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

(11) EP 4 682 287 A1

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

(43) Date of publication:
21.01.2026 Bulletin 2026/04

(21) Application number: **24774866.8**

(22) Date of filing: **15.03.2024**

(51) International Patent Classification (IPC):
C22C 38/00 *(2006.01)* ***C21D 8/10*** *(2006.01)*
C21D 9/08 *(2006.01)* ***C22C 38/60*** *(2006.01)*

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

(86) International application number:
PCT/JP2024/010269

(87) International publication number:
WO 2024/195730 (26.09.2024 Gazette 2024/39)

(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 ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
GE KH MA MD TN

(30) Priority: **17.03.2023 JP 2023043602**

(71) Applicant: **NIPPON STEEL CORPORATION**
Chiyoda-ku
Tokyo 100-8071 (JP)

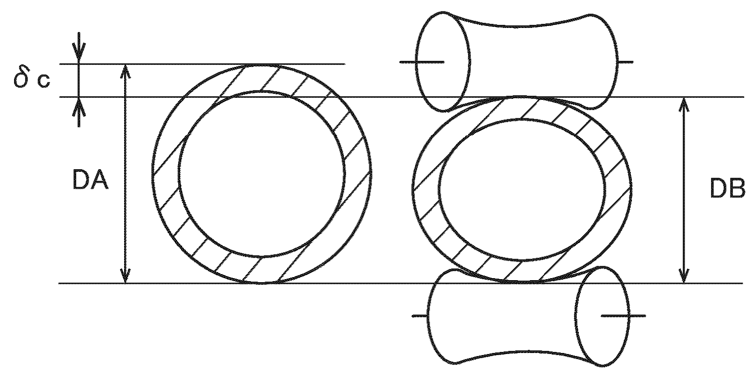
(72) Inventors:
- **OKADA, Seiya**
  Tokyo 100-8071 (JP)
- **ARAI, Yuji**
  Tokyo 100-8071 (JP)
- **KONDO, Keiichi**
  Tokyo 100-8071 (JP)

(74) Representative: **Zimmermann & Partner Patentanwälte mbB**
P.O. Box 330 920
80069 München (DE)

(54) **DUPLEX STAINLESS STEEL PIPE**

(57) A duplex stainless steel pipe in which high strength and excellent corrosion resistance are obtained is provided. A duplex stainless steel pipe according to the present disclosure contains, in mass%, C: 0.030% or less, Si: 0.20 to 1.00%, Mn: 0.5 to 7.0%, P: 0.040% or less, S: 0.020% or less, Al: 0.100% or less, Ni: 4.0 to 9.0%, Cr: 20.0 to 30.0%, Mo: 0.5 to 2.0%, Cu: 1.5 to 3.0%, N: 0.15 to 0.30%, V: 0.01 to 0.50%, Nb: 0.030 to 0.300%, Co: 0.10 to 0.50%, and Sn: 0.001 to 0.050%, and has a microstructure that is composed of, in volume ratio, ferrite in an amount of 35.0 to 65.0% and σ phase in an amount of 0 to less than 1.0%, with the balance being austenite. In the duplex stainless steel pipe, the content of undissolved Nb is 0.008% by mass or more, a ratio of the content of undissolved Nb to the content of undissolved Al is 1.0 or more, and the yield strength is 655 MPa or more.

FIG. 2



EP 4 682 287 A1

Description

TECHNICAL FIELD

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

BACKGROUND ART

[0002] Oil wells and gas wells (hereinafter, oil wells and gas wells are collectively referred to simply as "oil wells") are sometimes a corrosive environment containing a corrosive gas. Here, the term "corrosive gas" means carbon dioxide gas and/or hydrogen sulfide gas. Therefore, steel materials for use in oil wells are required to have excellent corrosion resistance in a corrosive environment.

[0003] To date, as means for improving the corrosion resistance of a steel material, means of forming a passive film mainly composed of Cr oxide on the surface of the steel material by increasing the content of chromium (Cr) is known. Therefore, in an environment where excellent corrosion resistance is required, in some cases a duplex stainless steel material in which the content of Cr has been made high is used.

[0004] In recent years, furthermore, deep wells below sea level are being actively developed. A steel material used in such deep wells is required to have high strength. Therefore, there is a need for a duplex stainless steel material that can achieve both high strength and excellent corrosion resistance as a steel material to be used in an oil well.

