respect to the entire steel pipe. On the other hand, in the case where a retained austenite phase is precipitated in a large amount of more than 25% in terms of volume fraction, since an austenite phase has lower strength than a martensitic phase and a ferrite phase, it is not possible to achieve the desired strength. Therefore, the volume fraction of a retained austenite phase is set to be 5% or more and 25% or less. It is preferable that the volume fraction of a retained austenite phase be more than 10%. It is preferable that the volume fraction of a retained austenite phase be 20% or less or more preferably 15% or less.

[0065] It is possible to measure the above-described phases according to the present invention by using the following method.

[0066] First, a test specimen for microstructure observation is taken from the central portion in the wall thickness direction of a cross section perpendicular to the pipe axis direction, the test specimen is etched in Vilella's reagent (reagent obtained by mixing picric acid, hydrochloric acid, and ethanol in the proportion of 2 g of picric acid and 10 ml of hydrochloric acid to 100 ml of ethanol), the photograph of a microstructure is taken by using a scanning electron microscope (at a magnification of 1000 times), the fraction (area fraction (%)) of a ferrite phase is calculated by using an image analyzer, and the obtained area fraction is regarded as the volume fraction (%).

[0067] Subsequently, a test specimen for X-ray diffraction is taken so that a cross section perpendicular to the pipe axis direction (C-cross section) is a measurement surface, the measurement surface is ground and polished, and the amount of retained austenite (y) is measured by performing X-ray diffraction analysis. The amount of retained austenite is calculated by using the following equation after the integral X-ray diffraction intensities of the (220) plane of γ and the (211) plane of α (ferrite) have been measured.

$$\gamma\ (\text{volume fraction}) = 100/(1 + (I\alpha R\gamma/I\gamma R\alpha))$$

Here, $I\alpha$: integral intensity of α, $R\alpha$: theoretically calculated value of α on the basis of crystallography, Iy: integral intensity of γ, and $R\gamma$: theoretically calculated value of y on the basis of crystallography.

[0068] In addition, the fraction (volume fraction) of a tempered martensitic phase is defined as that of the remainder which differs from a ferrite phase and a retained y phase.

[0069] Incidentally, it is possible to adjust the above-described microstructure according to the present invention by performing a heat treatment (quenching treatment and tempering treatment) under the specified conditions described below.

[0070] As described above, in the present invention, by forming a specified chemical composition, in which the contents of the constituents are within the ranges described above, and in which relational expression (1) and relational expression (2) are satisfied, and a microstructure including, in terms of volume fraction, 45% or more of a tempered martensitic phase, 20% to 40% of a ferrite phase, and 5% to 25% of a retained austenite phase, it is possible to achieve the above-described properties intended by the present invention.

[0071] Hereafter, one of the preferable embodiments of the method for manufacturing a stainless steel pipe according to the present invention will be described. Here, as an example of a method for manufacturing a stainless steel pipe, a method for manufacturing a high-strength seamless stainless steel pipe for oil wells will be described.

[0072] In the present invention, a material for a steel pipe having the chemical composition described above is used as a starting material. There is no particular limitation on the method for manufacturing the material for a steel pipe, that is, the starting material. For example, it is preferable that the material for a steel pipe be manufactured by preparing molten steel having the chemical composition described above with a steelmaking method such as one utilizing a converter and by making a cast piece such as a billet with a casting method such as a continuous casting method or an ingot casting-blooming method. Here, the method for manufacturing a material for a steel pipe is not limited to this method.

[0073] A steel piece which is made by further performing hot rolling on the cast piece to obtain desired dimensions may be used as the material for a steel pipe.

[0074] Subsequently, this material for a steel pipe is subjected to a heat treatment (heating process).

[0075] In the heating process, the material for a steel pipe (for example, billet) is heated to a heating temperature of

1100°C to 1350°C. In the case where the heating temperature is lower than 1100°C, since there is a deterioration in the hot workability of the billet, flaws occur frequently during pipe making. On the other hand, in the case where the heating temperature is higher than 1350°C, since there is an excessive increase in crystal grain size, there is a deterioration in low-temperature toughness. Therefore, the heating temperature in the heating process is set to be 1100°C to 1350°C. It is preferable that the heating temperature be 1150°C or higher. It is preferable that the heating temperature be 1300°C or lower.

[0076] Here, the expression a "deterioration in hot-workability" in the present invention denotes, as described in EXAMPLES below, a case where, when a round-bar test specimen having a round bar shape and a parallel portion diameter of 10 mm, which has been taken from a billet, is heated to a temperature of 1250°C in a Gleeble testing machine, held for 100 seconds, cooled to a temperature of 1000°C at a cooling rate of 1°C/sec, held for 10 seconds, and thereafter subjected to tension until the test specimen is broken, and when a cross-sectional area reduction ratio (%) is measured, the cross-sectional area reduction ratio is less than 70%.

[0077] Subsequently, the heated material for a steel pipe is subjected to hot working in a hot pipe making process so as to be made into a seamless steel pipe having a predetermined shape. It is preferable that the hot pipe making process be a Mannesmann-plug mill process or a Mannesmann-mandrel mill process. Here, a seamless steel pipe may be manufactured by using a hot extrusion process involving a pressing process. There is no particular limitation on the conditions applied for the hot pipe making process as long as it is possible to manufacture a seamless steel pipe having a predetermined shape.

[0078] After the hot pipe making process described above, the obtained seamless steel pipe may be subjected to a cooling treatment (cooling process). There is no particular limitation on the cooling process. In the case of the chemical composition according to the present invention, by cooling the steel pipe to room temperature at a cooling rate corresponding to natural cooling after hot working has been performed in the hot pipe making process, it is possible to control the microstructure of a steel pipe to be one including a martensitic phase as a main phase.

[0079] Subsequently, in the present invention, the seamless steel pipe is subjected to a heat treatment involving a quenching treatment and a tempering treatment.

[0080] The quenching treatment is a treatment in which, after the seamless steel pipe has been reheated to a temperature (heating temperature) of 850°C to 1150°C and has been held for a predetermined time, the held steel pipe is cooled at a cooling rate equal to or higher than that corresponding to natural cooling to a temperature (cooling stop temperature) of 50°C to 0°C (not inclusive) in terms of the surface temperature of the seamless steel pipe.

