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

(11) **EP 4 286 542 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
06.12.2023 Bulletin 2023/49

(21) Application number: **22775695.4**

(22) Date of filing: **23.03.2022**

(51) International Patent Classification (IPC):
C21D 8/02 $^{(2006.01)}$ ***C21D 8/06*** $^{(2006.01)}$
C21D 8/10 $^{(2006.01)}$ ***C21D 9/08*** $^{(2006.01)}$
C22C 38/00 $^{(2006.01)}$ ***C22C 38/60*** $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
C21D 8/02; C21D 8/06; C21D 8/10; C21D 9/08;
C22C 38/00; C22C 38/60

(86) International application number:
PCT/JP2022/013603

(87) International publication number:
WO 2022/202913 (29.09.2022 Gazette 2022/39)

(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:
KH MA MD TN

(30) Priority: **24.03.2021 JP 2021050578**

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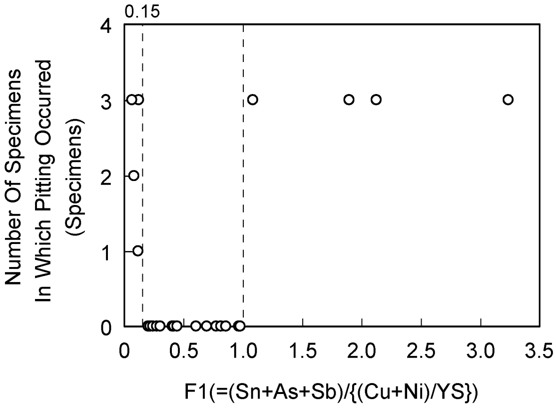
(54) MARTENSITE STAINLESS STEEL MATERIAL

(57) A martensitic stainless steel material that achieves both a high yield strength and excellent SSC resistance is provided. The martensitic stainless steel material according to the present disclosure consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cu: 0.01 to 3.50%, Cr: 10.00 to 14.00%, Ni: 4.50 to 7.50%, Mo: 1.00 to 4.00%, Ti: 0.050 to 0.300%, V: 0.01 to 1.00%, Al: 0.001 to 0.100%, Co: 0.010 to 0.500%, Ca: 0.0005 to 0.0050%, Sn: 0.0005 to 0.0500%, N: 0.0010 to 0.0500%, O: 0.050% or less, and the balance: Fe and impurities, and has a yield strength of 758 MPa or more. Within this range, the contents of elements and the yield strength satisfy Formula (1) described in the description.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a steel material, and more particularly relates to a martensitic stainless steel material.

BACKGROUND ART

[0002] The environments of oil wells and gas wells (hereinafter, oil wells and gas wells are collectively referred to as "oil wells") include environments which contain large amounts of corrosive substances. The corrosive substances are, for example, corrosive gases such as hydrogen sulfide (H_2S) gas and carbon dioxide (CO_2) gas. It is known that chromium (Cr) is effective for improving the carbonic-acid gas corrosion resistance of a steel material. Therefore, in an oil well in an environment containing a large amount of carbon dioxide gas, martensitic stainless steel materials containing about 13% by mass of Cr that are typified by API L80 13Cr steel material (normal 13Cr steel material) and Super 13Cr steel material in which the content of C is reduced are used according to the partial pressure and temperature of the carbon dioxide gas.

[0003] In recent years, with deeper oil wells, there is a demand to enhance the strength of steel materials for oil wells. Specifically, steel materials for oil wells of 80 ksi grade (yield strength is 80 to less than 95 ksi, that is, 552 to less than 655 MPa) and 95 ksi grade (yield strength is 95 to less than 110 ksi, that is, 655 to less than 758 MPa) are being widely utilized. Furthermore, recently steel materials for oil wells of 110 ksi grade or more (yield strength is 758 MPa or more) have also started to be demanded.

[0004] Here, in the present description, an environment containing hydrogen sulfide and carbon dioxide gas is referred to as a "sour environment". Steel materials for oil wells to be used in a sour environment are required to have sulfide stress cracking resistance (hereunder, referred to as "SSC resistance"). That is, in recent years, steel materials for oil wells are required to have both high strength and excellent SSC resistance.

[0005] Japanese Patent Application Publication No. 2000-192196 (Patent Literature 1), Japanese Patent Application Publication No. 2012-136742 (Patent Literature 2), and International Application Publication No. WO2008/023702 (Patent Literature 3) each proposes a steel material that has high strength and excellent SSC resistance.

[0006] The steel material proposed in Patent Literature 1 is a martensitic stainless steel for oil wells consisting of, in weight%, C: 0.001 to 0.05%, Si: 0.05 to 1%, Mn: 0.05 to 2%, P: 0.025% or less, S: 0.01% or less, Cr: 9 to 14%, Mo: 3.1 to 7%, Ni: 1 to 8%, Co: 0.5 to 7%, sol. Al: 0.001 to 0.1%, N: 0.05% or less, O (oxygen): 0.01% or less, Cu: 0 to 5%, and W: 0 to 5%, with the balance being Fe and unavoidable impurities. When a steel material contains Mo, the Ms point decreases. Therefore, because this steel material contains Co as well as Mo, a decrease in the Ms point is suppressed, and the microstructure is made a martensitic single-phase structure. It is described in Patent Literature 1 that, as a result, in this steel material, the SSC resistance can be increased while maintaining the strength at 80 ksi or more (552 MPa or more).

[0007] The steel material proposed in Patent Literature 2 is a martensitic stainless steel seamless pipe consisting of, in 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: 14.0 to 15.5%, Ni: 5.5 to 7.0%, Mo: 2.0 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, with the balance being Fe and unavoidable impurities. The steel material has a yield strength of 655 to 862 MPa, and a yield ratio of 0.90 or more. It is described in Patent Literature 2 that by setting the content of C to 0.01% or less, adjusting Cr, Ni and Mo to within a preferable range, and also containing suitable amounts of Cu and V or a suitable amount of W, excellent SSC resistance is obtained while also having a strength of 655 MPa or more.

[0008] The steel material proposed in Patent Literature 3 is a martensitic stainless steel that consists of, in mass%, C: 0.010 to 0.030%, Mn: 0.30 to 0.60%, P: 0.040% or less, S: 0.0100% or less, Cr: 10.00 to 15.00%, Ni: 2.50 to 8.00%, Mo: 1.00 to 5.00%, Ti: 0.050 to 0.250%, V: 0.25% or less, N: 0.07% or less, and one or more kinds of element among Si: 0.50% or less and Al: 0.10% or less, with the balance being Fe and impurities, and that satisfies the formula ($6.0 \leq Ti/C \leq 10.1$). The yield strength is 758 to 862 MPa. There is a correlation between a ratio (Ti/C) of the content of Ti to the content of C in the steel and a value obtained by subtracting the yield strength from the tensile strength. Further, when there are large hardness variations in a steel material, the SSC resistance of the steel material decreases. Therefore, it is described in Patent Literature 3 that in this steel material, by adjusting Ti/C to within a preferable range, hardness variations are suppressed and the yield strength is made 758 to 862 MPa.

CITATION LIST

PATENT LITERATURE

[0009]

Patent Literature 1: Japanese Patent Application Publication No. 2000-192196
Patent Literature 2: Japanese Patent Application Publication No. 2012-136742
Patent Literature 3: International Application Publication No. WO2008/023702

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0010] The aforementioned Patent Literatures 1 to 3 propose techniques for increasing the yield strength and improving the SSC resistance of a steel material. However, a martensitic stainless steel material that has excellent SSC resistance while also increasing the yield strength may be obtained by a technique other than the techniques proposed in the aforementioned Patent Literatures 1 to 3.

[0011] In addition, in recent years, oil wells with higher concentrations of hydrogen ions than in the past are being actively developed. In general, SSC is liable to occur in an environment in which there is a high hydrogen ion concentration (that is, the pH is low). Therefore, there is a need for a martensitic stainless steel material that has excellent SSC resistance even in a sour environment with a pH of 3.0 in which the hydrogen ion concentration is higher than has been the case in the past. However, the aforementioned Patent Literatures 1 to 3 contain no discussion regarding the SSC resistance of the steel materials in sour environments with a pH of 3.0.

[0012] An objective of the present disclosure is to provide a martensitic stainless steel material that can achieve both a high yield strength, and excellent SSC resistance in a sour environment with a pH of 3.0.

SOLUTION TO PROBLEM

[0013] A martensitic stainless steel material according to the present disclosure consists of, in mass%,

C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cu: 0.01 to 3.50%,
Cr: 10.00 to 14.00%,
Ni: 4.50 to 7.50%,
Mo: 1.00 to 4.00%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Al: 0.001 to 0.100%,
Co: 0.010 to 0.500%,
Ca: 0.0005 to 0.0050%,
Sn: 0.0005 to 0.0500%,
N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 0.50%,
Nb: 0 to 0.500%,
As: 0 to 0.0100%,
Sb: 0 to 0.0100%, and
the balance: Fe and impurities,
wherein:

a yield strength is 758 MPa or more; and
within a range of contents of elements and the yield strength of the martensitic stainless steel material, the contents of elements and the yield strength satisfy Formula (1);

$$0.15 \leq (\mathrm{Sn}+\mathrm{As}+\mathrm{Sb})/\{(\mathrm{Cu}+\mathrm{Ni})/\mathrm{YS}\} \leq 1.00 \qquad (1)$$

where, in Formula (1), a content of a corresponding element in percent by mass is substituted for each symbol of an element, and a yield strength in MPa is substituted for YS, and, if a corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] The martensitic stainless steel material according to the present disclosure can achieve both a high yield strength, and excellent SSC resistance in a sour environment with a pH of 3.0.

BRIEF DESCRIPTION OF DRAWING

[0015] [FIG. 1] FIG. 1 is a view illustrating the relation between F1 (= (Sn+As+Sb)/{(Cu+Ni)/YS}) and the number of specimens in which pitting occurred (specimens) that is an index of SSC resistance in the present Examples.

DESCRIPTION OF EMBODIMENTS

[0016] First, the present inventors conducted studies from the viewpoint of the chemical composition with respect to a martensitic stainless steel material that can achieve both a high yield strength, and excellent SSC resistance in a sour environment with a pH of 3.0. As a result, the present inventors considered that if a martensitic stainless steel material contains, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cu: 0.01 to 3.50%, Cr: 10.00 to 14.00%, Ni: 4.50 to 7.50%, Mo: 1.00 to 4.00%, Ti: 0.050 to 0.300%, V: 0.01 to 1.00%, Al: 0.001 to 0.100%, Co: 0.010 to 0.500%, Ca: 0.0005 to 0.0050%, N: 0.0010 to 0.0500%, O: 0.050% or less, W: 0 to 0.50%, and Nb: 0 to 0.500%, there is a possibility that both a yield strength of 758 MPa (110 ksi) or more, and excellent SSC resistance in a sour environment with a pH of 3.0 can be obtained.