[0005] Japanese Patent Application Publication No. 2018-193591 (Patent Literature 1) and International Application Publication No. WO2012/121232 (Patent Literature 2) each proposes a duplex stainless steel material that has high strength and excellent corrosion resistance.

[0006] The duplex stainless steel material disclosed in Patent Literature 1 has a chemical composition which contains, in mass%, C: 0.005 to 0.04%, Si: 0.2 to 1.0%, Mn: 0.1 to 2.0%, P: 0.040% or less, S: 0.010% or less, Ni: 3 to 7%, Cr: 23 to 28%, Mo: 0.5 to 1.5%, Cu: 2 to 4%, N: 0.10 to 0.35%, Al: 0.001 to 0.04%, W: 0 to 1.0%, Co: 0 to 1.0%, V: 0 to 1.0%, Nb: 0 to 0.2%, Ti: 0 to 0.2%, Ca: 0 to 0.02%, Mg: 0 to 0.02%, B: 0 to 0.02%, and rare earth metal (REM): 0 to 0.2%, with the balance being Fe and impurities, and which satisfies Formula (1) to Formula (3), and has a yield strength YS of 655 MPa or more. Here, Formula (1) to Formula (3) are as follows.

$$YS/150 \leq Ni + Mo + 0.5W + Cu - Mn \leq YS/75 \qquad (1)$$

$$Cr + 3.3 \times (Mo + 0.5W) + 16N \geq 30.0 \qquad (2)$$

$$Mo + 0.5W + Ni \leq 7.50 \qquad (3)$$

[0007] It is described in Patent Literature 1 that in this duplex stainless steel material, by adjusting the contents of the elements in the chemical composition and the yield strength so as to satisfy Formula (1) to Formula (3), high strength and excellent corrosion resistance are obtained.

[0008] The duplex stainless steel material disclosed in Patent Literature 2 has a chemical composition containing, in mass%, C: 0.03% or less, Si: 0.3% or less, Mn: 3.0% or less, P: 0.040% or less, S: 0.008% or less, Cu: 0.2 to 2.0%, Ni: 5.0 to 6.5%, Cr: 23.0 to 27.0%, Mo: 2.5 to 3.5%, W: 1.5 to 4.0%, and N: 0.24 to 0.40%, with the balance being Fe and impurities, in which a σ phase susceptibility index X (= 2.2Si + 0.5Cu + 2.0Ni + Cr + 4.2Mo + 0.2W) is 52.0 or less, a strength index Y (= Cr + 1.5Mo + 10N + 3.5W) is 40.5 or more, and a pitting resistance equivalent PREW (= Cr + 3.3(Mo + 0.5W) + 16N) is 40 or more. In the structure of the steel, in a cross section in the thickness direction which is parallel to the rolling elongation direction, when a straight line is drawn parallel to the thickness direction from the outer layer to a depth of 1 mm, the number of boundaries between a ferrite phase and an austenite phase which intersect with the straight line is 160 or more. It is described in Patent Literature 2 that in this duplex stainless steel, high strength can be achieved without loss of corrosion resistance.

CITATION LIST

PATENT LITERATURE

[0009]

Patent Literature 1: Japanese Patent Application Publication No. 2018-193591

Patent Literature 2: International Application Publication No. WO2012/121232

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0010] In the duplex stainless steel materials disclosed in Patent Literature 1 and Patent Literature 2, high strength and excellent corrosion resistance are obtained. However, high strength and excellent corrosion resistance may also be obtained by means other than the means disclosed in Patent Literature 1 and Patent Literature 2.

[0011] An objective of the present disclosure is to provide a duplex stainless steel pipe in which high strength and excellent corrosion resistance are obtained.

