(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 533 892 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
04.09.2019 Bulletin 2019/36

(21) Application number: **17865353.1**

(22) Date of filing: **13.09.2017**

(51) Int Cl.:
C22C 38/00 *(2006.01)*
C21D 8/10 *(2006.01)*
C21D 9/08 *(2006.01)*
C22C 38/46 *(2006.01)*
C22C 38/52 *(2006.01)*

(86) International application number:
PCT/JP2017/033008

(87) International publication number:
WO 2018/079111 (03.05.2018 Gazette 2018/18)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **25.10.2016 JP 2016208420**

(71) Applicant: **JFE Steel Corporation**
Tokyo 100-0011 (JP)

(72) Inventors:
- **ENDO Mami**
  Tokyo 100-0011 (JP)
- **EGUCHI Kenichiro**
  Tokyo 100-0011 (JP)
- **YUGA Masao**
  Tokyo 100-0011 (JP)

(74) Representative: **Grünecker Patent- und Rechtsanwälte**
PartG mbB
Leopoldstraße 4
80802 München (DE)

(54) SEAMLESS PIPE OF MARTENSITIC STAINLESS STEEL FOR OIL WELL PIPE, AND METHOD FOR PRODUCING SEAMLESS PIPE

(57) Provided herein is a martensitic stainless steel seamless pipe, intended for oil country tubular goods, having high strength, and excellent sulfide stress corrosion cracking resistance. A method for producing such a martensitic stainless steel seamless pipe is also provided. The martensitic stainless steel seamless pipe for oil country tubular goods has a composition that contains, in mass%, C: 0.035% or less, Si: 0.5% or less, Mn: 0.05 to 0.5%, P: 0.03% or less, S: 0.005% or less, Cu: 2. 6% or less, Ni: 5.3 to 7.3%, Cr: 11.8 to 14.5%, Al: 0.1% or less, Mo: 1.8 to 3.0%, V: 0.2% or less, N: 0.1% or less, and the balance Fe and unavoidable impurities, and in which C, Mn, Cr, Cu, Ni, Mo, W, Nb, N, and Ti satisfy the predetermined relations.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a martensitic stainless steel seamless pipe for use in oil country tubular goods used in oil well and gas well applications such as in crude oil wells and natural gas wells, and to a method for producing such a martensitic stainless steel seamless pipe. The invention particularly relates to improvement of corrosion resistance in a severe corrosive environment containing carbon dioxide gas (CO_2), chlorine ions (Cl^-), and the like, and improvement of sulfide stress corrosion cracking resistance (SSC resistance) in a hydrogen sulfide (H_2S)-containing environment.

Background Art

[0002] Rising crude oil prices, and the increasing shortage of petroleum resources have prompted active development of deep oil fields that were unthinkable in the past, and oil fields and gas fields of a severe corrosive environment containing carbon dioxide gas, chlorine ions, and hydrogen sulfide. Steel pipes for oil country tubular goods (OCTG) intended for such an environment need to be made of materials having high strength, and excellent corrosion resistance.

[0003] Oil country tubular goods used for mining of oil fields and gas fields of an environment containing CO_2 gas, Cl^-, and the like often use 13% Cr martensitic stainless steel pipes. In order to meet the increasing demand for higher SSC resistance arising out of the world-wide development of oil fields of a severe corrosive environment containing hydrogen sulfide, there has been increasing use of modified 13% Cr martensitic stainless steel pipes containing a reduced carbon content, and increased Ni and Mo contents.

[0004] PTL 1 discloses a 13% Cr steel basic composition containing Ni, Mo, and Cu, and a much smaller carbon content than in traditional compositions. These elements are contained to satisfy $Cr + 2Ni + 1.1Mo + 0.7Cu \leq 32.5$, and $Nb + V \geq 0.05\%$ for at least one of Nb: 0.20% or less, and V: 0.20% or less. The composition is described as being capable of providing high strength with a yield strength of 965 MPa or more, and high toughness with a Charpy absorption energy at -40°C of 50 J or more, in addition to desirable corrosion resistance.

[0005] PTL 2 describes a 13% Cr martensitic stainless steel pipe having an extremely low carbon content of 0.015% or less, and a Ti content of 0.03% or more. With such a composition, the 13% Cr martensitic stainless steel pipe can have high strength with a yield stress in the order of 95 ksi (655 to 758 MPa), low hardness with a Rockwell hardness HRC of less than 27, and excellent SSC resistance. PTL 3 describes a martensitic stainless steel that satisfies $6.0 \leq Ti/C \leq 10.1$, where Ti/C has a correlation with a value obtained by subtracting the yield stress from the tensile stress. The technique described in this publication can produce a value of 20.7 MPa or more as the difference of the yield stress from the tensile stress, and can reduce the hardness variation, which deteriorates the SSC resistance.