[0017] Next, with respect to a martensitic stainless steel material containing the contents of elements described above, the present inventors conducted detailed studies regarding means for increasing the SSC resistance while maintaining a yield strength of 758 MPa or more. As a result, the present inventors discovered that in a martensitic stainless steel material containing the contents of elements described above, there is a possibility that tin (Sn), arsenic (As) and antimony (Sb), which are elements on which attention had not been focused heretofore, increases the SSC resistance. As a result of further detailed studies conducted by the present inventors, it has been found that in a martensitic stainless steel material containing the contents of elements described above, there is a possibility that Sn, in particular, markedly increases the SSC resistance, and that As and Sb assist the effect of increasing SSC resistance produced by Sn.

[0018] Therefore, the present inventors conducted detailed studies regarding contents of Sn, As and Sb that can sufficiently increase the SSC resistance of a martensitic stainless steel material. As a result, it has been clarified that, in addition to the contents of elements described above, by the martensitic stainless steel material according to the present embodiment also containing Sn in an amount of 0.0005 to 0.0500%, As in an amount of 0 to 0.0100%, and Sb in an amount of 0 to 0.0100%, the SSC resistance of the steel material can be increased. That is, if a martensitic stainless steel material consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cu: 0.01 to 3.50%, Cr: 10.00 to 14.00%, Ni: 4.50 to 7.50%, Mo: 1.00 to 4.00%, Ti: 0.050 to 0.300%, V: 0.01 to 1.00%, Al: 0.001 to 0.100%, Co: 0.010 to 0.500%, Ca: 0.0005 to 0.0050%, Sn: 0.0005 to 0.0500%, N: 0.0010 to 0.0500%, O: 0.050% or less, W: 0 to 0.50%, Nb: 0 to 0.500%, As: 0 to 0.0100%, and Sb: 0 to 0.0100%, with the balance being Fe and impurities, there is a possibility that both a yield strength of 758 MPa or more, and excellent SSC resistance in a sour environment with a pH of 3.0 can be obtained.

[0019] On the other hand, the present inventors have found that even in the case of a martensitic stainless steel material having the aforementioned chemical composition, when the martensitic stainless steel material has a yield strength of 758 MPa or more, there are some cases where the SSC resistance is not stably increased in a sour environment with a pH of 3.0. Therefore, with respect to a martensitic stainless steel material having the aforementioned chemical composition, the present inventors conducted detailed studies regarding means for increasing the SSC resistance in a sour environment with a pH of 3.0 while maintaining a yield strength of 758 MPa or more. As a result, the present inventors obtained the following findings.

[0020] It has been clarified as a result of the detailed studies conducted by the present inventors that in a martensitic stainless steel material having the aforementioned chemical composition and in which the yield strength is 758 MPa or more, if the contents of elements and the yield strength satisfy Formula (1), the SSC resistance of the steel material is markedly increased in a sour environment with a pH of 3.0.

$$0.15 \leq (Sn+As+Sb)/\{(Cu+Ni)/YS\} \leq 1.00 \qquad (1)$$

[0021] Where, in Formula (1), a content of a corresponding element in percent by mass is substituted for each symbol of an element, and a yield strength in MPa is substituted for YS. Note that, if a corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

[0022] Let F1 be defined as F1 = (Sn+As+Sb)/{(Cu+Ni)/YS}. As described above, As and Sb assist the effect of increasing the SSC resistance of the steel material produced by Sn. In addition, the SSC resistance of the steel material markedly increases by making a ratio of the contents of Sn, As and Sb to the contents of Cu and Ni fall within a certain range. On the other hand, the higher that the yield strength of the steel material is, the more that the SSC resistance of the steel material tends to decrease. Therefore, the denominator of F1 is set to a ratio of the contents of Cu and Ni to the yield strength. Thus, a ratio of the contents of Sn, As and Sb to the contents of Cu and Ni that is adjusted according to the yield strength is defined as F1. That is, F1 is an index of an increase in the SSC resistance in a sour environment with a pH of 3.0 obtained by a synergetic effect between Sn, As and Sb, and Cu and Ni that is adjusted according to the yield strength. The relation between F1 and the SSC resistance in a sour environment with a pH of 3.0 is described specifically hereunder using the accompanying drawing.

[0023] FIG. 1 is a view illustrating the relation between F1 and SSC resistance in the present Examples. FIG. 1 was created using F1 and the number of specimens in which pitting occurred (specimens) that is an index of SSC resistance, with respect to Examples which had the aforementioned chemical composition and in which the yield strength was 758 MPa or more among Examples that are described later. Note that, the number of specimens in which pitting occurred was obtained by performing an SSC resistance evaluation test that assumed a sour environment with a pH of 3.0, which will be described later.

[0024] Referring to FIG. 1, when F1 was too low, pitting occurred in one or more specimens. Similarly, when F1 was too high, pitting also occurred in one or more specimens. On the other hand, when F1 was within the range of 0.15 to 1.00, pitting did not occur in even one specimen. That is, referring to FIG. 1, in a steel material having the aforementioned chemical composition and in which the yield strength is 758 MPa or more, when F1 is within the range of 0.15 to 1.00, excellent SSC resistance is obtained in a sour environment with a pH of 3.0.

[0025] Note that, with respect to a steel material having the aforementioned chemical composition and a yield strength of 758 MPa or more, the detailed mechanism whereby the SSC resistance of the steel material in a sour environment with a pH of 3.0 is increased by adjusting F1 to within the range of 0.15 to 1.00 has not been clarified. However, as illustrated also in FIG. 1, the fact that the SSC resistance in a sour environment with a pH of 3.0 of a martensitic stainless steel material having the aforementioned chemical composition and a yield strength of 758 MPa or more is increased by adjusting F1 to within the range of 0.15 to 1.00 has been proven by the Examples.

[0026] As described above, the martensitic stainless steel material according to the present embodiment has the aforementioned chemical composition, has a yield strength of 758 MPa or more, and furthermore, within the ranges of the contents of the elements and the yield strength, the contents of the elements and the yield strength satisfy Formula (1). As a result, the martensitic stainless steel material according to the present embodiment can achieve both a high yield strength of 758 MPa or more, and excellent SSC resistance in a sour environment with a pH of 3.0.

[0027] The gist of the martensitic stainless steel material according to the present embodiment, which has been completed based on the above findings, is as follows.

[1] A martensitic stainless steel material consisting of, in mass%,

C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cu: 0.01 to 3.50%,
Cr: 10.00 to 14.00%,
Ni: 4.50 to 7.50%,
Mo: 1.00 to 4.00%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Al: 0.001 to 0.100%,
Co: 0.010 to 0.500%,
Ca: 0.0005 to 0.0050%,
Sn: 0.0005 to 0.0500%,

N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 0.50%,
Nb: 0 to 0.500%,
As: 0 to 0.0100%,
Sb: 0 to 0.0100%, and
the balance: Fe and impurities,
wherein:

a yield strength is 758 MPa or more; and
within a range of contents of elements and the yield strength of the martensitic stainless steel material, the contents of elements and the yield strength satisfy Formula (1);

$$0.15 \leq (\mathrm{Sn}+\mathrm{As}+\mathrm{Sb})/\{(\mathrm{Cu}+\mathrm{Ni})/\mathrm{YS}\} \leq 1.00 \qquad (1)$$

where, in Formula (1), a content of a corresponding element in percent by mass is substituted for each symbol of an element, and a yield strength in MPa is substituted for YS, and, if a corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

[2] The martensitic stainless steel material according to [1], containing one or more elements selected from a group consisting of:

W: 0.01 to 0.50%,
Nb: 0.001 to 0.500%,
As: 0.0001 to 0.0100%, and
Sb: 0.0001 to 0.0100%.

[0028] The shape of the martensitic stainless steel material according to the present embodiment is not particularly limited. The martensitic stainless steel material according to the present embodiment may be a pipe, may be a round steel bar (solid material), or may be a steel plate. Note that, the term "round steel bar" refers to a steel bar in which a cross section in a direction perpendicular to the axial direction is a circular shape. Further, the pipe may be a seamless pipe or may be a welded pipe.

[0029] Hereunder, the martensitic stainless steel material according to the present embodiment is described in detail. The symbol "%" in relation to an element means mass percent unless otherwise stated. Further, in the following description, the martensitic stainless steel material is also referred to as simply "steel material".

[Chemical composition]

[0030] The martensitic stainless steel material according to the present embodiment contains the following elements.

C: 0.030% or less

[0031] Carbon (C) is unavoidably contained. That is, the lower limit of the content of C is more than 0%. C increases hardenability of the steel material and increases strength of the steel material. On the other hand, if the content of C is too high, even if the contents of other elements are within the range of the present embodiment, strength of the steel material will be too high. As a result, the SSC resistance of the steel material will decrease. Therefore, the content of C is to be 0.030% or less. A preferable upper limit of the content of C is 0.028%, more preferably is 0.025%, further preferably is 0.020%, and further preferably is 0.018%. The content of C is preferably as low as possible. However, extremely reducing the content of C will increase the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of C is 0.001%, more preferably is 0.003%, and further preferably is 0.005%.

Si: 1.00% or less

[0032] Silicon (Si) is unavoidably contained. That is, the lower limit of the content of Si is more than 0%. Si deoxidizes the steel. On the other hand, if the content of Si is too high, even if the contents of other elements are within the range of the present embodiment, hot workability of the steel material will decrease. Therefore, the content of Si is to be 1.00%

or less. A preferable lower limit of the content of Si for effectively obtaining the aforementioned advantageous effect is 0.01%, more preferably is 0.05%, further preferably is 0.10%, and further preferably is 0.15%. A preferable upper limit of the content of Si is 0.80%, more preferably is 0.60%, further preferably is 0.50%, and further preferably is 0.45%.

Mn: 1.00% or less

[0033] Manganese (Mn) is unavoidably contained. That is, the lower limit of the content of Mn is more than 0%. Mn increases hardenability of the steel material and increases strength of the steel material. On the other hand, if the content of Mn is too high, even if the contents of other elements are within the range of the present embodiment, in some cases Mn will segregate at grain boundaries together with impurity elements such as P and S. In such a case, the SSC resistance of the steel material will decrease. Therefore, the content of Mn is to be 1.00% or less. A preferable lower limit of the content of Mn for effectively obtaining the aforementioned advantageous effect is 0.01%, more preferably is 0.05%, further preferably is 0.10%, and further preferably is 0.15%. A preferable upper limit of the content of Mn is 0.80%, more preferably is 0.70%, further preferably is 0.60%, and further preferably is 0.50%.