SOLUTION TO PROBLEM

[0012] A duplex stainless steel pipe according to the present disclosure consists of, in mass%, C: 0.030% or less, Si: 0.20 to 1.00%, Mn: 0.5 to 7.0%, P: 0.040% or less, S: 0.020% or less, Al: 0.100% or less, Ni: 4.0 to 9.0%, Cr: 20.0 to 30.0%, Mo: 0.5 to 2.0%, Cu: 1.5 to 3.0%, N: 0.15 to 0.30%, V: 0.01 to 0.50%, Nb: 0.030 to 0.300%, Co: 0.10 to 0.50%, Sn: 0.001 to 0.050%, Ta: 0 to 0.100%, Ti: 0 to 0.100%, Zr: 0 to 0.100%, Hf: 0 to 0.100%, W: 0 to 0.200%, Sb: 0 to 0.100%, Ca: 0 to 0.020%, Mg: 0 to 0.020%, B: 0 to 0.020%, and rare earth metal: 0 to 0.200%, with the balance being Fe and impurities, and has a microstructure that is composed of, in volume ratio, ferrite in an amount of 35.0 to 65.0% and σ phase in an amount of 0 to less than 1.0%, with the balance being austenite, wherein a content of undissolved Nb is 0.008% by mass or more, and a ratio of the content of undissolved Nb to a content of undissolved Al is 1.0 or more, and a yield strength is 655 MPa or more.

ADVANTAGEOUS EFFECTS OF INVENTION

[0013] In the duplex stainless steel pipe according to the present disclosure, high strength and excellent corrosion resistance are obtained.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

[FIG. 1] FIG. 1 is a schematic diagram of an example of a straightening machine.
[FIG. 2] FIG. 2 is a front view of the straightening machine illustrated in FIG. 1.

DESCRIPTION OF EMBODIMENTS

[0015] The present inventors conducted studies from the viewpoint of the chemical composition with regard to a duplex stainless steel pipe in which high strength and excellent corrosion resistance can be obtained. As a result, the present inventors have considered that if a duplex stainless steel pipe consists of, in mass%, C: 0.030% or less, Si: 0.20 to 1.00%, Mn: 0.5 to 7.0%, P: 0.040% or less, S: 0.020% or less, Al: 0.100% or less, Ni: 4.0 to 9.0%, Cr: 20.0 to 30.0%, Mo: 0.5 to 2.0%, Cu: 1.5 to 3.0%, N: 0.15 to 0.30%, V: 0.01 to 0.50%, Nb: 0.030 to 0.300%, Co: 0.10 to 0.50%, Sn: 0.001 to 0.050%, Ta: 0 to 0.100%, Ti: 0 to 0.100%, Zr: 0 to 0.100%, Hf: 0 to 0.100%, W: 0 to 0.200%, Sb: 0 to 0.100%, Ca: 0 to 0.020%, Mg: 0 to 0.020%, B: 0 to 0.020%, and rare earth metal: 0 to 0.200%, with the balance being Fe and impurities, high strength and excellent corrosion resistance can be obtained.

[0016] Therefore, the present inventors conducted further studies from viewpoints other than the chemical composition with respect to means for obtaining even higher strength in a duplex stainless steel pipe that satisfies the chemical composition described above. First, the present inventors conducted studies regarding the microstructure of a duplex stainless steel pipe. The microstructure of a duplex stainless steel pipe having the chemical composition described above is mainly composed of ferrite and austenite. The present inventors have found that if the microstructure of a duplex stainless steel pipe having the chemical composition described above is made a structure in which the ferrite volume ratio is 35.0 to 65.0% and the balance is substantially austenite, strength and corrosion resistance can be stably increased.

[0017] In addition, the present inventors have considered that the strength of a duplex stainless steel pipe can be further increased by causing Nb carbo-nitrides to precipitate in the duplex stainless steel pipe. Nb carbo-nitrides are fine precipitates. Therefore, the strength of a duplex stainless steel pipe is increased by precipitation strengthening by Nb carbo-nitrides. However, σ phase also easily forms in a temperature range in which Nb carbo-nitrides form during a process for producing a duplex stainless steel pipe. The σ phase reduces the corrosion resistance of the duplex stainless steel pipe. Therefore, the present inventors investigated the relation between the formed amount of Nb carbo-nitrides, the formed amount of σ phase, and the strength and corrosion resistance. The formed amount of Nb carbo-nitrides correlates with the content of undissolved Nb. In a duplex stainless steel pipe satisfying the chemical composition described above, if the content of undissolved Nb is 0.008% by mass or more, Nb carbo-nitrides are sufficiently formed and the strength can be increased. In addition, even when the content of undissolved Nb is 0.008% by mass or more, by a microstructure that is composed of, in volume ratio, ferrite in an amount of 35.0 to 65.0% and σ phase in an amount of 0 to less than 1.0%, with the balance being austenite, excellent corrosion resistance can be maintained.