[0006] PTL 4 describes a martensitic stainless steel containing a specified amount of molybdenum satisfying $Mo \geq 2.3-0.89Si + 32.2C$, and having a metal structure that is configured primarily from tempered martensite, carbides that have precipitated during tempering, and intermetallic compounds, such as the Laves phase and the δ phase, that have finely precipitated during tempering. The technique described in this publication can achieve high strength with a 0.2% proof stress of 860 MPa or more, and excellent carbon dioxide corrosion resistance, and excellent sulfide stress corrosion cracking resistance.

Citation List

Patent Literature

[0007]

PTL 1: JP-A-2007-332442
PTL 2: JP-A-2010-242163
PTL 3: WO2008/023702
PTL 4: WO2004/057050

Summary of Invention

Technical Problem

[0008] Recent oil fields and gas fields are developed in severe corrosive environments containing CO_2, Cl^-, and H_2S. There are also rising concerns over increased H_2S concentrations due to aging. The oil country tubular goods used in these environments are thus required to have excellent sulfide stress corrosion cracking resistance (SSC resistance), in addition to carbon dioxide corrosion resistance. The technique of PTL 1 is described as providing excellent carbon dioxide corrosion resistance. However, there is no investigation of sulfide stress corrosion cracking resistance, and the technique cannot be said as providing the level of corrosion resistance that can withstand a severe corrosive environment.

[0009] It is stated in PTL 2 that sulfide stress corrosion cracking resistance can be maintained under an applied stress of 655 MPa in an atmosphere of a 5% NaCl aqueous solution (H_2S: 0.10 bar) with an adjusted pH of 3.5. PTL 3 describes providing sulfide stress corrosion cracking resistance in an atmosphere of a 20% NaCl aqueous solution (H_2S: 0.03 atm, CO_2 balance.) with an adjusted pH of 4.5. PTL 4 describes providing sulfide stress corrosion cracking resistance in an atmosphere of a 25% NaCl aqueous solution (H_2S: 0.003 MPa, CO_2 balance.) with an adjusted pH of 4.0. However, these techniques do not investigate sulfide stress corrosion cracking resistance in other atmospheres, and cannot be said as providing the level of sulfide stress corrosion cracking resistance that can withstand the today's more severe corrosive environments.

[0010] It is accordingly an object of the present invention to provide a martensitic stainless steel seamless pipe having high strength, and excellent sulfide stress corrosion cracking resistance, intended for oil country tubular goods. The invention is also intended to provide a method for producing such a martensitic stainless steel seamless pipe for oil country tubular goods.

[0011] As used herein, "high-strength" means a yield stress of 758 MPa (110 ksi) or more. Preferably, the yield stress is 896 MPa or less.

[0012] As used herein, "excellent sulfide stress corrosion cracking resistance" means that a test piece dipped in a test solution (a 0.165 mass% NaCl aqueous solution; liquid temperature: 25°C, H_2S: 1 bar, CO_2 balance) having an adjusted pH of 3.5 with addition of sodium acetate and hydrochloric acid does not crack even after 720 hours under an applied stress equal to 90% of the yield stress.

Solution to Problem

[0013] In order to achieve the foregoing objects, the present inventors conducted intensive studies of various alloy elements in a basic composition of a 13% Cr stainless steel pipe with regard to the effects of these elements on sulfide stress corrosion cracking resistance (SSC resistance) in a corrosive environment containing CO_2, Cl^-, and H_2S. As a result of the investigation, the present inventors have found that a martensitic stainless steel seamless pipe for oil country tubular goods having the desired strength, and excellent SSC resistance in a CO_2-, Cl^--, and H_2S-containing corrosive environment under an applied stress close to the yield stress can be produced when a composition containing C, Mn, Cr, Cu, Ni, Mo, W, Nb, N, and Ti in adjusted amounts that satisfy appropriate relations and ranges is subjected to appropriate quenching and tempering treatments.

[0014] The present invention was completed on the basis of these findings after further studies, and the gist of the invention is as follows.

[1] A martensitic stainless steel seamless pipe for oil country tubular goods,
the martensitic stainless steel seamless pipe having a composition that comprises, in mass%, C: 0.035% or less, Si: 0.5% or less, Mn: 0.05 to 0.5%, P: 0.03% or less, S: 0.005% or less, Cu: 2.6% or less, Ni: 5.3 to 7.3%, Cr: 11.8 to 14.5%, Al: 0.1% or less, Mo: 1.8 to 3.0%, V: 0.2% or less, N: 0.1% or less, and the balance Fe and unavoidable impurities, and that satisfies the following formula (4) with the following formulae (1), (2), and (3),
the martensitic stainless steel seamless pipe having a yield stress of 758 MPa or more.

Formula (1)

$$-109.37C + 7.307Mn + 6.399Cr + 6.329Cu + 11.343Ni - 13.529Mo + 1.276W + 2.925Nb + 196.775N - 2.621Ti - 120.307$$

Formula (2)

$$-0.0278Mn + 0.0892Cr + 0.00567Ni + 0.153Mo - 0.0219W - 1.984N + 0.208Ti - 1.83$$

Formula (3)

$$-1.324C + 0.0533Mn + 0.0268Cr + 0.0893Cu + 0.00526Ni + 0.0222Mo - 0.0132W - 0.473N - 0.5Ti - 0.514,$$

In the formulae (1) to (3), C, Mn, Cr, Cu, Ni, Mo, W, Nb, N, and Ti represent the content of each element in mass% (the content being 0 (zero) percent for elements that are not contained).