P: 0.030% or less

[0034] Phosphorus (P) is an impurity that is unavoidably contained. That is, the lower limit of the content of P is more than 0%. P segregates at grain boundaries and facilitates the occurrence of SSC. Therefore, if the content of P is too high, even if the contents of other elements are within the range of the present embodiment, the SSC resistance of the steel material will markedly decrease. Therefore, the content of P is to be 0.030% or less. A preferable upper limit of the content of P is 0.025%, more preferably is 0.020%, and further preferably is 0.018%. The content of P is preferably as low as possible. However, extremely reducing the content of P will raise the production cost. Accordingly, when taking industrial production into consideration, a preferable lower limit of the content of P is 0.001%, more preferably is 0.002%, and further preferably is 0.003%.

S: 0.0050% or less

[0035] Sulfur (S) is an impurity that is unavoidably contained. That is, the lower limit of the content of S is more than 0%. Similarly to P, S segregates at grain boundaries and facilitates the occurrence of SSC. Therefore, if the content of S is too high, even if the contents of other elements are within the range of the present embodiment, the SSC resistance of the steel material will markedly decrease. Therefore, the content of S is to be 0.0050% or less. A preferable upper limit of the content of S is 0.0040%, more preferably is 0.0030%, further preferably is 0.0025%, and further preferably is 0.0020%. The content of S is preferably as low as possible. However, extremely reducing the content of S will raise the production cost. Accordingly, when taking industrial production into consideration, a preferable lower limit of the content of S is 0.0001%, more preferably is 0.0002%, and further preferably is 0.0003%.

Cu: 0.01 to 3.50%

[0036] Copper (Cu) is an austenite forming element and causes the microstructure after quenching to become martensitic. Cu also increases the SSC resistance of the steel material in a sour environment with a pH of 3.0, by a synergetic effect with Sn, As and Sb. If the content of Cu is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Cu is too high, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will be saturated, and furthermore, hot workability of the steel material will markedly decrease. In this case, in addition, the production cost will rise. Therefore, the content of Cu is to be 0.01 to 3.50%. A preferable lower limit of the content of Cu is 0.02%, more preferably is 0.03%, and further preferably is 0.05%. A preferable upper limit of the content of Cu is 3.30%, more preferably is 3.10%, and further preferably is 2.90%.

Cr: 10.00 to 14.00%

[0037] Chromium (Cr) forms a passive film on the surface of the steel material and thereby increases the SSC resistance of the steel material. If the content of Cr is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Cr is too high, even if the contents of other elements are within the range of the present embodiment, in some cases ferrite will be included in the microstructure, and it will be difficult to secure sufficient strength. If the content of Cr is too high, in addition, even if the contents of other elements are within the range of the present embodiment, intermetallic compounds or Cr carbo-nitrides will easily form in the steel material. As a result, the SSC resistance of the steel material will decrease. Therefore, the content of Cr is to be 10.00 to 14.00%. A preferable lower limit of the content of Cr is 10.30%, more preferably is 10.50%, and further preferably is 11.00%. A preferable upper limit of the content of Cr is 13.80%, more preferably is 13.60%, further preferably is 13.50%, further preferably is 13.45%, further preferably is 13.40%, and further preferably is 13.35%.

Ni: 4.50 to 7.50%

[0038] Nickel (Ni) is an austenite forming element and causes the microstructure after quenching to become martensitic. Ni also forms sulfides on the passive film in a sour environment. The Ni sulfides inhibit chloride ions (Cl^-) and hydrogen sulfide ions (HS^-) from coming into contact with the passive film, thereby suppressing destruction of the passive film by chloride ions and hydrogen sulfide ions. As a result, the SSC resistance of the steel material increases. Furthermore, Ni increases the SSC resistance of the steel material in a sour environment with a pH of 3.0 by a synergetic effect with Sn, As and Sb. If the content of Ni is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Ni is too high, even if the contents of other elements are within the range of the present embodiment, the diffusion coefficient of hydrogen in the steel material may decrease. In such case, the SSC resistance of the steel material will decrease. Therefore, the content of Ni is to be 4.50 to 7.50%. A preferable lower limit of the content of Ni is 4.80%, more preferably is 5.00%, and further preferably is 5.50%. A preferable upper limit of the content of Ni is 7.30%, more preferably is 7.00%, and further preferably is 6.50%.

Mo: 1.00 to 4.00%

[0039] Molybdenum (Mo) forms sulfides on the passive film in a sour environment. The Mo sulfides inhibit chloride ions (Cl^-) and hydrogen sulfide ions (HS^-) from coming into contact with the passive film, thereby suppressing destruction of the passive film by chloride ions and hydrogen sulfide ions. As a result, the SSC resistance of the steel material increases. Mo also dissolves in the steel material, and thereby increases strength of the steel material. If the content of Mo is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Mo is too high, even if the contents of other elements are within the range of the present embodiment, it will be difficult to stabilize austenite. As a result, in some cases a large amount of ferrite will be included in the microstructure after tempering. If the content of Mo is too high, even if the contents of other elements are within the range of the present embodiment, in some cases a large amount of intermetallic compounds such as Laves phase-based intermetallic compounds may form, and the yield strength of the steel material may become too high. Therefore, the content of Mo is to be 1.00 to 4.00%. A preferable lower limit of the content of Mo is 1.30%, more preferably is 1.50%, and further preferably is 1.80%. A preferable upper limit of the content of Mo is 3.80%, more preferably is 3.60%, and further preferably is 3.40%.

Ti: 0.050 to 0.300%

[0040] Titanium (Ti) combines with C and/or N to form carbides or nitrides. In such case, coarsening of grains is suppressed by the pinning effect, and the yield strength of the steel material increases. If the content of Ti is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Ti is too high, even if the contents of other elements are within the range of the present embodiment, strength of the steel material will be too high, and the SSC resistance of the steel material will decrease. Therefore, the content of Ti is to be 0.050 to 0.300%. A preferable lower limit of the content of Ti is 0.060%, and more preferably is 0.080%. A preferable upper limit of the content of Ti is 0.250%, more preferably is 0.200%, and further preferably is 0.180%.

V: 0.01 to 1.00%

[0041] Vanadium (V) increases hardenability of the steel material and raises the yield strength of the steel material. If the content of V is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of V is too high, even if the contents of other elements are within the range of the present embodiment, strength of the steel material will be too high and the SSC resistance of the steel material will decrease. Therefore, the content of V is to be 0.01 to 1.00%. A preferable lower limit of the content of V is 0.02%, and more preferably is 0.03%. A preferable upper limit of the content of V is 0.80%, more preferably is 0.60%, and further preferably is 0.50%.

Al: 0.001 to 0.100%

[0042] Aluminum (Al) deoxidizes the steel. If the content of Al is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Al is too high, even if the contents of other elements are within the range of the present embodiment, coarse oxides will form and the SSC resistance of the steel material will decrease. Therefore, the content of Al is to be 0.001 to 0.100%. A preferable lower limit of the content of Al is 0.005%, more preferably is 0.010%, and further preferably is 0.015%. A preferable upper limit of the content of Al is 0.080%, more preferably is 0.060%, further preferably is 0.055%, and further preferably is 0.050%. As used in the present description, the term "content of Al" means the content of sol. Al (acid-soluble Al).

Co: 0.010 to 0.500%

[0043] Cobalt (Co) forms sulfides on the passive film in a sour environment. The Co sulfides inhibit chloride ions (Cl^-) and hydrogen sulfide ions (HS^-) from coming into contact with the passive film, thereby suppressing destruction of the passive film by chloride ions and hydrogen sulfide ions. As a result, the SSC resistance of the steel material increases. Co also increases hardenability of the steel material, and particularly during industrial production, ensures consistent high strength of the steel material. Specifically, Co suppresses the formation of retained austenite, and suppresses the occurrence of variations in strength of the steel material. If the content of Co is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Co is too high, even if the contents of other elements are within the range of the present embodiment, toughness of the steel material will decrease. Therefore, the content of Co is to be 0.010 to 0.500%. A preferable lower limit of the content of Co is 0.015%, more preferably is 0.020%, further preferably is 0.030%, further preferably is 0.050%, and further preferably is 0.100%. A preferable upper limit of the content of Co is 0.450%, more preferably is 0.400%, and further preferably is 0.350%.

Ca: 0.0005 to 0.0050%

[0044] Calcium (Ca) immobilizes S in the steel material as a sulfide to make it harmless, and thereby improves hot workability of the steel material. If the content of Ca is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Ca is too high, even if the contents of other elements are within the range of the present embodiment, coarse inclusions will be formed in the steel material and the SSC resistance of the steel material will decrease. Therefore, the content of Ca is to be 0.0005 to 0.0050%. A preferable lower limit of the content of Ca is 0.0006%, more preferably is 0.0008%, and further preferably is 0.0010%. A preferable upper limit of the content of Ca is 0.0045%, more preferably is 0.0040%, and further preferably is 0.0035%.

Sn: 0.0005 to 0.0500%

[0045] Tin (Sn) increases the SSC resistance of the steel material in a sour environment with a pH of 3.0. If the content of Sn is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Sn is too high, even if the contents of other elements are within the range of the present embodiment, Sn will segregate at grain boundaries and, on the contrary, the SSC resistance of the steel material will decrease. Therefore, the content of Sn is to be 0.0005 to 0.0500%. A preferable lower limit of the content of Sn is 0.0008%, more preferably is 0.0010%, and further preferably is 0.0015%. A preferable upper limit of the content of Sn is 0.0400%, more preferably is 0.0300%, further preferably is 0.0200%, further preferably is 0.0100%, and further preferably is 0.0080%.

N: 0.0010 to 0.0500%

[0046] Nitrogen (N) combines with Ti to form fine Ti nitrides. The fine TiN suppresses coarsening of grains by the pinning effect. As a result, the yield strength of the steel material increases. If the content of N is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of N is too high, even if the contents of other elements are within the range of the present embodiment, coarse nitrides will be formed and the SSC resistance of the steel material will decrease. Therefore, the content of N is to be 0.0010 to 0.0500%. A preferable lower limit of the content of N is 0.0015%, more preferably is 0.0020%, further preferably is 0.0030%, and further preferably is 0.0040%. A preferable upper limit of the content of N is 0.0450%, more preferably is 0.0400%, further preferably is 0.0350%, and further preferably is 0.0300%.

O: 0.050% or less

[0047] Oxygen (O) is an impurity that is unavoidably contained. That is, the lower limit of the content of O is more than 0%. O forms oxides and reduces the SSC resistance of the steel material. Accordingly, if the content of O is too high, even if the contents of other elements are within the range of the present embodiment, the SSC resistance of the steel material will markedly decrease. Therefore, the content of O is to be 0.050% or less. A preferable upper limit of the content of O is 0.040%, more preferably is 0.030%, and further preferably is 0.020%. The content of O is preferably as low as possible. However, extremely reducing the content of O will raise the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of O is 0.0005%, more preferably is 0.001%, and further preferably is 0.002%.