[0081] In the case where the heating temperature for a quenching treatment is lower than 850°C, since such a temperature is lower than the Ac_3 temperature, reverse transformation from martensite to austenite does not occur. In addition, when cooling for a quenching treatment is performed, transformation from austenite to martensite does not occur. As a result, it is not possible to achieve the strength intended by the present invention. On the other hand, in the case where the heating temperature for a quenching treatment is higher than 1150°C, there is an excessive increase in crystal grain size. As a result, there is a deterioration in low-temperature toughness. Therefore, the heating temperature for a quenching treatment is set to be 850°C to 1150°C. It is preferable that the heating temperature be 900°C or higher. It is preferable that the heating temperature be 1000°C or lower.

[0082] In a quenching treatment, the seamless steel pipe, which has been heated to the heating temperature described above, is held for a predetermined time. It is preferable that the soaking time be 5 min to 40 min to prevent a variation in material properties by providing uniform temperature distribution in the wall thickness direction of the seamless steel pipe. It is more preferable that the soaking time be 10 min or more.

[0083] In the case where the cooling stop temperature for a quenching treatment is higher than 50°C, since transformation from austenite to martensite does not sufficiently progress, there is an excessive increase in the fraction of an austenite phase. On the other hand, in the case where the cooling stop temperature for a quenching treatment is 0°C or lower, since transformation into a martensitic phase progresses excessively, it is not possible to achieve the fraction of an austenite phase necessary in the present invention. Therefore, in the present invention, the cooling stop temperature in cooling for a quenching treatment is set to be 50°C to 0°C (not inclusive). It is preferable that the cooling stop temperature be 10°C or higher. It is preferable that the cooling stop temperature be 40°C or lower.

[0084] Here, the expression a "cooling rate equal to or higher than that corresponding to natural cooling" denotes an average cooling rate of 0.01°C/sec or higher.

[0085] Subsequently, the seamless steel pipe, which has been subjected to a quenching treatment, is subjected to a tempering treatment. The tempering treatment is a treatment in which, after the seamless steel pipe has been heated to a temperature (tempering temperature) of 500°C to 650°C and has been held for a predetermined time, the held seamless steel pipe is allowed to be naturally cooled. Natural cooling is air cooling.

[0086] In the case where the tempering temperature is lower than 500°C, since the temperature is excessively low, it is not possible to expect for the desired effect of tempering to be obtained. On the other hand, in the case where the tempering temperature is higher than 650°C, since a martensitic phase in the quenched state is formed, it is not possible to provide high strength, high toughness (that is, excellent low-temperature toughness), and excellent corrosion resistance intended by the present invention at the same time. Therefore, the tempering temperature is set to be 500°C to 650°C. It is preferable that the tempering temperature be 520°C or higher or more preferably 550°C or higher. It is preferable that the tempering temperature be 630°C or lower or more preferably 600°C or lower.

[0087] In a tempering treatment, the seamless steel pipe, which has been heated to the tempering temperature described above, is held for a predetermined time. It is preferable that the soaking time (holding time) be 5 min to 90 min to prevent a variation in material properties by providing uniform temperature distribution in the wall thickness direction of the seamless steel pipe. It is more preferable that the soaking time (holding time) be 15 min or more. It is more preferable that the soaking time (holding time) be 60 min or less.

[0088] By performing the above-described heat treatment (quenching treatment and tempering treatment) on the seamless steel pipe, the microstructure of the obtained steel pipe includes a tempered martensitic phase as a main phase and, in addition, a ferrite phase and a retained austenite phase as described above. Consequently, it is possible to obtain a high-strength seamless stainless steel pipe for oil wells having high strength, high toughness, and excellent corrosion resistance intended by the present invention at the same time.

[0089] As described above, the stainless steel pipe obtained by using the present invention has a yield strength (YS) of 758 MPa or more, excellent low-temperature toughness, and excellent corrosion resistance. It is preferable that the yield strength be 800 MPa or higher. It is preferable that the yield strength be 1034 MPa or lower.

EXAMPLES

[0090] Hereafter, the present invention will be described in accordance with examples. Here, the present invention is not limited to the examples below.

[0091] Molten steels having the chemical compositions given in Table 1 were prepared by performing vacuum melting, and the obtained materials for a steel pipe (cast pieces) were subjected to a heating process in which heating was performed under the heating temperatures given in Table 2.

[0092] Subsequently, in a hot pipe making process, the heated materials for a steel pipe were subjected to hot working utilizing a seamless rolling mill so as to be made into seamless steel pipes (having an outer diameter of 297 mmϕ and a wall thickness of 34 mm), and the obtained seamless steel pipes were cooled by air to room temperature (25°C).

[0093] Subsequently, a test material was taken from the obtained seamless steel pipe, and the test material was subjected to a heat treatment (quenching treatment and tempering treatment) under the conditions given in Table 2. The test material was taken so that the longitudinal direction of the test material was the pipe axis direction. The average cooling rate when cooling for quenching treatment was performed was 11°C/sec, and the average cooling rate when air cooling (natural cooling) for a tempering treatment was performed was 0.04°C/sec.

[0094] Here, the sign "-" in the columns for "Chemical Composition" in Table 1 denotes a case where the corresponding element was not purposely added, that is, not only a case where the content of the corresponding element was 0% but also a case where the corresponding element was incidentally contained.

[0095] Subsequently, test specimens were taken from the obtained test material, which had been subjected to a heating treatment, and each of the test specimens was used for respective microstructure observation, a tensile test, an impact test, and corrosion resistance tests. The methods for the tests and the like are described below.

(1) Microstructure observation

[0096] From the obtained test material, which had been subjected to a heat treatment, a test specimen for microstructure observation was taken so that a cross section in the pipe axis direction was an observation surface. The obtained test specimen for microstructure observation was etched in Vilella's reagent (reagent obtained by mixing picric acid, hydrochloric acid, and ethanol in the proportion of 2 g of picric acid and 10 ml of hydrochloric acid to 100 ml of ethanol), the photograph of a microstructure was taken by using a scanning electron microscope (at a magnification of 1000 times), and the fraction (area fraction (%)) of a ferrite phase was calculated by using an image analyzer. The obtained area fraction was regarded as the volume fraction (%).