Formula (4)

$$-10 \leq \text{formula (1)} \leq 45,\ -0.25 \leq \text{formula (2)} \leq -0.20,\ \text{and}\ 0.10 \leq \text{formula (3)} \leq 0.20$$

[2] The martensitic stainless steel seamless pipe for oil country tubular goods according to item [1], wherein the composition further comprises, in mass%, at least one selected from Ti: 0.19% or less, Nb: 0.25% or less, W: 1.1% or less, and Co: 0.45% or less.

[3] A method for producing the martensitic stainless steel seamless pipe for oil country tubular goods of item [1] or [2], the method comprising:

making a steel pipe out of a steel pipe material;
subjecting the steel pipe to quenching in which the steel pipe is heated to a temperature equal to or greater than the Ac_3 transformation point, and air cooled to a cooling stop temperature of 100°C or less at a cooling rate of 0.1°C/s or more; and
tempering the steel pipe at a temperature equal to or less than the Ac_1 transformation point.

Advantageous Effects of Invention

[0015] The present invention can produce a martensitic stainless steel seamless pipe for oil country tubular goods having excellent sulfide stress corrosion cracking resistance (SSC resistance) in a CO_2-, Cl^--, and H_2S-containing corrosive environment, and high strength with a yield stress YS of 758 MPa (110 ksi) or more.

Description of Embodiments

[0016] A seamless stainless steel pipe of the present invention is a martensitic stainless steel seamless pipe for oil country tubular goods. The martensitic stainless steel seamless pipe has a composition that contains, in mass%, C: 0.035% or less, Si: 0.5% or less, Mn: 0.05 to 0.5%, P: 0.03% or less, S: 0.005% or less, Cu: 2.6% or less, Ni: 5.3 to 7.3%, Cr: 11.8 to 14.5%, Al: 0.1% or less, Mo: 1.8 to 3.0%, V: 0.2% or less, N: 0.1% or less, and the balance Fe and unavoidable impurities, and that satisfies the following formula (4), (5), or (6) with the following formulae (1), (2), and (3). The martensitic stainless steel seamless pipe has a yield stress of 758 MPa or more.

Formula (1)

$$-109.37C + 7.307Mn + 6.399Cr + 6.329Cu + 11.343Ni - 13.529Mo + 1.276W + 2.925Nb + 196.775N - 2.621Ti - 120.307$$

Formula (2)

$$-0.0278Mn + 0.0892Cr + 0.00567Ni + 0.153Mo - 0.0219W - 1.984N + 0.208Ti - 1.83$$

Formula (3)

$$-1.324C + 0.0533Mn + 0.0268Cr + 0.0893Cu + 0.00526Ni + 0.0222Mo - 0.0132W - 0.473N - 0.5Ti - 0.514$$

[0017] In the formulae (1) to (3), C, Mn, Cr, Cu, Ni, Mo, W, Nb, N, and Ti represent the content of each element in mass% (the content being 0 (zero) percent for elements that are not contained).

Formula (4)

$$-10 \leq \text{formula (1)} \leq 45,\ -0.25 \leq \text{formula (2)} \leq -0.20,\ \text{and}\ 0.10 \leq \text{formula (3)} \leq 0.20$$

Formula (5)

$$-10 \leq \text{formula (1)} \leq 5,\ -0.35 \leq \text{formula (2)} \leq -0.25,\ \text{and}\ 0.025 \leq \text{formula (3)} \leq 0.10$$

Formula (6)

$$-10 \leq \text{formula (1)} \leq -5,\ -0.39 \leq \text{formula (2)} \leq -0.35,\ \text{and}\ -0.15 \leq \text{formula (3)} \leq 0.025$$

[0018] The reasons for specifying the composition of the steel pipe of the present invention are as follows . In the following, "%" means percent by mass, unless otherwise specifically stated.

C: 0.035% or Less

[0019] Carbon is an important element involved in the strength of the martensitic stainless steel, and effectively improves the strength. However, a carbon content of more than 0.035% makes the hardness excessively high, and increases the sensitivity to sulfide stress corrosion cracking. For this reason, the C content is limited to 0.035% or less in the present invention. Preferably, the C content is 0.015% or less. More preferably, the C content is 0.0090% or less. Further preferably, the C content is 0.0075% or less. Desirably, carbon is contained in an amount of 0.005% or more to provide the desired strength.

Si: 0.5% or Less

[0020] Silicon acts as a deoxidizing agent, and should be contained in an amount of 0.05% or more. A Si content of more than 0.5% deteriorates carbon dioxide corrosion resistance and hot workability. For this reason, the Si content is limited to 0.5% or less. The lower limit of Si content is preferably 0.10% or more, and the upper limit of Si content is preferably 0.30% or less.