[0048] The balance in the martensitic stainless steel material according to the present embodiment is Fe and impurities. Here, the term "impurities" refers to elements which, when industrially producing the steel material, are mixed in from ore or scrap that is used as the raw material or from the production environment or the like, and which are not intentionally contained but are allowed within a range that does not adversely affect the martensitic stainless steel material according to the present embodiment.

[Optional elements]

[0049] The martensitic stainless steel material according to the present embodiment may also contain W in lieu of a part of Fe.

W: 0 to 0.50%

[0050] Tungsten (W) is an optional element and need not be contained. That is, the content of W may be 0%. When contained, W stabilizes the passive film in a sour environment, and suppresses destruction of the passive film by chloride ions and hydrogen sulfide ions. As a result, the SSC resistance of the steel material increases. If even a small amount of W is contained, the aforementioned effect will be obtained to a certain extent. On the other hand, if the content of W is too high, W will combine with C and form coarse carbides. In such case, the SSC resistance of the steel material will decrease even if the contents of other elements are within the range of the present embodiment. Therefore, the content of W is to be 0 to 0.50%. A preferable lower limit of the content of W is 0.01%, more preferably is 0.03%, and further preferably is 0.05%. A preferable upper limit of the content of W is 0.45%, more preferably is 0.40%, and further preferably is 0.35%.

[0051] In addition, W markedly increases the SSC resistance when the content of Cu is high. Specifically, when the content of Cu is 0.50% or more, it is preferable to set the content of W to 0.10% or more. When the content of Cu is 0.50% or more, a more preferable lower limit of the content of W is 0.12%, and further preferably is 0.15%.

[0052] The martensitic stainless steel material according to the present embodiment may also contain Nb in lieu of a part of Fe.

Nb: 0 to 0.500%

[0053] Niobium (Nb) is an optional element, and need not be contained. That is, the content of Nb may be 0%. When contained, Nb combines with C and/or N to form Nb carbides and Nb carbo-nitrides. In such case, coarsening of grains is suppressed by the pinning effect, and the yield strength of the steel material increases. If even a small amount of Nb is contained, the aforementioned effect will be obtained to a certain extent. On the other hand, if the content of Nb is too high, Nb carbides and/or Nb carbo-nitrides will excessively form even if the contents of other elements are within the range of the present embodiment. As a result, the SSC resistance of the steel material will decrease. Therefore, the content of Nb is to be 0 to 0.500%. A preferable lower limit of the content of Nb is 0.001%, more preferably is 0.002%, and further preferably is 0.003%. A preferable upper limit of the content of Nb is 0.450%, more preferably is 0.400%, and further preferably is 0.350%.

[0054] The martensitic stainless steel material according to the present embodiment may further contain one or more elements selected from the group consisting of As and Sb in lieu of a part of Fe. Each of these elements assists the effect of increasing the SSC resistance of the steel material produced by Sn.

As: 0 to 0.0100%

[0055] Arsenic (As) is an optional element, and need not be contained. That is, the content of As may be 0%. When contained, As assists the effect of increasing the SSC resistance of the steel material produced by Sn. If even a small amount of As is contained, the aforementioned effect will be obtained to a certain extent. On the other hand, if the content of As is too high, even if the contents of other elements are within the range of the present embodiment, As will segregate at grain boundaries and the SSC resistance of the steel material will decrease. Therefore, the content of As is to be 0 to 0.0100%. A preferable lower limit of the content of As is 0.0001%, more preferably is 0.0005%, and further preferably is 0.0010%. A preferable upper limit of the content of As is 0.0090%, and more preferably is 0.0080%.

Sb: 0 to 0.0100%

[0056] Antimony (Sb) is an optional element, and need not be contained. That is, the content of Sb may be 0%. When contained, Sb assists the effect of increasing the SSC resistance of the steel material produced by Sn. If even a small amount of Sb is contained, the aforementioned effect will be obtained to a certain extent. On the other hand, if the content of Sb is too high, even if the contents of other elements are within the range of the present embodiment, Sb will segregate at grain boundaries and the SSC resistance of the steel material will decrease. Therefore, the content of Sb is to be 0 to 0.0100%. A preferable lower limit of the content of Sb is 0.0001%, more preferably is 0.0005%, and further preferably is 0.0010%. A preferable upper limit of the content of Sb is 0.0090%, and more preferably is 0.0080%.

[Yield strength]

[0057] The yield strength of the martensitic stainless steel material according to the present embodiment is 758 MPa (110 ksi) or more, and more preferably is 862 MPa (125 ksi) or more. Although the upper limit of the yield strength is not particularly limited, the upper limit of the yield strength of the steel material of the present embodiment is, for example, 1034 MPa (150 ksi). A more preferable upper limit of the yield strength of the steel material is 1000 MPa (145 ksi). As used herein, the term "yield strength" means 0.2% offset yield stress (MPa) obtained by a tensile test at normal temperature (24 ± 3°C) conducted in conformity with ASTM E8/E8M (2013).

[0058] Specifically, in the present embodiment, the yield strength is determined by the following method. First, a tensile test specimen is prepared from the martensitic stainless steel material according to the present embodiment. If the steel material is a pipe, the tensile test specimen is prepared from a central position of the wall thickness. If the steel material is a round steel bar, the tensile test specimen is prepared from an R/2 position. Note that, in the present description, the term "R/2 position" of a round steel bar means the center position of a radius R in a cross section perpendicular to the axial direction of the round steel bar. If the steel material is a steel plate, the tensile test specimen is prepared from a central position of the thickness. The size of the tensile test specimen is not particularly limited. For example, a round bar tensile test specimen in which the diameter of the parallel portion is 8.9 mm and the gage length is 35.6 mm is used as the tensile test specimen. The longitudinal direction of the parallel portion of the tensile test specimen is to be made parallel to the rolling direction and/or axial direction of the steel material. A tensile test is conducted at normal temperature (24 ± 3°C) in accordance with ASTM E8/E8M (2013) using the prepared tensile test specimen, and the 0.2% offset yield stress (MPa) is determined. The determined 0.2% offset yield stress is defined as the yield strength (MPa).

[0059] As described above, the yield strength of the martensitic stainless steel material according to the present embodiment is 758 MPa or more, and preferably is 862 MPa or more. In the present embodiment, when the content of Cu is 1.00% or less and attempting to obtain a yield strength of 758 to less than 862 MPa, preferably the martensitic stainless steel material consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cu: 0.01 to 1.00%, Cr: 10.00 to 14.00%, Ni: 4.50 to 6.50%, Mo: 1.00 to 3.00%, Ti: 0.050 to 0.300%, V: 0.01 to 1.00%, Al: 0.001 to 0.100%, Co: 0.010 to 0.500%, Ca: 0.0005 to 0.0050%, Sn: 0.0005 to 0.0500%, N: 0.0010 to 0.0500%, O: 0.050% or less, W: 0 to 0.50%, Nb: 0 to 0.500%, As: 0 to 0.0100%, and Sb: 0 to 0.0100%, with the balance being Fe and impurities.

[0060] In addition, in the present embodiment, when the content of Cu is 1.00% or less and attempting to obtain a yield strength of 862 MPa or more, preferably the martensitic stainless steel material consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cu: 0.01 to 1.00%, Cr: 10.00 to 14.00%, Ni: 5.00 to 7.50%, Mo: 2.00 to 4.00%, Ti: 0.050 to 0.300%, V: 0.01 to 1.00%, Al: 0.001 to 0.100%, Co: 0.010 to 0.500%, Ca: 0.0005 to 0.0050%, Sn: 0.0005 to 0.0500%, N: 0.0010 to 0.0500%, O: 0.050% or less, W: 0 to 0.50%, Nb: 0 to 0.500%, As: 0 to 0.0100%, and Sb: 0 to 0.0100%, with the balance being Fe and impurities.

[0061] In the present embodiment, when the content of Cu is 0.50% or more and attempting to obtain a yield strength of 862 MPa or more, preferably the martensitic stainless steel material consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cu: 0.50 to 3.50%, Cr: 10.00 to 14.00%, Ni: 5.00 to 7.50%, Mo: 2.00 to 4.00%, Ti: 0.050 to 0.300%, V: 0.01 to 1.00%, Al: 0.001 to 0.100%, Co: 0.010 to 0.500%, Ca: 0.0005 to 0.0050%, Sn: 0.0005 to 0.0500%, N: 0.0010 to 0.0500%, O: 0.050% or less, W: 0.10 to 0.50%, Nb: 0 to 0.500%, As: 0 to 0.0100%, and Sb: 0 to 0.0100%, with the balance being Fe and impurities.

[Regarding Formula (1)]

[0062] In the martensitic stainless steel material according to the present embodiment, within the range of the contents of elements described above and a yield strength of 758 MPa or more, the contents of elements and the yield strength satisfy Formula (1). As a result, on the condition that the other requirements of the present embodiment are satisfied, the martensitic stainless steel material according to the present embodiment has excellent SSC resistance in a sour environment with a pH of 3.0.

$$0.15 \leq (\mathrm{Sn+As+Sb})/\{(\mathrm{Cu+Ni})/\mathrm{YS}\} \leq 1.00 \qquad (1)$$

[0063] Where, in Formula (1), a content of a corresponding element in percent by mass is substituted for each symbol of an element, and a yield strength in MPa is substituted for YS. Note that, if a corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

[0064] F1 (= (Sn+As+Sb)/{(Cu+Ni)/YS}) is an index of an increase in the SSC resistance in a sour environment with a pH of 3.0 obtained by a synergetic effect between Sn, As and Sb, and Cu and Ni that is adjusted according to the yield strength. When F1 is too low, the steel material will not exhibit excellent SSC resistance in a sour environment with a pH of 3.0. Similarly, when F1 is too high, the steel material will not exhibit excellent SSC resistance in a sour environment with a pH of 3.0. On the other hand, if F1 is in the range of 0.15 to 1.00, the steel material will exhibit excellent SSC resistance in a sour environment with a pH of 3.0.

[0065] Therefore, in the martensitic stainless steel material according to the present embodiment, in addition to satisfying the requirements regarding the contents of elements described above and the yield strength of 758 MPa or more, F1 is to be within the range of 0.15 to 1.00. A preferable lower limit of F1 is 0.16, and more preferably is 0.18. A preferable upper limit of F1 is 0.95, and more preferably is 0.90.

[Microstructure of steel material]

[0066] The microstructure of the martensitic stainless steel material according to the present embodiment is mainly composed of martensite. As used herein, the phrase "mainly composed of martensite" means that the microstructure is composed of, in volume ratio, 0 to 5.0% of retained austenite and 0 to 5.0% of ferrite, and the balance is martensite. In the present description, the phrase "composed of retained austenite, ferrite, and tempered martensite" means that the amount of any phase other than retained austenite, ferrite, and tempered martensite is negligible. For example, in the chemical composition of the martensitic stainless steel material according to the present embodiment, the volume ratios of precipitates and inclusions are negligible as compared with the volume ratios of retained austenite, ferrite, and tempered martensite. That is, the microstructure of the martensitic stainless steel material according to the present embodiment may contain minute amounts of precipitates, inclusions and the like, in addition to retained austenite, ferrite, and tempered martensite.