[0097] In addition, a test specimen for X-ray diffraction was taken so that a cross section perpendicular to the pipe axis direction (C-cross section) was a measurement surface from the obtained test material, which had been subjected to a heat treatment, the measurement surface was ground and polished, and the amount of retained austenite (y) was measured by performing X-ray diffraction analysis. The amount of a retained austenite was calculated by using the following equation after the integral X-ray diffraction intensities of the (220) plane of y and the (211) plane of α (ferrite) had been measured.

$$\gamma\ (\text{volume fraction}) = 100/(1 + (I\alpha R\gamma/I\gamma R\alpha))$$

Here, Iα: integral intensity of α, Rα: theoretically calculated value of α on the basis of crystallography, Iy: integral intensity of y, and Ry: theoretically calculated value of y on the basis of crystallography.

[0098] Here, the fraction (volume fraction) of a tempered martensite phase was that of the remainder which differs from a ferrite phase and a retained y phase.

(2) Tensile test

[0099] An API (American Petroleum Institute) arc-shaped tensile test specimen was taken so that the pipe axis direction was the tensile direction from the obtained test material, which had been subjected to a heat treatment, and a tensile test was performed in accordance with the prescription by API to obtain tensile properties (yield strength (YS) and tensile strength (TS)).

[0100] Here, a case of a yield strength (YS) of 758 MPa or higher was judged as a case of high strength and as satisfactory. On the other hand, a case of a yield strength of lower than 758 MPa was judged as unsatisfactory.

(3) Impact test

[0101] A V-notch test specimen (having a thickness of 10 mm) was taken so that longitudinal direction of the test specimen was the pipe axis direction in accordance with the prescription in JIS Z 2242 (2018) from the obtained test material, which had been subjected to a heat treatment, and a Charpy impact test was performed. The test temperature was -10°C, and the absorbed energy at a temperature of - 10°C, that is vE_{-10}, was determined to evaluate low-temperature toughness. Here, the number of the test specimens was three, and the arithmetic average of the determined values was defined as the absorbed energy (J) of the related steel pipe.

[0102] Here, a case of an absorbed energy at a temperature of -10°C, that is vE_{-10}, of 40 J or more was judged as a case of high toughness (excellent low-temperature toughness) and as satisfactory. On the other hand, a case of a vE_{-10} of less than 40 J was judged as unsatisfactory.

(4) Corrosion resistance test

[0103] Here, each of the taken test specimens was used for respective corrosion tests as described below to evaluate carbon dioxide corrosion resistance and sulfide stress cracking resistance.

<Evaluation of carbon dioxide corrosion resistance>

[0104] A corrosion test specimen having a thickness of 3 mm, a width of 30 mm, and a length of 40 mm was taken by performing machining from the obtained test material, which had been subjected to a heat treatment. Each of the taken test specimens was used for respective corrosion tests as described below.

(Corrosion test A)

[0105] A corrosion test was performed by immersing the test specimen described above in a testing solution, that is, a 25 mass% NaCl aqueous solution (having a temperature of 250°C in a CO_2 gas environment under a pressure of 30 atm), which was contained in an autoclave, for an immersion time of 14 days (336 hours). The weight of the test specimen after the corrosion test had been performed was measured, and the corrosion rate was calculated from the difference in weight before and after the corrosion test.

[0106] Here, a case of a corrosion rate of 0.125 mm/y or lower was judged as satisfactory, and a case of a corrosion rate of more than 0.125 mm/y was judged as unsatisfactory.

[0107] In addition, the surface of the test specimen after the corrosion test had been performed was observed by using a loupe at a magnification of 10 times to determine whether or not pitting corrosion occurred. The expression "with pitting corrosion" denotes a case where pitting corrosion having a diameter of 0.2 mm or more was observed. The expression "without pitting corrosion" denotes a case where no pitting corrosion was observed or only pitting corrosion having a diameter of less than 0.2 mm was observed. Here, a case without pitting corrosion was judged as satisfactory, and a case with pitting corrosion was judged as unsatisfactory.

(Corrosion test B)

[0108] A corrosion test was performed by immersing the test specimen described above in a testing solution, that is, a 0.01 mol/L H_2SO_4 aqueous solution (having a temperature of 250°C in a CO_2 gas environment under a pressure of 30 atm), which was contained in an autoclave, for an immersion time of 14 days (336 hours). The weight of the test specimen after the corrosion test had been performed was measured, and the corrosion rate was calculated from the difference in weight before and after the corrosion test.

[0109] Here, a case of a corrosion rate of 0.125 mm/y or lower was judged as satisfactory, and a case of a corrosion rate of more than 0.125 mm/y was judged as unsatisfactory.

[0110] In addition, the surface of the test specimen after the corrosion test had been performed was observed by using a loupe at a magnification of 10 times to determine whether or not pitting corrosion occurred. The expression "with pitting corrosion" denotes a case where pitting corrosion having a diameter of 0.2 mm or more was observed. The expression "without pitting corrosion" denotes a case where no pitting corrosion was observed or only pitting corrosion having a diameter of less than 0.2 mm was observed. Here, a case without pitting corrosion was judged as satisfactory, and a case with pitting corrosion was judged as unsatisfactory.

[0111] In the present EXAMPLES, a case where a result with a corrosion rate of 0.125 mm/y or less and without pitting corrosion was obtained in corrosion test A and a result with a corrosion rate of 0.125 mm/y or less and without pitting corrosion was obtained in corrosion test B was judged as a case of excellent carbon dioxide corrosion resistance.

<Evaluation of sulfide stress cracking resistance>

[0112] A round bar-shaped test specimen (having a diameter of 6.4 mmϕ) was taken by performing machining in accordance with Method A in NACE (National Association of Corrosion and Engineers) TM0177 from the obtained test material, which had been subjected to a heat treatment. A sulfide stress cracking resistance test (SSC resistance test) was performed on the taken round bar-shaped test specimen as described below.

[0113] An SSC resistance test was performed by immersing the test specimen described above in an aqueous solution, which had been prepared by adding acetic acid and sodium acetate to a testing solution, that is, a 5 mass% NaCl aqueous solution (having a temperature of 25°C in an atmosphere containing CO_2 gas corresponding to a pressure of 0.95 atm and H_2S corresponding to a pressure of 0.05 atm) so that the pH was 3.5, under a loading stress equal to 90% of its yield stress for an immersion time of 720 hours. The test specimen after the SSC resistance test had been performed was observed to determine whether or not cracking occurred.