Mn: 0.05 to 0.5%

[0021] Manganese is an element that improves hot workability, and is contained in an amount of 0.05% or more. When contained in excess of 0.5%, the effect becomes saturated, and this leads to increased cost. For this reason, the Mn content is limited to 0.05 to 0.5%. Preferably, the Mn content is 0.40% or less.

P: 0.03% or Less

[0022] Phosphorus is an element that deteriorates carbon dioxide corrosion resistance, pitting corrosion resistance, and sulfide stress corrosion cracking resistance, and should be contained in as small an amount as possible in the present invention. However, an excessively small P content leads to increased manufacturing cost. The P content is therefore limited to 0.03% or less, a content that does not bring about an excessive loss of characteristics, and that is industrially feasible in terms of cost. Preferably, the P content is 0.02% or less.

S: 0.005% or Less

[0023] Sulfur is an element that seriously deteriorates hot workability, and should desirably be contained in as small an amount as possible. A S content of 0.005% or less enables pipe production using common procedures, and accordingly the S content is limited to 0.005% or less in the present invention. Preferably, the S content is 0.003% or less.

Cu: 2.6% or Less

[0024] Copper adds strength to the protective coating, and improves sulfide stress corrosion cracking resistance. However, a Cu content of more than 2.6% causes precipitation of CuS, and deteriorates hot workability. For this reason, the Cu content is limited to 2.6% or less. The lower limit of Cu content is preferably 0.5% or more, and the upper limit of Cu content is preferably 2.0% or less.

Ni: 5.3 to 7.3%

[0025] When contained in an amount of 5.3% or more, nickel adds strength to the protective coating, and improves corrosion resistance. Nickel also forms a solid solution, and increases the steel strength in this content range. A Ni content of more than 7.3% makes the martensite phase unstable, and the strength deteriorates. For this reason, the Ni content is limited to 5.3 to 7.3%. Preferably, the Ni content is 5.7% or more, more preferably 6.0% or more.

Cr: 11.8 to 14.5%

[0026] Chromium is an element that forms a protective coating, and improves the corrosion resistance. Chromium provides the corrosion resistance necessary for oil country tubular goods applications when contained in an amount of 11.8% or more. A Cr content or more than 14.5% facilitates ferrite generation, and the martensite phase cannot remain stable. For this reason, the Cr content is limited to 11.8 to 14.5%. The lower limit of Cr content is preferably 12.0% or more, and the upper limit of Cr content is preferably 13.5% or less.

Al: 0.1% or Less

[0027] Aluminum acts as a deoxidizing agent. An Al content of 0.01% or more effectively provides this effect. Because an Al content of more than 0.1% adversely affects toughness, the Al content is limited to 0.1% or less in the present invention. Preferably, the Al content is 0.01 to 0.03%.

Mo: 1.8 to 3.0%

[0028] Molybdenum is an element that improves the pitting corrosion resistance caused by Cl^-. Molybdenum needs to be contained in an amount of 1.8% or more to obtain the corrosion resistance necessary for a severe corrosive environment. The effect becomes saturated when the Mo content is more than 3.0%. Molybdenum is also an expensive element, and increases the manufacturing cost. For these reasons, the Mo content is limited to 1.8 to 3.0%. The lower limit of Mo content is preferably 2.4% or more, and the upper limit of Mo content is preferably 2.9% or less.

V: 0.2% or Less

[0029] Vanadium is contained in an amount of desirably 0.01% or more, in order to improve steel strength by precipitation strengthening, and to improve sulfide stress corrosion cracking resistance. A V content of more than 0.2% deteriorates toughness, and the V content is limited to 0.2% or less in the present invention. The lower limit of V content is preferably 0.01% or more, and the upper limit of V content is preferably 0.08% or less.

N: 0.1% or Less

[0030] Nitrogen is an element that greatly improves the pitting corrosion resistance. However, a N content of more than 0.1% causes formation of various nitrides, and deteriorates toughness. For this reason, the N content is limited to 0.1% or less in the present invention. Preferably, the N content is 0.003% or more. The lower limit of N content is more preferably 0.004% or more, further preferably 0.005% or more. The upper limit of N content is more preferably 0.08% or less, further preferably 0.05% or less.

[0031] In the present invention, C, Mn, Cr, Cu, Ni, Mo, W, Nb, N, and Ti are contained in the foregoing ranges, and these are contained so as to satisfy the formula (4), (5), or (6) with the formulae (1), (2), and (3) below. Formula (1) is a formula that correlates with the residual γ amount. By making the calculated value of formula (1) smaller, the residual austenite is reduced, and the hardness reduces, with the result that the sulfide stress corrosion cracking resistance improves. Formula (2) is a formula that correlates with the repassivation potential. Regeneration of the passivation coating occurs more easily, and repassivation improves by containing C, Mn, Cr, Cu, Ni, Mo, W, Nb, N, and Ti in such amounts that formula (1) yields a value that satisfies the range of formula (4), (5), or (6), and by containing Mn, Cr, Cu, Ni, Mo, W, N, and Ti in such amounts that formula (2) yields a value that satisfies the range of formula (4), (5), or (6). Formula (3) is a formula that correlates with the pitting corrosion potential. Pitting corrosion, which becomes an origin of sulfide stress corrosion cracking, can be suppressed, and the sulfide stress corrosion cracking resistance greatly improves by containing C, Mn, Cr, Cu, Ni, Mo, W, N, and Ti in such amounts that formula (3) yields a value that satisfies the range of formula (4), (5), or (6) . With the calculated value of formula (1) satisfying the range of formula (4), the hardness increases when the calculated value of formula (1) is 10 or more. However, regeneration of a passivation coating occurs more prominently, and the pitting corrosion can be suppressed more effectively when the calculated values of formulae (2) and (3) satisfy the range of formula (4). This improves the sulfide stress corrosion cracking resistance.