[0018] However, it has been revealed that even when duplex stainless steel pipes satisfied the features described above, sufficient strength was still not obtained in some cases. Therefore, the present inventors conducted further studies. As a result, it has newly been revealed that in a duplex stainless steel pipe having the chemical composition described above, Al nitrides are a factor that causes a reduction in strength.

[0019] In the chemical composition described above, in order to obtain high strength by means of dissolved N, the content of N is higher than the content of C. It is considered that in the case of such a chemical composition, the content of N in the Nb carbo-nitrides is higher than the content of C. That is, in the chemical composition described above, N not only contributes to solid-solution strengthening as dissolved N, but also contributes to precipitation strengthening by means of Nb carbo-nitrides.

[0020] On the other hand, N also combines with Al to form Al nitrides. Al nitrides are coarser precipitates than Nb carbo-nitrides. Therefore, Al nitrides make almost no contribution to precipitation strengthening. Therefore, in a duplex stainless steel pipe having the chemical composition described above, if the formed amount of Al nitrides is relatively larger than the formed amount of Nb carbo-nitrides, a case will occur in which the dissolved N and Nb nitrides are insufficient. In such case, the strength of the duplex stainless steel pipe cannot be sufficiently increased.

[0021] Al nitrides correlate with the content of undissolved Al. Therefore, the present inventors conducted further studies regarding the relation between the content of undissolved Nb and content of undissolved Al and the strength and corrosion resistance. As a result, the present inventors have discovered that if an undissolved Nb/Al ratio that is a ratio of the content of undissolved Nb to the content of undissolved Al is 1.0 or more, a sufficient amount of Nb nitrides and a sufficient amount of dissolved N can be secured, and as a result, both high strength and excellent corrosion resistance can be achieved.

[0022] Note that, there is also a possibility that in a duplex stainless steel pipe satisfying the chemical composition and microstructure described above, by making the content of undissolved Nb 0.008% by mass or more and making the undissolved Nb/Al ratio 1.0 or more, both a yield strength of 655 MPa or more and excellent corrosion resistance are achieved by a mechanism that is different from the mechanism described above. However, the fact that in a duplex stainless steel pipe having the chemical composition and microstructure described above, both a high yield strength of 655 MPa or more and excellent corrosion resistance can be achieved by making the content of undissolved Nb 0.008% by mass or more and making the undissolved Nb/Al ratio 1.0 or more has been demonstrated by examples that are described later.

[0023] A duplex stainless steel pipe according to the present embodiment, which was completed based on the findings described above, is as follows.

[0024] A duplex stainless steel pipe according to a first aspect has a chemical composition consisting of, in mass%, C: 0.030% or less, Si: 0.20 to 1.00%, Mn: 0.5 to 7.0%, P: 0.040% or less, S: 0.020% or less, Al: 0.100% or less, Ni: 4.0 to 9.0%, Cr: 20.0 to 30.0%, Mo: 0.5 to 2.0%, Cu: 1.5 to 3.0%, N: 0.15 to 0.30%, V: 0.01 to 0.50%, Nb: 0.030 to 0.300%, Co: 0.10 to 0.50%, Sn: 0.001 to 0.050%, Ta: 0 to 0.100%, Ti: 0 to 0.100%, Zr: 0 to 0.100%, Hf: 0 to 0.100%, W: 0 to 0.200%, Sb: 0 to 0.100%, Ca: 0 to 0.020%, Mg: 0 to 0.020%, B: 0 to 0.020%, and rare earth metal: 0 to 0.200%, with the balance being Fe and impurities. The microstructure of the aforementioned duplex stainless steel pipe is composed of, in volume ratio, ferrite in an amount of 35.0 to 65.0% and σ phase in an amount of 0 to less than 1.0%, with the balance being austenite. In addition, in the aforementioned duplex stainless steel pipe, a content of undissolved Nb is 0.008% by mass or more, and a ratio of the content of undissolved Nb to a content of undissolved Al is 1.0 or more, and the yield strength is 655 MPa or more.