[0067] In the present description, the term "martensite" includes not only fresh martensite but also tempered martensite. The lower limit of the volume ratio of martensite in the microstructure of the martensitic stainless steel material according to the present embodiment is 90.0%, and more preferably is 95.0%. Further preferably, the microstructure of the steel material is composed of single-phase martensite.

[0068] In the microstructure, a small amount of retained austenite does not result in a significant decrease in strength, and significantly increases toughness of the steel material. However, if the volume ratio of retained austenite is too high, the strength of the steel material will markedly decrease. Accordingly, in the microstructure of the steel material of the present embodiment, the volume ratio of retained austenite is to be 0 to 5.0%. From the viewpoint of ensuring strength, a preferable upper limit of the volume ratio of retained austenite is 4.0%, and more preferably is 3.0%. The volume ratio of retained austenite may be 0%. On the other hand, in the case of containing even a small amount of retained austenite, the volume ratio of retained austenite is to be more than 0 to 5.0%, more preferably is to be more than 0 to 4.0%, and further preferably is to be more than 0 to 3.0%.

[0069] A small amount of ferrite may be included in the microstructure. However, if the volume ratio of ferrite is too high, toughness of the steel material will markedly decrease. Accordingly, in the microstructure of the steel material of the present embodiment, the volume ratio of ferrite is to be 0 to 5.0%. A preferable upper limit of the volume ratio of ferrite is 3.0%, more preferably is 2.0%, and further preferably is 1.0%. The volume ratio of ferrite may be 0%. On the other hand, in the case of containing even a small amount of ferrite, the volume ratio of ferrite is to be more than 0 to 5.0%, more preferably more than 0 to 3.0%, further preferably more than 0 to 2.0%, and further preferably more than 0 to 1.0%.

[Method for measuring volume ratio of martensite]

[0070] In the present embodiment, the volume ratio (%) of martensite in the microstructure of the steel material is determined by subtracting a volume ratio (%) of retained austenite determined by a method described hereunder and a volume ratio (%) of ferrite determined by a method described hereunder from 100%.

[Method for measuring volume ratio of retained austenite]

[0071] The volume ratio of retained austenite in the microstructure of the steel material is determined by an X-ray diffraction method. Specifically, a test specimen for measuring the volume ratio of retained austenite is prepared from the steel material according to the present embodiment. If the steel material is a pipe, the test specimen is taken from a central position of the wall thickness. If the steel material is a round steel bar, the test specimen is taken from an R/2 position. If the steel material is a steel plate, the test specimen is taken from a central position of the thickness. The size of the test specimen is not particularly limited. The test specimen is for example, 15 mm × 15 mm × a thickness of 2 mm. If the steel material is a pipe, the thickness direction of the test specimen is the pipe diameter direction. If the steel material is a round steel bar, the thickness direction of the test specimen is the radial direction. If the steel material is a steel plate, the thickness direction of the test specimen is the plate thickness direction. Using the prepared test specimen, the X-ray diffraction intensity of each of the (110) plane of α phase (martensite), the (200) plane of α phase, the (211) plane of α phase, the (111) plane of y phase (retained austenite), the (200) plane of y phase, and the (220) plane of y phase are measured, and an integrated intensity of the respective planes is calculated.

[0072] In the measurement of the X-ray diffraction intensity, the target of the X-ray diffraction apparatus is Co (Co Kα radiation), and the output is set to 30 kV - 100 mA. The measurement angle (2θ) is set to 45 to 105°. After calculation, the volume ratio Vy (%) of retained austenite is calculated using Formula (I) for combinations (3 × 3 = 9 pairs) of each plane of the α phase and each plane of the y phase. Then, an average value of the volume ratios Vy of retained austenite of the nine pairs is defined as the volume ratio (%) of retained austenite.

$$V\gamma = 100/\{1+(I\alpha\times R\gamma)/(I\gamma\times R\alpha)\} \qquad (I)$$

[0073] Where, $I\alpha$ is the integrated intensity of α phase. $R\alpha$ is a crystallographic theoretical calculation value of α phase. Iy is the integrated intensity of y phase. Ry is a crystallographic theoretical calculation value of y phase. Values incorporated into a retained y quantitative analysis system belonging to RINT-TTR (product name) manufactured by Rigaku Corporation can be used for the values of $R\alpha$ and $R\gamma$ for each plane. Note that, a value obtained by rounding off the second decimal place of the obtained numerical value is adopted as the volume ratio of retained austenite.

[Method for measuring volume ratio of ferrite]

[0074] The volume ratio of ferrite in the microstructure of the steel material is determined by a point counting method. Specifically, a test specimen for measuring the volume ratio of ferrite is prepared from the steel material according to the present embodiment. If the steel material is a pipe, the test specimen is taken from a central position of the wall thickness. If the steel material is a round steel bar, the test specimen is taken from an R/2 position. If the steel material is a steel plate, the test specimen is taken from a central position of the thickness. The test specimen is not particularly limited as long as the test specimen has a face that is parallel to the rolling direction as an observation surface. For example, if the steel material is a pipe, the observation surface of the test specimen is parallel to the axial direction of the pipe. After the observation surface is mechanically polished, the observation surface is subjected to electrolytic etching to reveal the microstructure. The electrolytic etching is performed using a 30% sodium hydroxide aqueous solution as the electrolyte, at a current density of 1 A/cm^2, for an electrolysis time of 1 minute.

[0075] On the observation surface subjected to the electrolytic etching, 30 visual fields are observed using an optical microscope. Each observation visual field is set as a rectangle of 250 μm × 250 μm. Note that, the observation magnification is ×400. Those skilled in the art can distinguish ferrite from other phases (retained austenite or tempered martensite) based on contrast in each observation visual field. Therefore, ferrite in each observation visual field is identified based on contrast. The area fraction of the identified ferrite is determined by a point counting method conforming to ASTM E562 (2019).

[0076] Specifically, for each observation visual field, 20 vertical lines are drawn at regular intervals from the top end to the bottom end of the observation visual field. That is, the observation visual field is divided into 21 regions in the left-right direction by the 20 vertical lines. Further, for each observation visual field, 20 horizontal lines are also drawn at regular intervals from the left end to the right end of the observation visual field. That is, the observation visual field is divided into 21 regions in the vertical direction by the 20 horizontal lines. At this time, intersections between the vertical lines and the horizontal lines are called lattice points. That is, in each observation visual field, 400 lattice points are arranged at regular intervals. In accordance with ASTM E562 (2019), the lattice points that overlap with ferrite in the observation visual field are counted. The number of lattice points overlapping with ferrite obtained in the 30 visual fields is divided by the total number of lattice points (400×30 = 12000), and the resultant value is defined as the ferrite area fraction. In the present embodiment, the area fraction of ferrite determined by the above method is defined as the volume ratio (%) of ferrite. Note that, a value obtained by rounding off the second decimal place of the obtained numerical value is adopted as the volume ratio of ferrite.

[0077] Using the volume ratio (%) of retained austenite obtained by the aforementioned X-ray diffraction method, and the volume ratio (%) of ferrite obtained by the aforementioned point counting method, the volume ratio (%) of martensite in the microstructure of the steel material is determined by the following formula.

$$\text{Volume ratio (\%) of martensite} = 100.0 - \{\text{volume ratio (\%) of retained austenite} + \text{volume ratio (\%) of ferrite}\}$$

[SSC resistance of steel material]

[0078] Even though the martensitic stainless steel material according to the present embodiment has a high yield strength of 758 MPa or more, the martensitic stainless steel material has excellent SSC resistance in a sour environment with a pH of 3.0. The SSC resistance of the martensitic stainless steel material according to the present embodiment can be evaluated by an SSC resistance evaluation test at normal temperature. The SSC resistance evaluation test is performed by a method in conformity with NACE TM0177-2016 Method A.

[0079] Specifically, a round bar specimen is prepared from the steel material according to the present embodiment. If the steel material is a pipe, the round bar specimen is prepared from a central position of the wall thickness. If the steel material is a round steel bar, the round bar specimen is prepared from an R/2 portion. If the steel material is a steel plate, the round bar specimen is prepared from a central position of the thickness. The size of the round bar specimen is not particularly limited. The round bar specimen, for example, is a specimen in which the diameter of the parallel portion is 6.35 mm and the length of the parallel portion is 25.4 mm. Note that, the axial direction of the round bar specimen is to be made parallel to the rolling direction and/or axial direction of the steel material.

[0080] An aqueous solution containing 0.17% sodium chloride by mass and having a pH of 3.0 is used as the test solution. The test solution is prepared by adding acetic acid to an aqueous solution containing 0.17% sodium chloride by mass and 0.41 g/L of sodium acetate to adjust the pH to 3.0. A stress equivalent to 90% of the actual yield stress is applied to the round bar specimen prepared as described above. The test solution at 24°C is poured into a test vessel so that the round bar specimen to which the stress has been applied is immersed therein to form a test bath. After degassing the test bath, H_2S gas at 0.03 bar and CO_2 gas at 0.97 bar are blown into the test bath to saturate the test bath with H_2S gas. The test bath in which the H_2S gas is saturated is held at 24°C for 720 hours. After the test specimen has been held for 720 hours, the surface of the parallel portion of the test specimen is observed with a magnifying glass having a magnification of ×10 to confirm the presence or absence of pitting. In the martensitic stainless steel material according to the present embodiment, the presence of pitting is not confirmed after 720 hours elapse in an SSC resistance evaluation test conducted by the method described above.

[Shape and uses of steel material]

[0081] As mentioned above, the shape of the martensitic stainless steel material according to the present embodiment is not particularly limited. Specifically, the martensitic stainless steel material according to the present embodiment may be a pipe, may be a round steel bar (solid material), or may be a steel plate. The pipe may be a seamless pipe or may be a welded pipe. The pipe is, for example, a pipe for oil country tubular goods. The term "pipe for oil country tubular goods" means a pipe that is to be used in oil country tubular goods. Oil country tubular goods are, for example, casing pipes, tubing pipes, and drilling pipes which are used for drilling an oil well or a gas well, collecting crude oil or natural gas, and the like. Preferably, the steel material of the present embodiment is a seamless pipe for oil country tubular goods.

[0082] As described above, in the martensitic stainless steel material according to the present embodiment, the content of each element is within the range of the present embodiment, the yield strength is 758 MPa or more, and within the range of the contents of elements described above and the yield strength of 758 MPa or more, a condition that F1 is 0.15 to 1.00 is satisfied. As a result, the steel material according to the present embodiment has both a high yield strength and excellent SSC resistance in a sour environment with a pH of 3.0.