[0114] Here, a case where no cracking was observed was judged as satisfactory, and a case where cracking was observed was judged as unsatisfactory.

<Evaluation of hot workability>

[0115] For the evaluation of hot workability, a round-bar test specimen having a round bar shape and a parallel portion diameter of 10 mm, which had been taken from a billet, was used. The obtained round-bar test specimen was heated to a temperature of 1250°C in a Gleeble testing machine, held for 100 seconds, cooled to a temperature of 1000°C at an average cooling rate of 1°C /sec, held for 10 seconds, and thereafter subjected to tension until the test specimen was broken to determine a cross-sectional area reduction ratio (%).

[0116] Here, a case of a cross-sectional area reduction ratio of 70% or more was judged as a case of excellent hot workability and as satisfactory. On the other hand, a case of a cross-sectional area reduction ratio of less than 70% was judged as unsatisfactory.

[0117] The obtained results were given in Table 3.

[Table 1]

Steel No.	Chemical Composition (mass%)																									Relational Expression (1) *1		Relational Expression (2) *2		Note
	C	Si	Mn	P	S	Cr	Mo	Cu	Ni	Al	N	O	Nb	V	Ti	Ta	B	Ca	REM	Mg	Zr	Sn	Sb	Co	W	Left-hand Side Value	Satisfaction	Left-hand Side Value	Satisfaction	
A	0.008	0.37	0.28	0.013	0.0007	18.5	1.0	2.6	4.0	0.036	0.0115	22	-	-	-	-	-	-	-	-	-	-	-	-	-	22.9	○	21.6	○	Example
B	0.007	0.35	0.25	0.018	0.0007	19.1	0.7	2.5	4.0	0.025	0.0122	37	-	-	-	-	-	-	-	-	-	-	-	-	0.3	23.4	○	21.8	○	Example
C	0.006	0.37	0.48	0.011	0.0014	18.6	1.3	2.7	3.9	0.022	0.0135	34	-	-	-	-	-	-	-	-	-	-	-	-	-	23.2	○	22.7	○	Example
D	0.009	0.33	0.19	0.011	0.0010	16.6	1.3	2.7	4.3	0.024	0.0115	20	-	-	-	-	-	-	-	-	-	-	-	-	2.0	22.1	○	24.0	○	Example
E	0.009	0.31	0.15	0.013	0.0009	19.3	0.7	1.6	4.3	0.025	0.0113	43	-	-	-	-	-	-	-	-	-	-	-	-	-	23.2	○	21.5	○	Example
F	0.007	0.30	0.31	0.020	0.0011	18.6	1.0	0.6	4.0	0.031	0.0126	33	-	-	-	-	-	-	-	-	-	-	-	-	-	22.0	○	21.7	○	Example
G	0.007	0.33	0.35	0.016	0.0007	18.6	1.2	2.3	3.3	0.032	0.0131	42	-	-	-	-	-	-	-	-	-	-	-	-	-	22.6	○	22.4	○	Example
H	0.009	0.45	0.14	0.010	0.0013	18.6	1.1	1.5	4.9	0.022	0.0136	37	-	-	-	-	-	-	-	-	-	-	-	-	-	23.1	○	22.0	○	Example
I	0.031	0.46	0.27	0.010	0.0009	18.6	1.1	1.3	3.9	0.035	0.0113	46	-	-	-	-	-	-	-	-	-	-	-	-	-	21.9	○	21.7	○	Example
J	0.008	0.49	0.23	0.017	0.0011	18.8	1.1	2.6	3.3	0.030	0.0540	50	-	-	-	-	-	-	-	-	-	-	-	-	-	22.8	○	22.3	○	Example
K	0.006	0.30	0.17	0.020	0.0013	18.8	1.1	2.7	4.2	0.026	0.0131	27	0.10	-	-	-	-	-	-	-	-	-	-	-	-	23.5	○	22.3	○	Example
L	0.006	0.47	0.46	0.018	0.0013	18.7	1.0	2.5	4.0	0.027	0.0120	33	-	0.10	-	-	-	-	-	-	-	-	-	-	-	23.1	○	21.9	○	Example
M	0.007	0.42	0.33	0.015	0.0008	18.7	1.1	2.7	4.0	0.035	0.0120	39	-	0.40	-	-	-	-	-	-	-	-	-	-	-	23.3	○	22.2	○	Example
N	0.008	0.41	0.23	0.012	0.0009	18.7	1.0	2.6	4.3	0.022	0.0120	27	-	-	-	0.06	-	-	-	-	-	-	-	-	-	23.3	○	21.8	○	Example
O	0.007	0.37	0.12	0.018	0.0013	18.6	1.1	2.6	3.9	0.026	0.0135	24	-	-	-	-	0.0040	-	-	-	-	-	-	-	-	23.0	○	22.1	○	Example
P	0.007	0.42	0.35	0.017	0.0011	18.8	0.9	2.6	4.0	0.030	0.0131	50	-	-	0.07	-	-	-	-	-	-	-	-	-	-	23.2	○	21.6	○	Example
Q	0.005	0.40	0.10	0.018	0.0007	18.4	1.1	2.4	4.2	0.029	0.0129	40	-	-	-	-	-	0.0020	-	-	-	-	-	-	-	23.0	○	21.9	○	Example