[0025] A duplex stainless steel pipe according to the second aspect is in accordance with the duplex stainless steel pipe according to the first aspect, wherein the chemical composition contains one or more types of element selected from a group consisting of Ta: 0.001 to 0.100%, Ti: 0.001 to 0.100%, Zr: 0.001 to 0.100%, Hf: 0.001 to 0.100%, W: 0.001 to 0.200%, Sb: 0.001 to 0.100%, Ca: 0.001 to 0.020%, Mg: 0.001 to 0.020%, B: 0.001 to 0.020%, and rare earth metal: 0.001 to 0.200%.

[0026] Hereunder, the duplex stainless steel pipe according to the present embodiment is described in detail. Note that, in the following description, the duplex stainless steel pipe is also referred to simply as "steel pipe". Further, the symbol "%" in relation to an element means mass percent unless otherwise stated.

[Features of duplex stainless steel pipe of present embodiment]

[0027] The duplex stainless steel pipe of the present embodiment satisfies the following feature 1 to feature 4.

(Feature 1)

[0028] The chemical composition consists of, in mass%, C: 0.030% or less, Si: 0.20 to 1.00%, Mn: 0.5 to 7.0%, P: 0.040% or less, S: 0.020% or less, Al: 0.100% or less, Ni: 4.0 to 9.0%, Cr: 20.0 to 30.0%, Mo: 0.5 to 2.0%, Cu: 1.5 to 3.0%, N: 0.15 to 0.30%, V: 0.01 to 0.50%, Nb: 0.030 to 0.300%, Co: 0.10 to 0.50%, Sn: 0.001 to 0.050%, Ta: 0 to 0.100%, Ti: 0 to 0.100%, Zr: 0 to 0.100%, Hf: 0 to 0.100%, W: 0 to 0.200%, Sb: 0 to 0.100%, Ca: 0 to 0.020%, Mg: 0 to 0.020%, B: 0 to 0.020%, and rare earth metal: 0 to 0.200%, with the balance being Fe and impurities.

(Feature 2)

[0029] The microstructure is composed of, in volume ratio, ferrite in an amount of 35.0 to 65.0% and σ phase in an amount of 0 to less than 1.0%, with the balance being austenite.

(Feature 3)

[0030] The content of undissolved Nb is 0.008% by mass or more, and a ratio of the content of undissolved Nb to the content of undissolved Al is 1.0 or more.

(Feature 4)

[0031] The yield strength is 655 MPa or more.
[0032] Feature 1 to feature 4 are described hereunder.

[(Feature 1) Regarding chemical composition]

[0033] The chemical composition of the duplex stainless steel pipe according to the present embodiment contains the following elements.

C: 0.030% or less

[0034] Carbon (C) is unavoidably contained. That is, the lower limit of the content of C is more than 0%. C forms Cr carbides at grain boundaries and increases the corrosion susceptibility at the grain boundaries. Therefore, if the content of C is more than 0.030%, the corrosion resistance of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment. Therefore, the C content is 0.030% or less.
[0035] The content of C is preferably as low as possible. However, excessive reduction of the content of C will significantly increase the production cost. Therefore, when industrial manufacturing is taken into consideration, a preferable lower limit of the content of C is 0.001%, more preferably is 0.002%, and further preferably is 0.005%.
[0036] A preferable upper limit of the content of C is 0.029%, more preferably is 0.028%, and further preferably is 0.027%.

Si: 0.20 to 1.00%

[0037] Silicon (Si) deoxidizes the steel. If the content of Si is less than 0.20%, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.
[0038] On the other hand, if the content of Si is more than 1.00%, toughness and hot workability of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment.
[0039] Therefore, the content of Si is 0.20 to 1.00%.
[0040] A preferable lower limit of the content of Si is 0.21%, more preferably is 0.22%, further preferably is 0.25%, and further preferably is 0.30%.
[0041] A preferable upper limit of the content of Si is 0.95%, more preferably is 0.92%, further preferably is 0.91%, and further preferably is 0.90%.

Mn: 0.5 to 7.0%

[0042] Manganese (Mn) deoxidizes the steel and desulfurizes the steel. Furthermore, Mn enhances hot workability of the steel pipe. If the content of Mn is less than 0.5%, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.
[0043] On the other hand, Mn segregates to grain boundaries together with impurities such as P and S. Therefore, if the

content of Mn is more than 7.0%, even if the contents of other elements are within the range of the present embodiment, the corrosion resistance of the steel pipe in high temperature environments will decrease.
[0044] Therefore, the content of Mn is 0.5 to 7.0%.
[0045] A preferable lower limit of the content of Mn is 0.6%, more preferably is 0.8%, further preferably is 1.0%, and further preferably is 1.2%.
[0046] A preferable upper limit of the content of Mn is 6.8%, more preferably is 6.5%, further preferably is 6.3%, further preferably is 6.2%, and further preferably is 6.0%.