[0032] The calculated value of formula (1) is preferably 5 to 45 in the following formula (4), and is preferably -5 to 5 in the following formula (5).

Formula (1)

$$-109.37C + 7.307Mn + 6.399Cr + 6.329Cu + 11.343Ni - 13.529Mo + 1.276W + 2.925Nb + 196.775N - 2.621Ti - 120.307$$

Formula (2)

$$-0.0278Mn + 0.0892Cr + 0.00567Ni + 0.153Mo - 0.0219W - 1.984N + 0.208Ti - 1.83$$

Formula (3)

$$-1.324C + 0.0533Mn + 0.0268Cr + 0.0893Cu + 0.00526Ni + 0.0222Mo - 0.0132W - 0.473N - 0.5Ti - 0.514$$

[0033] In the formulae (1) to (3), C, Mn, Cr, Cu, Ni, Mo, W, Nb, N, and Ti represent the content of each element in mass% (the content is 0 (zero) percent for elements that are not contained)

Formula (4)

$$-10 \leq \text{formula (1)} \leq 45,\ -0.25 \leq \text{formula (2)} \leq -0.20, \text{ and } 0.10 \leq \text{formula (3)} \leq 0.20$$

Formula (5)

$$-10 \leq \text{formula (1)} \leq 5,\ -0.35 \leq \text{formula (2)} \leq -0.25, \text{ and } 0.025 \leq \text{formula (3)} \leq 0.10$$

Formula (6)

$$-10 \leq \text{formula (1)} \leq -5,\ -0.39 \leq \text{formula (2)} \leq -0.35, \text{ and } -0.15 \leq \text{formula (3)} \leq 0.025$$

[0034] In addition to the foregoing components, the composition contains the balance Fe and unavoidable impurities. The foregoing basic composition may further contain one or more selectable elements selected from Ti: 0.19% or less, Nb: 0.25% or less, W: 1.1% or less, and Co: 0.45% or less, as needed.

[0035] Titanium and niobium form carbides, and can reduce the solid-solution carbon. This makes it possible to reduce hardness. Excessively high Ti and Nb contents may deteriorate toughness, and the Ti and Nb contents are limited to 0.19% or less for Ti, and 0.25% or less for Nb when containing these elements.

[0036] Tungsten and cobalt are elements that improve the pitting corrosion resistance. However, excessively high W and Co contents may deteriorate toughness, and increase the material cost. For this reason, the W and Co contents are limited to 1.1% or less for W, and 0.45% or less for Co when containing these elements.

[0037] A preferred method for producing the martensitic stainless steel seamless pipe for oil country tubular goods of the present invention is described below.

[0038] The present invention uses a steel pipe material of the composition described above. The method of production of the steel pipe material, or a seamless stainless steel pipe, is not particularly limited, and any known seamless steel pipe production method may be used.

[0039] Preferably, a molten steel of the foregoing composition is made into steel using a steel making process such as by using a converter furnace, and formed into a steel pipe material, for example, a billet, using a method such as continuous casting, and ingot casting-slab rolling. The steel pipe material is heated, and hot worked using a known pipe manufacturing process, for example, such as the Mannesmann-plug mill process, and the Mannesmann-mandrel mill process to produce a seamless steel pipe of the foregoing composition.

[0040] The process that follows the production of the steel pipe from the steel pipe material is not particularly limited. Preferably, the steel pipe is subjected to quenching, in which the steel pipe is heated to a temperature equal to or greater than the Ac_3 transformation point, and air cooled to a cooling stop temperature of 100°C or less at a cooling rate of 0.1°C/s or more, and this is followed by tempering at a temperature equal to or less than the Ac_1 transformation point.

Quenching

[0041] In the present invention, the steel pipe is subjected to quenching, in which the steel pipe is reheated to a temperature equal to or greater than the Ac_3 transformation point, maintained for preferably at least 5 min, and air cooled to a cooling stop temperature of 100°C or less. This produces a fine martensite phase, and high toughness. When the quenching heating temperature is less than the Ac_3 transformation point, heating cannot be made in the single austenite phase region, and a sufficient martensite structure cannot be obtained in the subsequent cooling. In this case, the desired high strength cannot be obtained. For this reason, the quenching heating temperature is limited to a temperature equal to or greater than the AC_3 transformation point. Here, "air cooling" means a cooling rate of 0.1°C/s or more.