R	0.008	0.44	0.12	0.019	0.0014	18.5	1.1	2.4	4.3	0.025	0.0115	35	-	-	-	-	-		0.005	-	-	-	-	-	-	23.1	○	22.0	○	Example
S	0.007	0.44	0.42	0.017	0.0009	18.4	0.9	2.4	4.1	0.020	0.0136	37	-	-	-	-	-	-	-	0.0040	-	-	-	-	-	22.7	○	21.2	○	Example
T	0.008	0.48	0.13	0.014	0.0009	18.6	0.9	2.3	4.0	0.031	0.0112	44	-	-	-	-	-	-	-	-	-	0.1	-	-	-	22.8	○	21.4	○	Example
U	0.008	0.34	0.40	0.012	0.0011	18.7	1.0	2.5	4.0	0.028	0.0119	41	-	-	-	-	-	-	-	-	-	-	0.1	-	-	23.1	○	21.8	○	Example
V	0.007	0.36	0.37	0.019	0.0009	18.6	1.0	2.4	4.1	0.038	0.0126	24	-	-	-	-	-	-	-	-	0.04	-	-	-	-	23.0	○	21.7	○	Example
W	0.008	0.44	0.15	0.014	0.0011	18.6	1.1	2.4	3.9	0.033	0.0113	37	-	-	-	-	-	-	-	-	-	-	-	0.07	-	22.9	○	22.1	○	Example
X	0.009	0.39	0.20	0.010	0.0013	19.7	0.1	2.4	4.1	0.034	0.0072	45	-	-	-	-	-	-	-	-	-	-	-	-	-	23.6	○	19.9	×	Comparative Example
Y	0.058	0.47	0.41	0.017	0.0010	18.4	1.0	2.7	4.3	0.036	0.0113	39	-	-	-	-	-	-	-	-	-	-	-	-	-	22.1	○	20.7	×	Comparative Example
Z	0.007	0.45	0.22	0.019	0.0012	15.8	1.0	2.6	3.9	0.036	0.0133	50	-	-	-	-	-	-	-	-	-	-	-	-	-	20.2	×	19.0	×	Comparative Example
AA	0.007	0.41	0.45	0.017	0.0010	20.3	1.1	2.5	4.2	0.036	0.0133	31	-	-	-	-	-	-	-	-	-	-	-	-	-	24.9	○	23.8	○	Comparative Example
AB	0.005	0.41	0.34	0.020	0.0009	18.5	1.7	2.5	4.3	0.021	0.0133	28	-	-	-	-	-	-	-	-	-	-	-	-	-	23.6	○	24.0	○	Comparative Example
AC	0.007	0.31	0.15	0.014	0.0010	18.5	1.1	3.7	4.0	0.032	0.0114	43	-	-	-	-	-	-	-	-	-	-	-	-	-	23.6	○	22.0	○	Comparative Example
AD	0.008	0.50	0.18	0.016	0.0012	18.8	1.0	2.3	2.8	0.025	0.0126	43	-	-	-	-	-	-	-	-	-	-	-	-	-	22.3	○	21.9	○	Comparative Example
AE	0.006	0.30	0.41	0.016	0.0014	18.6	1.1	2.4	5.3	0.021	0.0123	30	-	-	-	-	-	-	-	-	-	-	-	-	-	23.9	○	22.1	○	Comparative Example
AF	0.009	0.48	0.37	0.020	0.0008	18.5	0.9	2.5	4.3	0.020	0.0120	27	-	-	-	-	-	-	-	-	-	-	-	-	3.2	24.0	○	26.6	○	Comparative Example
AG	0.047	0.39	0.24	0.017	0.0007	18.5	1.1	2.7	4.1	0.035	0.0111	22	-	-	-	-	-	-	-	-	-	-	-	-	-	22.4	○	21.3	○	Example
AH	0.013	0.10	0.28	0.014	0.0008	18.5	0.9	2.5	4.1	0.032	0.0139	20	-	-	-	-	-	-	-	-	-	-	-	-	-	22.8	○	21.2	○	Example
AI	0.007	0.33	1.92	0.013	0.0011	18.4	1.1	2.7	4.0	0.035	0.0105	23	-	-	-	-	-	-	-	-	-	-	-	-	-	23.0	○	21.9	○	Example
AJ	0.013	0.37	0.25	0.016	0.0042	18.5	1.0	2.5	3.9	0.040	0.0110	21	-	-	-	-	-	-	-	-	-	-	-	-	-	22.8	○	21.6	○	Example
AK	0.010	0.33	0.33	0.012	0.0003	20.0	1.0	2.5	4.0	0.036	0.0103	21	-	-	-	-	-	-	-	-	-	-	-	-	-	24.4	○	23.1	○	Example
AL	0.003	0.40	0.24	0.010	0.0010	18.5	1.0	2.6	4.0	0.068	0.0134	19	-	-	-	-	-	-	-	-	-	-	-	-	-	23.1	○	21.7	○	Example
AM	0.010	0.39	0.32	0.015	0.0008	18.5	0.9	2.7	3.9	0.040	0.0211	19	-	-	-	-	-	-	-	-	-	-	-	-	-	22.9	○	21.3	○	Example
AN	0.008	0.33	0.27	0.013	0.0011	18.4	0.9	3.4	4.0	0.033	0.0116	19	-	-	-	-	-	-	-	-	-	-	-	-	-	23.3	○	21.2	○	Example
AO	0.005	0.38	0.31	0.014	0.0011	18.4	1.0	2.7	4.0	0.031	0.0128	24	-	-	0.19	-	-	-	-	-	-	-	-	-	-	23.0	○	21.6	○	Example
AP	0.003	0.33	0.26	0.016	0.0009	18.5	1.0	2.6	4.0	0.039	0.0105	20	-	-	-	0.12	-	-	-	-	-	-	-	-	-	23.1	○	21.7	○	Example
AQ	0.011	0.41	0.31	0.010	0.0003	18.5	0.9	2.7	4.1	0.034	0.0112	25	-	-	-	-	-	-	-	-	-	-	-	0.51	-	23.0	○	21.3	○	Example

*1) Cr + 0.65 × Ni + 0.6(Mo + 0.5 × W) + 0.55 × Cu - 20 × C ≥ 21.7

*2) Cr + 3.3 × (Mo + 0.5 × W) - 17 × C ≥ 21.0

*3) Here, the content of O (oxygen) is expressed in units of "mass ppm".