[Production method]

[0083] An example of a method for producing the martensitic stainless steel material according to the present embodiment will now be described. Note that, the production method described hereunder is an example, and a method for producing the martensitic stainless steel material according to the present embodiment is not limited to the production method described hereunder. That is, as long as the martensitic stainless steel material according to the present embodiment that is composed as described above can be produced, a method for producing the martensitic stainless steel material is not limited to the production method described hereunder. However, the production method described hereunder is a favorable method for producing the martensitic stainless steel material according to the present embodiment.
[0084] One example of a method for producing the martensitic stainless steel material according to the present embodiment includes a process of preparing an intermediate steel material (preparation process), and a process of subjecting the intermediate steel material to quenching and tempering (heat treatment process). Each of these processes is described in detail hereunder.

[Preparation process]

[0085] In the preparation process, an intermediate steel material having the aforementioned chemical composition is prepared. The method for preparing the intermediate steel material is not particularly limited as long as the intermediate steel material has the aforementioned chemical composition. As used here, the term "intermediate steel material" refers to a plate-shaped steel material in a case where the end product is a steel plate or a welded pipe, and refers to a hollow shell in a case where the end product is a seamless pipe.
[0086] The preparation process may include a process of preparing a starting material (starting material preparation process), and a process of subjecting the starting material to hot working to produce an intermediate steel material (hot working process). Hereunder, a case where the preparation process includes a starting material preparation process and a hot working process is described in detail.

[Starting material preparation process]

[0087] In the starting material preparation process, a starting material is produced using a molten steel having the aforementioned chemical composition. The method for producing the starting material is not particularly limited, and it suffices to use a well-known method. Specifically, a cast piece (a slab, a bloom, or a billet) may be produced by a continuous casting process using the molten steel. An ingot may also be produced by an ingot-making process using the molten steel. As necessary, the slab, bloom, or ingot may be subjected to blooming to produce a billet. A starting material (a slab, a bloom, or a billet) is produced by the above-described process.

[Hot working process]

[0088] In the hot working process, the prepared starting material is subjected to hot working to produce an intermediate steel material. If the steel material is a seamless pipe, the intermediate steel material corresponds to a hollow shell. First, a billet is heated in a reheating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. After the billet is extracted from the reheating furnace, the billet is subjected to hot working to produce a hollow shell (seamless pipe). The method of hot working is not particularly limited, and it suffices to use a well-known method.
[0089] For example, the Mannesmann process may be performed as hot working to produce a hollow shell. In this case, a round billet is subjected to piercing-rolling using a piercing machine. When performing piercing-rolling, although not particularly limited, for example, the piercing ratio is 1.0 to 4.0. The round billet subjected to piercing-rolling is further subjected to hot rolling with a mandrel mill, a reducer, a sizing mill or the like to produce a hollow shell. The cumulative reduction of area in the hot working process is, for example, 20 to 70%.
[0090] A hollow shell may be produced from the billet by performing another hot working method. For example, in a case where the steel material is a heavy-wall pipe of a short length such as a coupling, a hollow shell may be produced by forging by the Ehrhardt process or the like. A hollow shell is produced by the above process. Although not particularly limited, the wall thickness of the hollow shell is, for example, 9 to 60 mm.
[0091] If the steel material is a round steel bar, first, the starting material is heated in a reheating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. The starting material extracted from the reheating furnace is subjected to hot working to produce an intermediate steel material in which a cross section perpendicular to the axial direction is a circular shape. The hot working is, for example, blooming performed using a blooming mill or hot rolling performed using a continuous mill. In a continuous mill, a horizontal stand having a pair of grooved rolls arranged one on the other in the vertical direction, and a vertical stand having a pair of grooved rolls

arranged side by side in the horizontal direction are alternately arranged.

[0092] If the steel material is a steel plate, first, the starting material is heated in a reheating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. The starting material extracted from the reheating furnace is subjected to hot rolling using a blooming mill and a continuous mill to produce an intermediate steel material having a steel plate shape.

[0093] The hollow shell produced by hot working may be air-cooled (as-rolled). The hollow shell produced by hot working may be subjected to direct quenching after hot working without being cooled to normal temperature, or may be subjected to quenching after undergoing supplementary heating (reheating) after hot working.

[0094] In a case of performing direct quenching after hot working, or performing quenching after supplementary heating, cooling may be stopped midway through the quenching process or slow cooling may be performed. In this case, the occurrence of quench cracking in the hollow shell can be suppressed. In addition, in the case of performing direct quenching after hot working, or performing quenching after supplementary heating, stress relief annealing (SR) may be performed at a time that is after quenching and before the heat treatment of the next process. In this case, residual stress of the hollow shell is eliminated.

[0095] As described above, an intermediate steel material is prepared in the preparation process. The intermediate steel material may be produced by the aforementioned preferable process, or may be an intermediate steel material produced by a third party, or an intermediate steel material produced in another factory other than the factory in which a quenching process and a tempering process to be described later are performed, or at a different place of business may be prepared. The heat treatment process is described in detail hereunder.

[Heat treatment process]

[0096] The heat treatment process includes a quenching process and a tempering process.

[Quenching process]

[0097] In the heat treatment process, first, the intermediate steel material produced in the hot working process is subjected to quenching (quenching process). The quenching is performed by a well-known method. Specifically, the intermediate steel material after the hot working process is charged into a heat treatment furnace and held at a quenching temperature. The quenching temperature is equal to or higher than the Acs transformation point, and for example is 900 to 1000°C. After being held at the quenching temperature, the intermediate steel material is rapidly cooled (quenched). Although not particularly limited, the holding time at the quenching temperature is, for example, 10 to 60 minutes. The quenching method is, for example, water cooling. The quenching method is not particularly limited. In a case where the intermediate steel material is a hollow shell, for example, the hollow shell may be rapidly cooled by immersing the hollow shell in a water bath or an oil bath, or the hollow shell may be rapidly cooled by pouring or jetting cooling water onto the outer surface and/or inner surface of the hollow shell by shower cooling or mist cooling.

[0098] Note that, as mentioned above, after the hot working process, quenching (direct quenching) may be performed immediately after the hot working, without cooling the intermediate steel material to normal temperature, or quenching may be performed after the intermediate steel material has been held at the quenching temperature after being charged into a holding furnace before the temperature of the hollow shell decreased after the hot working.

[Tempering process]

[0099] The intermediate steel material after quenching is also subjected to a tempering process. In the tempering process, the yield strength of the steel material is adjusted. In the present embodiment, the tempering temperature is to be set in the range of 540 to 620°C. Although not particularly limited, the holding time at the tempering temperature is, for example, 10 to 180 minutes. It is well-known by those skilled in the art that the yield strength of a steel material can be adjusted by appropriately adjusting the tempering temperature according to the chemical composition. Therefore, the tempering conditions are adjusted so that the yield strength of the steel material becomes 758 MPa or more.

[0100] The martensitic stainless steel material according to the present embodiment can be produced by the process described above. Note that, as mentioned above, a method for producing the martensitic stainless steel material according to the present embodiment is not limited to the above production method. Specifically, as long as a martensitic stainless steel material in which the content of each element in the chemical composition is within the range of the present embodiment, and which has a microstructure composed of, in vol%, 0 to 5.0% of retained austenite and 0 to 5.0% of ferrite, with the balance being tempered martensite, has a yield strength of 758 MPa or more, and in which, in addition, F1 is 0.15 to 1.00 can be produced, the production method of the present embodiment is not limited to the production method described above. Hereunder, the martensitic stainless steel material according to the present embodiment is described more specifically by way of examples.

EXAMPLES

[0101] Molten steels having the chemical compositions shown in Table 1 were produced. Note that, the symbol "-" in Table 1 means that the content of the corresponding element was at an impurity level. For example, it means that the content of W of Test No. 1 was 0% when rounded off to two decimal places. It means that the content of Nb of Test No. 1 was 0% when rounded off to three decimal places. It means that the content of AS and the content of Sb of Test No. 1 were each 0% when rounded off to four decimal places.

[Table 1]

TABLE 1

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)																			
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Ti	V	Al	Co	Ca	Sn	N	O	W	Nb	As	Sb
1	0.011	0.25	0.41	0.011	0.0007	0.32	12.34	6.08	1.94	0.102	0.03	0.032	0.245	0.0014	0.0018	0.0075	0.002	-	-	-	-
2	0.010	0.31	0.37	0.015	0.0009	0.05	12.53	5.37	1.92	0.136	0.04	0.032	0.167	0.0006	0.0008	0.0058	0.003	0.11	-	-	0.0005
3	0.010	0.27	0.35	0.015	0.0008	0.08	11.92	5.44	2.03	0.087	0.05	0.038	0.171	0.0018	0.0015	0.0098	0.001	-	0.002	0.0012	-
4	0.008	0.24	0.42	0.014	0.0012	0.10	12.28	5.38	1.88	0.102	0.06	0.027	0.159	0.0016	0.0034	0.0086	0.003	-	-	0.0011	0.0008
5	0.014	0.25	0.40	0.014	0.0008	0.06	12.25	5.12	2.12	0.115	0.05	0.025	0.141	0.0012	0.0048	0.0086	0.003	-	-	0.0010	-
6	0.011	0.22	0.38	0.013	0.0008	0.11	12.38	5.64	2.12	0.105	0.06	0.032	0.126	0.0020	0.0028	0.0078	0.003	-	-	0.0028	-
7	0.010	0.24	0.40	0.014	0.0008	0.20	12.04	5.48	2.08	0.112	0.05	0.028	0.086	0.0018	0.0017	0.0087	0.002	-	-	0.0053	-
8	0.010	0.24	0.36	0.013	0.0008	1.54	12.76	6.08	2.48	0.113	0.05	0.031	0.124	0.0015	0.0064	0.0086	0.002	0.25	-	-	-
9	0.009	0.20	0.41	0.015	0.0006	0.04	11.90	7.05	3.01	0.105	0.04	0.042	0.120	0.0021	0.0020	0.0078	0.002	-	-	0.0012	-
10	0.007	0.24	0.48	0.012	0.0008	0.05	12.16	7.21	2.96	0.102	0.05	0.038	0.262	0.0020	0.0010	0.0087	0.004	0.12	-	0.0011	-
11	0.013	0.18	0.47	0.015	0.0007	0.06	12.32	6.88	2.93	0.103	0.05	0.045	0.023	0.0025	0.0012	0.0068	0.002	-	0.007	-	0.0008
12	0.009	0.21	0.40	0.013	0.0008	0.02	11.96	6.91	3.03	0.096	0.05	0.040	0.100	0.0017	0.0050	0.0081	0.002	0.01	0.004	0.0010	-
13	0.011	0.22	0.42	0.015	0.0006	0.25	12.05	7.15	2.98	0.114	0.05	0.035	0.243	0.0022	0.0007	0.0094	0.002	-	-	0.0076	-
14	0.012	0.25	0.42	0.013	0.0010	1.89	12.58	6.11	2.73	0.112	0.06	0.035	0.211	0.0022	0.0018	0.0093	0.002	0.18	-	-	-
15	0.010	0.23	0.40	0.015	0.0007	2.30	12.74	6.02	2.61	0.095	0.05	0.028	0.206	0.0006	0.0021	0.0071	0.003	0.38	-	0.0014	-
16	0.015	0.24	0.38	0.014	0.0008	2.13	13.09	5.98	2.76	0.108	0.04	0.032	0.165	0.0016	0.0042	0.0083	0.003	0.16	0.012	-	0.0010
17	0.008	0.23	0.46	0.017	0.0010	2.02	13.22	6.12	2.56	0.100	0.05	0.027	0.112	0.0021	0.0012	0.0078	0.004	0.32	0.004	0.0007	0.0007
18	0.012	0.27	0.42	0.018	0.0011	2.08	13.26	5.95	2.62	0.121	0.06	0.031	0.185	0.0028	0.0068	0.0123	0.003	-	-	0.0012	-
19	0.012	0.25	0.43	0.016	0.0008	2.32	12.86	6.12	2.60	0.108	0.04	0.032	0.175	0.0024	0.0048	0.0077	0.003	-	-	0.0031	-
20	0.011	0.24	0.41	0.015	0.0009	1.98	13.38	6.45	2.58	0.106	0.05	0.027	0.134	0.0026	0.0018	0.0106	0.002	-	-	0.0048	-
21	0.009	0.25	0.38	0.014	0.0007	2.15	13.18	6.32	2.54	0.113	0.05	0.032	0.156	0.0018	0.0012	0.0124	0.002	-	-	0.0078	-
22	0.008	0.24	0.40	0.015	0.0007	0.21	11.95	5.34	1.98	0.106	0.38	0.031	0.088	0.0025	0.0018	0.0076	0.003	-	-	-	-
23	0.012	0.28	0.41	0.012	0.0008	0.05	11.95	6.32	2.15	0.100	0.05	0.034	0.203	0.0019	0.0006	0.0077	0.004	-	-	-	-
24	0.023	0.22	0.38	0.015	0.0006	0.06	12.08	7.12	3.02	0.092	0.05	0.030	0.212	0.0018	0.0010	0.0092	0.002	-	-	-	-
25	0.012	0.24	0.38	0.015	0.0005	2.12	13.05	6.32	2.62	0.098	0.06	0.033	0.188	0.0025	0.0005	0.0082	0.003	0.15	-	-	-