Tempering

[0042] Quenching of the steel pipe is followed by tempering. The tempering is a process by which the steel pipe is heated to a temperature equal to or less than the Ac_1 transformation point, maintained for preferably at least 10 min, and air cooled. When the tempering temperature is higher than the Ac_1 transformation point, the martensite phase precipitates after the tempering, and it is not possible to obtain the desired high toughness and excellent corrosion resistance. For this reason, the tempering temperature is limited to a temperature equal to or less than the Ac_1 transformation point. The Ac_3 transformation point (°C), and the Ac_1 transformation point (°C) can be measured by a Formaster test, in which the test piece is given a heating and cooling temperature history, and the transformation point is detected from a small displacement due to expansion and contraction.

Examples

[0043] The present invention is further described below through Examples.

[0044] Molten steels of the compositions shown in Table 1 were made into steel with a converter furnace, and cast into billets (steel pipe material) by continuous casting. The steel pipe material was then hot worked with a model seamless rolling machine, and air cooled (cooling rate of 0.5°C/s) to produce a seamless steel pipe measuring 83.8 mm in outer diameter and 12.7 mm in wall thickness.

[0045] The seamless steel pipe was cut to obtain a test material, which was then subjected to quenching and tempering under the conditions shown in Table 2. A test piece for structure observation was collected from the quenched and tempered test material, and was polished, and measured for residual austenite (γ) amount by an X-ray diffraction method.

[0046] Specifically, the diffraction X-ray integral intensities of the γ (220) plane and the α (211) plane were measured. The results were then converted using the following equation.

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

[0047] In the equation, Ia represents the integral intensity of α, Rα represents a crystallographic theoretical value for α, Iγ represents the integral intensity of γ, and Rγ represents a crystallographic theoretical value for γ.

[0048] A strip specimen specified by API standard 5CT was collected from the quenched and tempered test material, and subjected to a tensile test according to the API specifications to determine its tensile characteristics (yield stress YS, tensile stress TS). The Ac_3 point (°C)and the Ac_1 point (°C) shown in Table 2 were measured by conducting a Formaster test for a test piece (measuring 4 mm in diameter $\phi \times$ 10 mm) collected from the quenched test material. Specifically, the test piece was heated to 500°C at 5°C/s, maintained for 10 minutes after raising the temperature to 920°C at 0.25°C/s, and cooled to room temperature at 2°C/s. The Ac_3 point (°C) and the Ac_1 point (°C) were found by detecting the expansion and contraction of the test piece with the temperature history.

[0049] The SSC test was conducted according to NACE TM0177, Method A. The test environment was created by using a 0.165 mass% NaCl test solution after adjusting the solution pH to 3.5 by addition of 0.41 g/L of CH_3COONa and HCl, and the test was conducted under a hydrogen sulfide partial pressure of 0.1 MPa, and an applied stress equal to 90% of the yield stress.

[0050] The results are presented in Table 2.

[Table 1]

Steel No.	Composition (mass%)																Applied formula (*4)	Remarks
	C	Si	Mn	P	S	Cu	Ni	Cr	Al	Mo	V	N	Ti, Nb, W, Co	Value of formula (1) (*1)	Value of formula (2) (*2)	Value of formula (3) (*3)		
A	0.0088	0.205	0.11	0.013	0.0009	2.04	7.25	14.16	0.052	2.513	0.010	0.0471	Nb: 0.091	40.8	-0.238	0.114	(4)	Compliant Example
B	0.0075	0.200	0.45	0.015	0.0010	2.50	6.40	13.30	0.020	2.600	0.015	0.0085	Ti: 0.025, Nb: 0.08	22.4	-0.234	0.155	(4)	Compliant Example
C	0.0075	0.200	0.40	0.015	0.0010	2.40	6.25	13.20	0.020	2.550	0.015	0.0085	Ti:0.05, Nb: 0.01	19.4	-0.245	0.126	(4)	Compliant Example
D	0.0075	0.200	0.40	0.015	0.0010	1.80	6.00	12.30	0.040	2.850	0.015	0.0075	Ti:0.05, Nb: 0.005	2.8	-0.278	0.054	(5)	Compliant Example
E	0.0075	0.200	0.40	0.015	0.0010	0.40	5.70	12.00	0.040	2.550	0.015	0.0075	Ti:0.05, Nb: 0.005	-7.4	-0.353	-0.087	(6)	Compliant Example
F	0.0075	0.200	0.40	0.015	0.0010	1.60	5.70	12.20	0.040	2.600	0.015	0.0075	Ti:0.05, Nb: 0.005	0.8	-0.327	0.026	(5)	Compliant Example
G	0.0075	0.204	0.41	0.015	0.0009	2.40	6.24	13.22	0.020	2.553	0.015	0.0043	-	18.7	-0.245	0.154	(4)	Compliant Example
H	0.0059	0.198	0.41	0.014	0.0010	1.81	5.99	12.32	0.042	2.850	0.014	0.0065	-	3.0	-0.285	0.084	(5)	Compliant Example
I	0.0063	0.200	0.40	0.015	0.0009	0.41	5.71	12.02	0.043	2.552	0.014	0.0066	-	-7.0	-0.359	-0.059	(6)	Compliant Example
J	0.0076	0.210	0.45	0.014	0.0011	2.51	6.40	13.30	0.020	2.605	0.015	0.0032	W:0.16	21.3	-0.231	0.168	(4)	Compliant Example
K	0.0072	0.195	0.40	0.013	0.0010	0.39	5.71	12.00	0.042	2.550	0.016	0.0074	Co:0.2	-7.2	-0.363	-0.063	(6)	Compliant Example