[Table 2]

Steel Pipe No.	Steel No.	Heating Process	Heat Treatment						
			Quenching Treatment				Tempering Treatment		
		Heating Temperature (°C)	Heating Temperature (°C)	Soaking Time (min)	Cooling	Cooling Stop Temperature (°C)	Tempering Temperature (°C)	Holding Time (min)	Cooling
1	A	1184	971	36	Water Cooling	34	574	16	Natural Cooling
2	8	1229	942	28	Water Cooling	18	551	41	Natural Cooling
3	C	1216	972	36	Water Cooling	31	583	47	Natural Cooling
4	D	1342	967	18	Water Cooling	24	573	23	Natural Cooling
5	E	1308	949	37	Water Cooling	34	597	58	Natural Cooling
6	F	1189	957	28	Water Cooling	31	553	36	Natural Cooling
7	G	1248	941	32	Water Cooling	26	590	21	Natural Cooling
8	H	1283	956	21	Water Cooling	33	588	26	Natural Cooling
9	I	1257	941	11	Water Cooling	35	577	37	Natural Cooling
10	J	1272	967	13	Water Cooling	32	565	24	Natural Cooling
11	K	1198	950	29	Water Cooling	17	580	22	Natural Cooling
12	L	1244	974	16	Water Cooling	24	553	46	Natural Cooling
13	M	1200	958	20	Water Cooling	34	560	58	Natural Cooling

(continued)

Steel Pipe No.	Steel No.	Heating Process	Heat Treatment						
			Quenching Treatment				Tempering Treatment		
		Heating Temperature (°C)	Heating Temperature (°C)	Soaking Time (min)	Cooling	Cooling Stop Temperature (°C)	Tempering Temperature (°C)	Holding Time (min)	Cooling
14	N	1191	972	21	Water Cooling	22	599	34	Natural Cooling
15	O	1286	969	24	Water Cooling	16	575	49	Natural Cooling
16	P	1240	973	18	Water Cooling	26	583	58	Natural Cooling
17	Q	1260	966	17	Water Cooling	23	564	51	Natural Cooling
18	R	1262	964	22	Water Cooling	26	590	46	Natural Cooling
19	S	1158	964	13	Water Cooling	22	586	18	Natural Cooling
20	T	1296	943	21	Water Cooling	18	585	47	Natural Cooling
21	U	1330	959	19	Water Cooling	19	598	35	Natural Cooling
22	V	1216	956	24	Water Cooling	22	587	34	Natural Cooling
23	W	1234	945	10	Water Cooling	34	569	30	Natural Cooling
24	X	1206	945	17	Water Cooling	31	594	24	Natural Cooling
25	Y	1278	942	24	Water Cooling	26	570	21	Natural Cooling
26	Z	1187	956	10	Water Cooling	32	590	43	Natural Cooling

(continued)

Steel Pipe No.	Steel No.	Heating Process	Heat Treatment						
			Quenching Treatment				Tempering Treatment		
		Heating Temperature (°C)	Heating Temperature (°C)	Soaking Time (min)	Cooling	Cooling Stop Temperature (°C)	Tempering Temperature (°C)	Holding Time (min)	Cooling
27	AA	1172	961	19	Water Cooling	30	561	15	Natural Cooling
28	AB	1215	945	12	Water Cooling	17	587	43	Natural Cooling
29	AC	1286	946	38	Water Cooling	24	585	26	Natural Cooling
30	AD	1309	965	20	Water Cooling	15	573	20	Natural Cooling
31	AE	1229	940	16	Water Cooling	34	577	43	Natural Cooling
32	AF	1246	952	39	Water Cooling	28	591	23	Natural Cooling
33	O	1367	978	16	Water Cooling	15	575	49	Natural Cooling
34	O	1224	845	26	Water Cooling	42	575	49	Natural Cooling
35	O	1240	1185	27	Water Cooling	19	575	49	Natural Cooling
36	O	1288	937	9	Water Cooling	57	575	49	Natural Cooling
37	O	1231	967	18	Water Cooling	-9	575	49	Natural Cooling
38	O	1297	928	33	Water Cooling	23	474	49	Natural Cooling
39	O	1322	967	5	Water Cooling	10	665	49	Natural Cooling

(continued)

Steel Pipe No.	Steel No.	Heating Process	Heat Treatment						
			Quenching Treatment				Tempering Treatment		
		Heating Temperature (°C)	Heating Temperature (°C)	Soaking Time (min)	Cooling	Cooling Stop Temperature (°C)	Tempering Temperature (°C)	Holding Time (min)	Cooling
40	AG	1201	961	22	Water Cooling	25	571	19	Natural Cooling
41	AH	1195	989	32	Water Cooling	41	570	15	Natural Cooling
42	AI	1176	981	40	Water Cooling	29	575	12	Natural Cooling
43	AJ	1188	977	24	Water Cooling	24	582	25	Natural Cooling
44	AK	1186	981	15	Water Cooling	28	568	13	Natural Cooling
45	AL	1173	967	21	Water Cooling	30	577	18	Natural Cooling
46	AM	1165	962	29	Water Cooling	28	580	26	Natural Cooling
47	AN	1164	961	32	Water Cooling	40	581	8	Natural Cooling
48	AO	1191	971	9	Water Cooling	24	579	16	Natural Cooling
49	AP	1169	987	18	Water Cooling	30	584	26	Natural Cooling
50	AQ	1197	957	26	Water Cooling	39	572	13	Natural Cooling
51	M	1200	958	20	Water Cooling	34	540	10	Natural Cooling

[Table 3]