26	0.013	0.20	0.42	0.014	0.0007	2.11	12.86	6.89	2.48	0.104	0.05	0.031	0.202	0.0021	0.0011	0.0078	0.002	0.09	-	-	-
27	0.009	0.24	0.40	0.013	0.0011	0.03	11.82	5.38	2.04	0.095	0.06	0.025	0.182	0.0023	0.0121	0.0082	0.003	-	-	-	-
28	0.015	0.26	0.42	0.021	0.0008	0.01	12.12	6.98	2.86	0.102	0.05	0.036	0.208	0.0028	0.0150	0.0086	0.003	-	-	-	-
29	0.011	0.25	0.42	0.016	0.0008	1.75	12.68	5.94	2.42	0.097	0.05	0.032	0.157	0.0016	0.0030	0.0110	0.003	0.22	-	0.0032	0.0025
30	0.015	0.26	0.46	0.013	0.0009	0.87	12.78	5.75	2.74	0.102	0.05	0.036	0.147	0.0018	0.0221	0.0091	0.003	0.21	-	-	-
31	0.012	0.32	0.45	0.013	0.0012	0.02	11.85	6.75	2.92	0.082	0.04	0.032	0.163	0.0025	-	0.0076	0.003	-	-	0.0012	-
32	0.027	0.19	0.40	0.011	0.0005	0.15	12.20	5.10	1.80	0.093	0.03	0.025	0.106	0.0025	-	0.0069	0.001	-	-	-	-
33	0.008	0.18	0.46	0.018	0.0009	0.04	12.11	6.88	2.78	0.088	0.04	0.041	0.098	0.0028	-	0.0084	0.002	-	-	-	0.0010
34	0.016	0.24	0.38	0.017	0.0006	2.15	13.12	6.12	2.51	0.108	0.05	0.032	0.242	0.0022	-	0.0105	0.003	0.12	-	-	-
35	0.010	0.35	0.45	0.016	0.0005	0.01	11.80	4.65	2.49	0.069	0.06	0.028	0.221	0.0009	-	0.0048	0.001	-	-	0.0046	0.0015
36	0.022	0.25	0.41	0.015	0.0008	1.58	12.78	6.15	2.38	0.120	0.05	0.030	0.005	0.0026	0.0012	0.0082	0.003	-	-	-	-
37	0.013	0.26	0.40	0.014	0.0005	1.38	12.85	4.81	2.20	0.112	0.05	0.028	0.006	0.0020	0.0007	0.0088	0.003	-	-	-	-

[0102] The respective molten steels described above were melted in a 180-kg vacuum furnace, and ingots were produced by an ingot-making process. The ingots were heated for three hours at 1250°C. The ingot after heating was subjected to hot forging to produce a block. A block after hot forging was heated for three hours at 1230°C, and thereafter the block was subjected to hot rolling. In this way, a steel material (a steel plate) having a thickness of 13 mm was produced.

[0103] The produced steel material of each test number was subjected to quenching. Specifically, the steel plate of each test number was heated so as to reach a quenching temperature (°C) described in Table 2. The steel plate of each test number was held at the quenching temperature for 15 minutes, and thereafter subjected to water cooling. The steel material of each test number after quenching was subjected to tempering in which the steel material was held at a tempering temperature (°C) described in Table 2 for 30 minutes.

[Table 2]

[0104]

TABLE 2

Test Number	Quenching Temperature (°C)	Tempering Temperature (°C)	Retained γ (%)	Ferrite (%)	Martensite (%)	YS (MPa)	F1	Number of Specimens in which Pitting Occurred (Specimens)
1	900	600	0.3	0.0	99.7	845	0.24	0
2	900	610	0.1	0.0	99.9	830	0.20	0
3	900	600	0.2	0.0	99.8	824	0.40	0
4	900	600	0.0	0.0	100.0	795	0.77	0
5	900	610	0.4	0.0	99.6	858	0.96	0
6	900	600	0.2	0.0	99.8	815	0.79	0
7	900	610	0.1	0.0	99.9	798	0.98	0
8	910	610	4.7	0.0	95.3	824	0.69	0
9	900	560	0.3	0.0	99.7	980	0.44	0
10	900	560	0.5	0.0	99.5	921	0.27	0
11	900	540	0.2	0.0	99.8	945	0.27	0
12	900	560	0.2	0.0	99.8	933	0.81	0
13	900	560	0.3	0.0	99.7	870	0.98	0
14	900	600	1.5	0.0	98.5	1003	0.23	0
15	900	600	2.1	0.0	97.9	985	0.41	0
16	900	590	0.6	0.0	99.4	942	0.60	0
17	900	590	0.7	1.2	98.1	935	0.30	0
18	900	590	1.2	0.5	98.3	982	0.98	0
19	900	590	3.4	0.0	96.6	913	0.85	0
20	900	590	2.8	0.0	97.2	1002	0.78	0
21	910	590	3.6	0.0	96.4	886	0.94	0
22	900	590	0.1	0.0	99.9	804	0.26	0
23	900	600	0.5	0.0	99.5	836	0.08	2
24	900	560	1.3	0.0	98.7	978	0.14	3
25	900	590	0.4	0.0	99.6	940	0.06	3
26	900	570	1.8	0.0	98.2	970	0.12	1

(continued)

Test Number	Quenching Temperature (°C)	Tempering Temperature (°C)	Retained γ (%)	Ferrite (%)	Martensite (%)	YS (MPa)	F1	Number of Specimens in which Pitting Occurred (Specimens)
27	900	600	0.2	0.0	99.8	847	1.89	3
28	900	540	1.0	0.0	99.0	988	2.12	3
29	900	590	0.3	0.0	99.7	956	1.08	3
30	900	610	0.2	0.0	99.8	968	3.23	3
31	900	560	0.4	0.0	99.6	912	0.16	1
32	900	610	0.3	0.0	99.7	788	0.00	2
33	900	540	0.2	0.0	99.8	956	0.14	1
34	900	600	1.3	0.4	98.3	980	0.00	2
35	900	590	0.0	0.0	100.0	861	1.13	3
36	900	570	0.8	0.0	99.2	980	0.15	1
37	900	600	0.5	0.0	99.5	798	0.09	3

[0105] The steel plate of each test number was produced by the above production process.

[Evaluation Tests]

[0106] The produced steel plate of each test number was subjected to a microstructure observation test, a tensile test, and a SSC resistance evaluation test.

[Microstructure observation test]

[0107] The steel plate of each test number was subjected to a microstructure observation test. First, the volume ratio (%) of retained austenite in the steel plate of each test number was determined by the aforementioned X-ray diffraction method. Note that, in the measurement of the X-ray diffraction intensity, an apparatus with the product name "RINT-TTR" manufactured by Rigaku Corporation was used as the X-ray diffraction apparatus. Measurement was conducted using Co Kα radiation as the radiation source, with the output set to 30 kV - 100 mA, and the measurement angle (2θ) set to 45 to 105°. The obtained volume ratio (%) of retained austenite in the steel plate of each test number is shown in the column "Retained y (%)" in Table 2.

[0108] Further, the volume ratio (%) of ferrite was determined by the aforementioned point counting method. Specifically, a test specimen was prepared from a central position of the thickness of the steel plate of each test number. For each test specimen, a surface parallel to the rolling direction was adopted as the observation surface. Note that, in the present Examples, an area fraction of ferrite determined by a method conforming to ASTM E562 (2019) described above was defined as the volume ratio (%) of ferrite. The obtained volume ratio of ferrite in the steel plate of each test number is shown in the column "Ferrite (%)" in Table 2.

[0109] In addition, for the steel plate of each test number, the volume ratio (%) of martensite was determined by the following formula using the volume ratio (%) of retained austenite and the volume ratio (%) of ferrite.

$$\text{Volume ratio (\%) of martensite} = 100 - \{\text{volume ratio (\%) of retained austenite} + \text{volume ratio (\%) of ferrite}\}$$

[0110] The obtained volume ratio (%) of martensite in each test number is shown in the "Martensite (%)" column in Table 2.