(continued)

Steel No.	Composition (mass%)																Applied formula (*4)	Remarks
	C	Si	Mn	P	S	Cu	Ni	Cr	Al	Mo	V	N	Ti, Nb, W, Co	Value of formula (1) (*1)	Value of formula (2) (*2)	Value of formula (3) (*3)		
L	0.0069	0.189	0.42	0.014	0.0009	1.95	6.34	12.57	0.046	2.555	0.018	0.0070	-	13.5	-0.307	0.097	(4)	Comparative Example
M	0.0080	0.192	0.11	0.013	0.0009	2.03	7.21	12.32	0.052	2.529	0.013	0.0067	-	20.2	-0.320	0.084	(4)	Comparative Example
N	0.0060	0.195	0.10	0.012	0.0008	2.00	7.16	12.38	0.043	2.519	0.014	0.0064	-	20.0	-0.315	0.084	(4)	Comparative Example
O	0.0064	0.216	0.21	0.018	0.0011	0.01	5.85	12.62	0.044	2.179	0.018	0.0056	-	-0.7	-0.355	-0.096	(5)	Comparative Example
P	0.0072	0.223	0.20	0.014	0.0011	0.01	5.98	12.04	0.037	2.168	0.018	0.0076	-	-2.5	-0.411	-0.113	(6)	Comparative Example

The balance is Fe and unavoidable impurities

(*1) Formula (1): -109.37C+7.307Mn+6.399Cr+6.329Cu+11,343Ni-13.529Mo+1,276W+2.925Nb+196.775N-2.621Ti-120.307

(*2) Formula (2): -0.0278Mn+0.0892Cr+0.00567Ni+0.153Mo-0.0219W-1.984N+0.208Ti-1.83

(*3) Formula (3): -1.324C+0.0533Mn+0.0268Cr+0.0893Cu+0.00526Ni+0.0222Mo-0.0132W-0.473N-0.5Ti-0.514

(*4) The formula used for determination

Formula (4): -10 ≤ formula (1) ≤ 45, -0.25 ≤ formula (2) ≤ -0.20, and 0.10 ≤ formula (3) ≤ 0.20

Formula (5): -10 ≤ formula (1) ≤ 5, -0.35 ≤ formula (2) ≤ -0.25, and 0.025 ≤ formula (3) ≤ 0.10

Formula (6): -10 ≤ formula (1) ≤ -5, -0.39 ≤ formula (2) ≤ -0.35, and -0.15 ≤ formula (3) ≤ 0.025

[Table 2]

Steel pipe No.	Steel No.	Quenching					Tempering			Structure	Tensile characteristics		SSC resistance test	Remarks
		Ac_3 point (°C)	Heating temperature (°C)	Holding time (min)	Cooling	Cooling stop temperature (°C)	Ac_1 point (°C)	Heating temperature (°C)	Holding time (min)	Residual γ (*1) (volume%)	Yield stress YS (MPa)	Tensile stress TS (MPa)	Cracking	
1	A	750	920	20	Air cooling	25	640	615	60	43.5	835	986	Absent	Present Example
2	B	750	920	20	Air cooling	25	645	625	60	25.6	828	952	Absent	Present Example
3	C	755	920	20	Air cooling	25	635	630	60	21.7	851	967	Absent	Present Example
4	D	750	920	20	Air cooling	25	630	615	60	5.3	846	929	Absent	Present Example
5	E	755	920	20	Air cooling	25	660	565	60	0.0	829	864	Absent	Present Example
6	F	745	920	20	Air cooling	25	635	625	60	2.4	863	892	Absent	Present Example
7	G	755	920	20	Air cooling	25	635	625	60	22.1	830	964	Absent	Present Example
8	H	750	920	20	Air cooling	25	625	615	60	6.3	851	903	Absent	Present Example
9	I	755	920	20	Air cooling	25	655	600	60	0.0	832	871	Absent	Present Example
10	J	750	920	20	Air cooling	25	640	605	60	24.2	842	975	Absent	Present
11	K	750	920	20	Air cooling	25	660	610	60	0.0	836	862	Absent	Example
12	L	755	990	20	Air cooling	25	630	605	60	15.3	906	1009	Present	Comparative Example

(continued)