Steel Pipe No.	Steel No.	Microstructure				Hot Workability	Tensile Property		Low-Temperature Toughness	Corrosion Test A		Corrosion Test B		SSC Resistance Test	Note
		Kind*	TM Phase Volume Fraction (%)	F Phase Volume Fraction (%)	γ Phase Volume Fraction (%)	Cross-sectional Area Reduction Ratio (%)	Yield Strength YS (MPa)	Tensile Strength TS (MPa)	vE_{-10} (J)	Corrosion Rate (mm/y)	with or without Pitting Corrosion	Corrosion Rate (mm/y)	with or without Pitting Corrosion	with or without Cracking	
1	A	TM+F+γ	60	30	10	76	905	1044	90	0.046	without	0.069	without	without	Example
2	B	TM+F+γ	54	33	13	77	921	1101	122	0.033	without	0.081	without	without	Example
3	C	TM+F+γ	56	35	9	75	869	992	53	0.047	without	0.067	without	without	Example
4	D	TM+F+γ	66	29	5	74	816	863	63	0.119	without	0.097	without	without	Example
5	E	TM+F+γ	56	32	12	75	878	1037	61	0.041	without	0.070	without	without	Example
6	F	TM+F+γ	60	35	5	76	915	989	81	0.093	without	0.100	without	without	Example
7	G	TM+F+γ	59	36	5	73	860	910	140	0.062	without	0.093	without	without	Example
8	H	TM+F+γ	62	27	11	75	902	1053	153	0.047	without	0.086	without	without	Example
9	I	TM+F+γ	57	33	10	74	844	974	114	0.107	without	0.112	without	without	Example
10	J	TM+F+γ	58	32	10	77	865	998	110	0.064	without	0.086	without	without	Example
11	K	TM+F+γ	64	31	5	74	872	952	109	0.047	without	0.074	without	without	Example
12	L	TM+F+γ	59	31	10	73	882	1018	94	0.048	without	0.087	without	without	Example
13	M	TM+F+γ	52	31	17	74	990	1242	43	0.056	without	0.083	without	without	Example
14	N	TM+F+γ	54	35	11	73	830	969	126	0.052	without	0.069	without	without	Example
15	O	TM+F+γ	60	29	11	73	851	993	49	0.055	without	0.076	without	without	Example
16	P	TM+F+γ	49	33	18	77	881	1120	65	0.051	without	0.075	without	without	Example
17	Q	TM+F+γ	60	31	9	74	906	1034	107	0.044	without	0.081	without	without	Example
18	R	TM+F+γ	55	35	10	76	837	966	141	0.051	without	0.085	without	without	Example
19	S	TM+F+γ	61	30	9	73	846	965	128	0.050	without	0.083	without	without	Example
20	T	TM+F+γ	58	33	9	75	843	962	124	0.053	without	0.081	without	without	Example

(continued)

Steel Pipe No.	Steel No.	Microstructure				Hot Workability	Tensile Property		Low-Temperature Toughness	Corrosion Test A		Corrosion Test B		SSC Resistance Test	Note
		Kind*	TM Phase Volume Fraction (%)	F Phase Volume Fraction (%)	γ Phase Volume Fraction (%)	Cross-sectional Area Reduction Ratio (%)	Yield Strength YS (MPa)	Tensile Strength TS (MPa)	vE_{-10} (J)	Corrosion Rate (mm/y)	with or without Pitting Corrosion	Corrosion Rate (mm/y)	with or without Pitting Corrosion	with or without Cracking	
21	U	TM+F+γ	59	34	7	75	809	903	128	0.055	without	0.079	without	without	Example
22	V	TM+F+γ	58	35	7	74	845	943	128	0.044	without	0.086	without	without	Example
23	W	TM+F+γ	63	29	8	75	902	1018	89	0.042	without	0.074	without	without	Example
24	X	TM+F+γ	62	29	9	76	854	974	82	0.031	without	0.069	without	with	Comparative Example
25	Y	TM+F+γ	57	21	22	73	845	1130	124	0.097	without	0.108	without	with	Comparative Example
26	Z	TM+F	82	18	0	77	837	867	121	0.352	with	0.149	with	without	Comparative Example
27	AA	TM+F+γ	36	44	20	77	745	902	143	0.012	without	0.063	without	without	Comparative Example
28	AB	TM+F+γ	44	43	13	74	810	968	31	0.038	without	0.069	without	with	Comparative Example
29	AC	TM+F+γ	57	30	13	67	917	1195	88	0.039	without	0.059	without	with	Comparative Example
30	AD	TM+F	60	40	0	75	887	919	124	0.175	with	0.188	with	without	Comparative Example
31	AE	TM+F+γ	52	22	26	64	706	1096	168	0.031	without	0.075	without	without	Comparative Example
32	AF	TM+F+γ	40	43	17	75	910	1142	34	0.031	without	0.061	without	with	Comparative Example
33	O	TM+F+γ	63	27	10	73	843	1001	30	0.058	without	0.079	without	without	Comparative Example

(continued)

Steel Pipe No.	Steel No.	Microstructure				Hot Workability	Tensile Property		Low-Temperature Toughness	Corrosion Test A		Corrosion Test B		SSC Resistance Test	Note
		Kind*	TM Phase Volume Fraction (%)	F Phase Volume Fraction (%)	γ Phase Volume Fraction (%)	Cross-sectional Area Reduction Ratio (%)	Yield Strength YS (MPa)	Tensile Strength TS (MPa)	vE_{-10} (J)	Corrosion Rate (mm/y)	with or without Pitting Corrosion	Corrosion Rate (mm/y)	with or without Pitting Corrosion	with or without Cracking	
34	O	TM+F+γ	59	31	10	73	751	901	48	0.059	without	0.069	without	without	Comparative Example
35	O	TM+F+γ	61	30	9	74	855	1013	31	0.051	without	0.079	without	without	Comparative Example
36	O	TM+F+γ	42	29	29	71	701	1022	50	0.055	without	0.066	without	without	Comparative Example
37	O	TM+F+γ	70	29	1	71	954	1086	33	0.060	without	0.076	without	without	Comparative Example
38	O	TM+F+γ	58	30	12	71	898	1055	34	0.051	without	0.066	without	without	Comparative Example
39	O	TM+F+γ	59	29	12	73	748	885	29	0.055	without	0.085	without	without	Comparative Example
40	AG	TM+F+γ	66	26	8	70	922	1043	214	0.072	without	0.087	without	without	Example
41	AH	TM+F+γ	67	28	5	72	929	990	47	0.048	without	0.084	without	without	Example
42	AI	TM+F+γ	65	30	5	77	950	1037	210	0.056	without	0.081	without	without	Example
43	AJ	TM+F+γ	63	32	5	72	935	1011	215	0.050	without	0.079	without	without	Example
44	AK	TM+F+γ	55	39	6	70	899	985	216	0.021	without	0.053	without	without	Example
45	AL	TM+F+γ	61	34	5	76	926	987	234	0.040	without	0.074	without	without	Example
46	AM	TM+F+γ	64	31	5	77	907	980	193	0.063	without	0.089	without	without	Example
47	AN	TM+F+γ	66	29	5	70	937	1013	199	0.035	without	0.078	without	without	Example
48	AO	TM+F+γ	64	31	5	73	954	1041	53	0.057	without	0.073	without	without	Example
49	AP	TM+F+γ	62	33	5	77	933	1008	208	0.048	without	0.073	without	without	Example

(continued)