[Tensile test]

[0111] The steel plate of each test number was subjected to a tensile test in accordance with ASTM E8/E8M (2013). Specifically, from a central position of the thickness of the steel plate of each test number, a round bar tensile test specimen in which the diameter of the parallel portion was made 8.9 mm, and the gage length was made 35.6 mm was prepared. The longitudinal direction of the round bar tensile test specimen was parallel to the rolling direction of the steel plate. A tensile test was performed at normal temperature (24 ± 3°C) in the atmosphere using the round bar tensile test specimen of each test number, and the 0.2% offset yield stress (MPa) was determined. The determined 0.2% offset yield stress was defined as the yield strength (MPa). The obtained yield strength of each test number is shown in the column "YS (MPa)" in Table 2. In addition, for the steel plate of each test number, F1 was determined using the chemical composition, the yield strength, and Formula (1). The obtained value of F1 for each test number is shown in the column "F1" in Table 2.

[SSC resistance evaluation test]

[0112] The steel plate of each test number was subjected to a SSC resistance evaluation test. Specifically, round bar specimens having a diameter of 6.35 mm and in which the length of the parallel portion was 25.4 mm were prepared from a central position of the thickness of the steel plate of each test number. Three of the prepared round bar specimens were subjected to a SSC resistance evaluation test conducted in conformity with NACE TM0177-2016 Method A. Note that, the axial direction of each round bar specimen was parallel to the rolling direction.

[0113] An aqueous solution containing 0.17% sodium chloride by mass and having a pH of 3.0 was used as the test solution. The test solution was prepared by adding acetic acid to an aqueous solution containing 0.17% sodium chloride by mass and 0.41 g/L of sodium acetate to adjust the pH to 3.0. A stress equivalent to 90% of the actual yield stress was applied to the round bar specimen of each test number. The test solution at 24°C was poured into a test vessel so that the round bar specimen to which the stress was applied was immersed therein to form a test bath. After degassing the test bath, H_2S gas at 0.03 bar and CO_2 gas at 0.97 bar were blown into the test bath to saturate the test bath with H_2S gas. The test bath in which the H_2S gas was saturated was held at 24°C for 720 hours.

[0114] The surface of the parallel portion of each round bar specimen after being held for 720 hours was observed with a magnifying glass having a magnification of ×10, and the presence or absence of pitting was confirmed. The number of specimens in which the occurrence of pitting was confirmed among the three round bar specimens is shown in Table 2 as "Number of Specimens in which Pitting Occurred (Specimens)"

[Evaluation results]

[0115] Referring to Table 1 and Table 2, in the steel plates of Test Nos. 1 to 22, the chemical composition was appropriate and each of these steel plates had a microstructure composed of 0 to 5.0 vol% of retained austenite and 0 to 5.0 vol% of ferrite, with the balance being martensite. In addition, each of these steel plates had a high strength which was a yield strength of 758 MPa or more. Further, in these steel plates, the condition that F1 was within the range of 0.15 to 1.00 was satisfied. As a result, with respect to these steel plates, in the sour environment with a pH of 3.0, the number of specimens in which pitting occurred was 0 specimens, and hence these steel plates had excellent SSC resistance.

[0116] On the other hand, in the steel plates of Test Nos. 23 to 26, F1 was too low. As a result, with respect to each of these steel plates, in the sour environment with a pH of 3.0, pitting occurred in at least one of the specimens, and hence these steel plates did not have excellent SSC resistance.

[0117] In the steel plates of Test Nos. 27 to 30, F1 was too high. As a result, with respect to each of these steel plates, in the sour environment with a pH of 3.0, pitting occurred in three specimens, and hence these steel plates did not have excellent SSC resistance.

[0118] The steel plate of Test No. 31 did not contain Sn. As a result, with respect to this steel plate, in the sour environment with a pH of 3.0, pitting occurred in one specimen, and hence the steel plate did not have excellent SSC resistance.

[0119] The steel plates of Test Nos. 32 to 34 did not contain Sn. In addition, F1 was too low in these steel plates. As a result, with respect to each of these steel plates, in the sour environment with a pH of 3.0, pitting occurred in at least one of the specimens, and hence these steel plates did not have excellent SSC resistance.

[0120] The steel plate of Test No. 35 did not contain Sn. In addition, F1 was too high in this steel plate. As a result, with respect to this steel plate, in the sour environment with a pH of 3.0, pitting occurred in three specimens, and hence the steel plate did not have excellent SSC resistance.

[0121] In the steel plate of Test No. 36, the content of Co was too low. As a result, with respect to this steel plate, in the sour environment with a pH of 3.0, pitting occurred in one specimen, and hence the steel plate did not have excellent

SSC resistance.

[0122] In the steel plate of Test No. 37, the content of Co was too low. In addition, F1 was too low in this steel plate. As a result, with respect to this steel plate, in the sour environment with a pH of 3.0, pitting occurred in three specimens, and hence the steel plate did not have excellent SSC resistance.

[0123] An embodiment of the present disclosure has been described above. However, the embodiment described above is merely an example for carrying out the present disclosure. Therefore, the present disclosure is not limited to the above-described embodiment, and can be implemented by appropriately modifying the above-described embodiment within a range not departing from the spirit thereof.

Claims

1. A martensitic stainless steel material consisting of, in mass%,

C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cu: 0.01 to 3.50%,
Cr: 10.00 to 14.00%,
Ni: 4.50 to 7.50%,
Mo: 1.00 to 4.00%,
Ti: 0.050 to 0.300%,
V: 0.01 to 1.00%,
Al: 0.001 to 0.100%,
Co: 0.010 to 0.500%,
Ca: 0.0005 to 0.0050%,
Sn: 0.0005 to 0.0500%,
N: 0.0010 to 0.0500%,
O: 0.050% or less,
W: 0 to 0.50%,
Nb: 0 to 0.500%,
As: 0 to 0.0100%,
Sb: 0 to 0.0100%, and
the balance: Fe and impurities,
wherein:

a yield strength is 758 MPa or more; and
within a range of contents of elements and the yield strength of the martensitic stainless steel material, the contents of elements and the yield strength satisfy Formula (1);

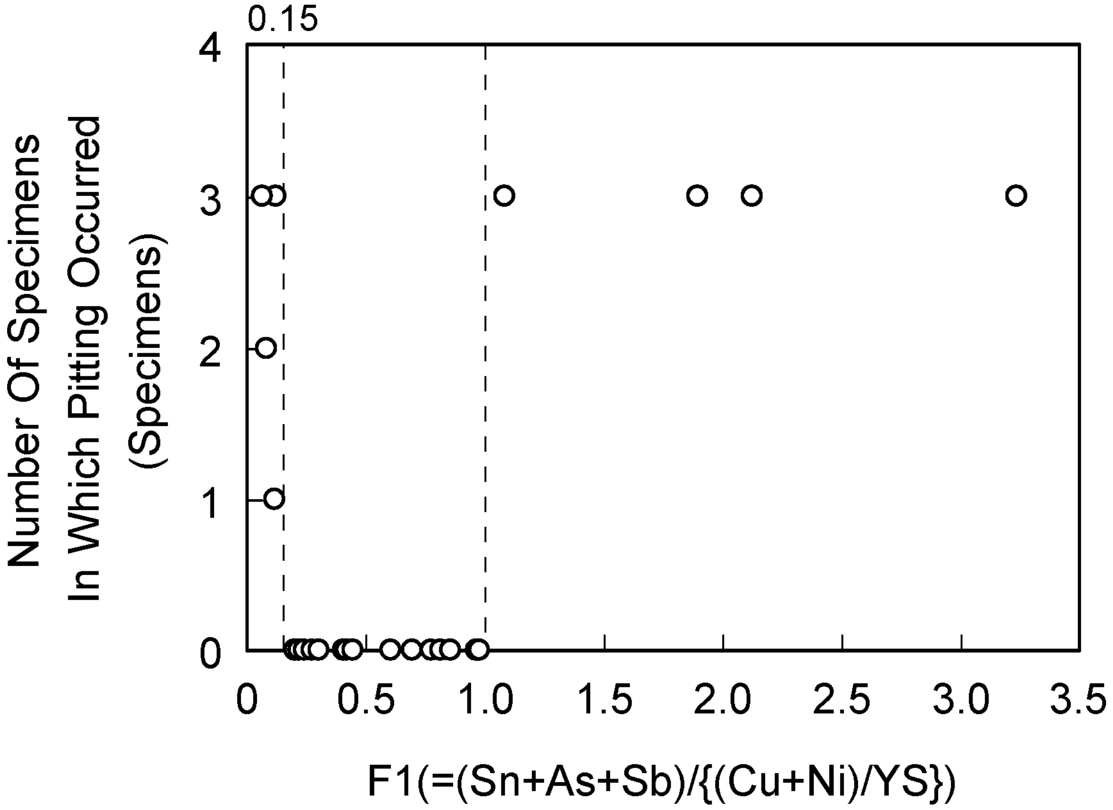
$$0.15 \leq (\mathrm{Sn}+\mathrm{As}+\mathrm{Sb})/\{(\mathrm{Cu}+\mathrm{Ni})/\mathrm{YS}\} \leq 1.00 \qquad (1)$$

where, in Formula (1), a content of a corresponding element in percent by mass is substituted for each symbol of an element, and a yield strength in MPa is substituted for YS, and, if a corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

2. The martensitic stainless steel material according to claim 1, containing one or more elements selected from a group consisting of:

W: 0.01 to 0.50%,
Nb: 0.001 to 0.500%,
As: 0.0001 to 0.0100%, and
Sb: 0.0001 to 0.0100%.

FIG. 1


0.15
4
3
2
1
0
Number Of Specimens In Which Pitting Occurred (Specimens)
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
F1(=(Sn+As+Sb)/{(Cu+Ni)/YS})

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/013603

A. CLASSIFICATION OF SUBJECT MATTER

C21D 8/02(2006.01)i; ***C21D 8/06***(2006.01)i; ***C21D 8/10***(2006.01)i; ***C21D 9/08***(2006.01)i; ***C22C 38/00***(2006.01)i; ***C22C 38/60***(2006.01)i
FI: C22C38/00 302Z; C22C38/60; C21D9/08 E; C21D8/02 D; C21D8/06 B; C21D8/10 D

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)

C21D8/02; C21D8/06; C21D8/10; C21D9/08; C22C38/00; C22C38/60

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.
A	WO 2020/202957 A1 (JFE STEEL CORP) 08 October 2020 (2020-10-08)	1-2
A	WO 2019/240127 A1 (NIPPON STEEL STAINLESS STEEL CORP) 19 December 2019 (2019-12-19)	1-2

☐ 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 **03 June 2022**	Date of mailing of the international search report **14 June 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.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/013603

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2020/202957 A1	08 October 2020	EP 3916120 A1	
WO 2019/240127 A1	19 December 2019	KR 10-2020-0124751 A	

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2000192196 A **[0005] [0009]**
- JP 2012136742 A **[0005] [0009]**
- WO 2008023702 A **[0005] [0009]**