Steel pipe No.	Steel No.	Quenching					Tempering			Structure	Tensile characteristics		SSC resistance test	Remarks
		Ac_3 point (°C)	Heating temperature (°C)	Holding time (min)	Cooling	Cooling stop temperature (°C)	Ac_1 point (°C)	Heating temperature (°C)	Holding time (min)	Residual γ (*1) (volume%)	Yield stress YS (MPa)	Tensile stress TS (MPa)	Cracking	
13	M	720	920	20	Air cooling	25	625	620	60	24.1	835	965	Present	Comparative Example
14	N	730	930	20	Air cooling	25	620	600	60	23.5	859	958	Present	Comparative Example
15	O	740	920	20	Air cooling	25	660	595	60	0.1	852	885	Present	Comparative Example
16	P	730	920	20	Air cooling	25	630	590	60	0.0	847	880	Present	Comparative Example
17	A	750	730	20	Air cooling	25	640	615	60	49.8	792	866	Present	Comparative Example
18	C	755	920	20	Air cooling	25	635	650	60	34.6	772	811	Present	ComparativeExample

(*1) Residual γ: Residual austenite

[0051] The martensitic stainless steel seamless pipes of the present examples all had high strength with a yield stress of 758 MPa or more, and excellent SSC resistance that did not involve cracking even under the applied stress in the H_2S environment. Comparative Examples outside the range of the present invention did not show excellent SSC resistance, though the desired levels of high strength were obtained.

Claims

1. A martensitic stainless steel seamless pipe for oil country tubular goods,
the martensitic stainless steel seamless pipe having a composition that comprises, in mass%, C: 0.035% or less, Si: 0.5% or less, Mn: 0.05 to 0.5%, P: 0.03% or less, S: 0.005% or less, Cu: 2.6% or less, Ni: 5.3 to 7.3%, Cr: 11.8 to 14.5%, Al: 0.1% or less, Mo: 1.8 to 3.0%, V: 0.2% or less, N: 0.1% or less, and the balance Fe and unavoidable impurities, and that satisfies the following formula (4) with the following formulae (1), (2), and (3),
the martensitic stainless steel seamless pipe having a yield stress of 758 MPa or more.

Formula (1)

$$-109.37C + 7.307Mn + 6.399Cr + 6.329Cu + 11.343Ni - 13.529Mo + 1.276W + 2.925Nb + 196.775N - 2.621Ti - 120.307$$

Formula (2)

$$-0.0278Mn + 0.0892Cr + 0.00567Ni + 0.153Mo - 0.0219W - 1.984N + 0.208Ti - 1.83$$

Formula (3)

$$-1.324C + 0.0533Mn + 0.0268Cr + 0.0893Cu + 0.00526Ni + 0.0222Mo - 0.0132W - 0.473N - 0.5Ti - 0.514$$

In the formulae (1) to (3), C, Mn, Cr, Cu, Ni, Mo, W, Nb, N, and Ti represent the content of each element in mass% (the content being 0 (zero) percent for elements that are not contained).

Formula (4)

$$-10 \leq \text{formula (1)} \leq 45,\ -0.25 \leq \text{formula (2)} \leq -0.20, \text{ and } 0.10 \leq \text{formula (3)} \leq 0.20$$

2. The martensitic stainless steel seamless pipe for oil country tubular goods according to claim 1, wherein the composition further comprises, in mass%, at least one selected from Ti: 0.19% or less, Nb: 0.25% or less, W: 1.1% or less, and Co: 0.45% or less.

3. A method for producing the martensitic stainless steel seamless pipe for oil country tubular goods of claim 1 or 2, the method comprising:

making a steel pipe out of a steel pipe material;
subjecting the steel pipe to quenching in which the steel pipe is heated to a temperature equal to or greater than the Ac_3 transformation point, and air cooled to a cooling stop temperature of 100°C or less at a cooling rate of 0.1°C/s or more; and
tempering the steel pipe at a temperature equal to or less than the Ac_1 transformation point.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/033008

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl. C22C38/00(2006.01)i, C21D8/10(2006.01)i, C21D9/08(2006.01)i, C22C38/46(2006.01)i, C22C38/52(2006.01)i

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-C22C38/60, 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	1971-2017
Registered utility model specifications of Japan	1996-2017
Published registered utility model applications of Japan	1994-2017

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 2006-144069 A (SUMITOMO METAL INDUSTRIES, LTD.) 08 June 2006, & US 2008/0213120 A1 & WO 2006/054430 A1 & EP 1826285 A1 & CN 100549204 C & CN 101061245 A	1-3
A	WO 2015/178022 A1 (JFE STEEL CORP.) 26 November 2015, & US 2017/0096722 A1 & EP 3121306 A1 & CN 106414785 A & MX 2016015099 A	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
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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
"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	Date of mailing of the international search report
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/033008

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/112353 A1 (JFE STEEL CORP.) 24 July 2014, & US 2015/0354022 A1 & EP 2947167 A1 & CN 104937126 A	1-3
A	JP 2012-136742 A (JFE STEEL CORP.) 19 July 2012, (Family: none)	1-3
A	JP 2003-3243 A (SUMITOMO METAL INDUSTRIES, LTD.) 08 January 2003 (Family: none)	1-3

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2007332442 A **[0007]**
- JP 2010242163 A **[0007]**
- WO 2008023702 A **[0007]**
- WO 2004057050 A **[0007]**