Steel Pipe No.	Steel No.	Microstructure				Hot Workability	Tensile Property		Low-Temperature Toughness	Corrosion Test A		Corrosion Test B		SSC Resistance Test	Note
		Kind*	TM Phase Volume Fraction (%)	F Phase Volume Fraction (%)	γ Phase Volume Fraction (%)	Cross-sectional Area Reduction Ratio (%)	Yield Strength YS (MPa)	Tensile Strength TS (MPa)	vE_{-10} (J)	Corrosion Rate (mm/y)	with or without Pitting Corrosion	Corrosion Rate (mm/y)	with or without Pitting Corrosion	with or without Cracking	
50	AQ	TM+F+γ	64	30	6	73	930	1019	187	0.041	without	0.088	without	without	Example
51	M	TM+F+γ	52	31	17	71	1033	1213	41	0.044	without	0.074	without	without	Example

*) TM: tempered martensite, F: ferrite, γ: retained austenite

[0118] All of the examples of the present invention had a high strength represented by a yield strength (YS) of 758 MPa or more, excellent low-temperature toughness, and excellent corrosion resistance (excellent carbon dioxide corrosion resistance and excellent sulfide stress cracking resistance) in a harsh corrosive environment having a high temperature of 250°C or higher and containing CO_2 and Cl^-.

[0119] On the other hand, in the case of each of the comparative examples, which were out of the range of the present invention, the characteristic value intended by the present invention was not achieved regarding at least one of yield strength, low-temperature toughness, carbon dioxide corrosion resistance, or sulfide stress cracking resistance.

Claims

1. A stainless steel pipe having

    a chemical composition comprising, by mass%,

    C: 0.05% or less,
    Si: 1.0% or less,
    Mn: 0.10% to 2.0%,
    P: 0.05% or less,
    S: less than 0.005%,
    Cr: 16.0% (not inclusive) to 20.0%,
    Mo: 0.6% (not inclusive) to 1.4% (not inclusive),
    Ni: 3.0% to 5.0% (not inclusive),
    Al: 0.001% to 0.10%,
    N: 0.010% to 0.100%,
    O: 0.01% or less,
    Cu: 0.3% to 3.5%, and
    a balance of Fe and incidental impurities, in which relational expression (1) and relational expression (2) are satisfied,

    a microstructure including, in terms of volume fraction, 45% or more of a tempered martensitic phase, 20% to 40% of a ferrite phase, and 5% to 25% of a retained austenite phase,
    a yield strength of 758 MPa or higher, and
    an absorbed energy at a temperature of -10°C vE_{-10} of 40 J or more:

$$\mathrm{Cr} + 0.65 \times \mathrm{Ni} + 0.6 \times (\mathrm{Mo} + 0.5 \times \mathrm{W}) + 0.55 \times \mathrm{Cu} - 20 \times \mathrm{C} \geq 21.7 \quad \cdots (1),$$

$$\mathrm{Cr} + 3.3 \times (\mathrm{Mo} + 0.5 \times \mathrm{W}) - 17 \times \mathrm{C} \geq 21.0 \quad \cdots (2),$$

    where, in both relational expressions, each of Cr, Ni, Mo, W, Cu, and C denotes the content (mass%) of the corresponding element and is assigned a value of zero when the corresponding element is not added.

2. The stainless steel pipe according to Claim 1, wherein the chemical composition further comprises, by mass%, one, two, or more selected from group A to group E below:

    group A: one, two, or more selected from Ti: 0.3% or less, Nb: 0.5% or less, V: 0.5% or less, and Ta: 0.5% or less,
    group B: one, two, or all selected from B: 0.0050% or less, Ca: 0.0050% or less, and REM: 0.010% or less,
    group C: one or both selected from Mg: 0.010% or less and Zr: 0.2% or less,
    group D: one or both selected from Sn: 0.20% or less and Sb: 0.20% or less, and
    group E: one or both selected from Co: 1.0% or less and W: 3.0% or less.

3. A method for manufacturing the stainless steel pipe according to Claim 1 or 2, the method comprising

    heating a steel pipe material to a heating temperature of 1100°C to 1350°C and performing hot working on the

heated material to obtain a seamless steel pipe having a predetermined shape,
performing a quenching treatment of reheating the seamless steel pipe after the hot working to a temperature of 850°C to 1150°C and cooling the heated steel pipe to a cooling stop temperature of 0°C (not inclusive) to 50°C in terms of surface temperature at a cooling rate equal to or higher than a cooling rate corresponding to natural cooling, and
performing a tempering treatment of heating the quenched steel pipe to a tempering temperature of 500°C to 650°C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/011814

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; ***C21D 8/10***(2006.01)i; ***C21D 9/08***(2006.01)i; ***C22C 38/58***(2006.01)i; ***C22C 38/60***(2006.01)i
FI: C22C38/00 302Z; C21D8/10 D; C21D9/08 E; C22C38/58; C22C38/60

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00-38/60; C21D8/10; 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 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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.
X	JP 2017-031493 A (NIPPON STEEL & SUMITOMO METAL CORP.) 09 February 2017 (2017-02-09) claims, paragraphs [0001], [0042], [0058]-[0068], [0080]-[0097]	1-3
X A	WO 2016/079922 A1 (JFE STEEL CORP.) 26 May 2016 (2016-05-26) claims, paragraphs [0001], [0031], [0034], [0036], [0037], [0058], [0067]-[0087]	2-3 1
A	JP 2017-039998 A (JFE STEEL CORP.) 23 February 2017 (2017-02-23)	1-3
A	JP 2017-048424 A (NIPPON STEEL & SUMITOMO METAL CORP.) 09 March 2017 (2017-03-09)	1-3

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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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
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **12 May 2022**	Date of mailing of the international search report **24 May 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. **PCT/JP2022/011814**

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2017-031493 A	09 February 2017	(Family: none)	
WO 2016/079922 A1	26 May 2016	AR 102673 A1	
JP 2017-039998 A	23 February 2017	(Family: none)	
JP 2017-048424 A	09 March 2017	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2005336595 A **[0014]**
- JP 2008081793 A **[0014]**
- JP 2010050519 A **[0014]**
- JP 2010134498 A **[0014]**
- JP 2010209402 A **[0014]**
- JP 2012149317 A **[0014]**
- JP 2013146046 A **[0014]**
- JP 2019073789 A **[0014]**