P: 0.040% or less

[0047] Phosphorus (P) is unavoidably contained. That is, the lower limit of the content of P is more than 0%. P segregates to grain boundaries. Therefore, if the content of P is more than 0.040%, the corrosion resistance of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment. Therefore, the content of P is 0.040% or less.
[0048] The content of P is preferably as low as possible. However, excessive reduction of the content of P will significantly increase the production cost. Therefore, when industrial manufacturing is taken 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%.
[0049] A preferable upper limit of the content of P is 0.038%, more preferably is 0.036%, further preferably is 0.035%, and further preferably is 0.030%.

S: 0.020% or less

[0050] Sulfur (S) is unavoidably contained. That is, a lower limit of the content of S is more than 0%. S segregates to grain boundaries. Therefore, if the content of S is more than 0.020%, toughness and hot workability of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment. Therefore, the content of S is 0.020% or less.
[0051] The content of S is preferably as low as possible. However, excessive reduction of the content of S will significantly increase the production cost. Therefore, when industrial manufacturing is taken into consideration, a preferable lower limit of the content of S is 0.001%, more preferably is 0.002%, further preferably is 0.003%, further preferably is 0.004%, and further preferably is 0.005%.
[0052] A preferable upper limit of the content of S is 0.018%, more preferably is 0.016%, and further preferably is 0.014%.

Al: 0.100% or less

[0053] Aluminum (Al) is unavoidably contained. That is, the lower limit of the content of Al is more than 0%. Al deoxidizes the steel. On the other hand, if the content of Al is more than 0.100%, coarse oxide-based inclusions will form. Consequently, even if the contents of other elements are within the range of the present embodiment, the toughness of the steel pipe will decrease. Therefore, the content of Al is 0.100% or less.
[0054] A preferable lower limit of the content of Al is 0.001%, more preferably is 0.005%, further preferably is 0.007%, and further preferably is 0.010%.
[0055] A preferable upper limit of the content of Al is 0.095%, more preferably is 0.092%, further preferably is 0.090%, and further preferably is 0.085%.
[0056] Note that, the content of Al in the chemical composition of the duplex stainless steel pipe of the present embodiment means the content of "acid-soluble Al," that is, the content of sol. Al.

Ni: 4.0 to 9.0%

[0057] Nickel (Ni) stabilizes the austenitic structure of the steel pipe. That is, Ni stabilizes the duplex microstructure consisting of ferrite and austenite. Ni also enhances the corrosion resistance of the steel pipe. If the content of Ni is less than 4.0%, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.
[0058] On the other hand, if the content of Ni is more than 9.0%, the volume ratio of austenite will be too high. In such case, the strength of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment.
[0059] Therefore, the content of Ni is 4.0 to 9.0%.
[0060] A preferable lower limit of the content of Ni is 4.1%, more preferably is 4.3%, and further preferably is 4.5%.
[0061] A preferable upper limit of the content of Ni is 8.8%, more preferably is 8.6%, further preferably is 8.4%, further

preferably is 8.2%, and further preferably is 8.0%.

Cr: 20.0 to 30.0%

[0062] Chromium (Cr) forms a passive film as an oxide on the surface of the steel pipe and thereby enhances the corrosion resistance of the steel pipe. Cr also increases the volume ratio of the ferritic structure of the steel pipe. By obtaining a sufficient ferritic structure, the corrosion resistance of the steel pipe is stabilized. If the content of Cr is less than 20.0%, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.
[0063] On the other hand, if the content of Cr is more than 30.0%, hot workability of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment.
[0064] Therefore, the content of Cr is 20.0 to 30.0%.
[0065] A preferable lower limit of the content of Cr is 20.2%, more preferably is 20.5%, further preferably is 21.0%, and further preferably is 21.5%.
[0066] A preferable upper limit of the content of Cr is 29.8%, more preferably is 29.6%, further preferably is 29.5%, further preferably is 29.0%, and further preferably is 28.5%.

Mo: 0.5 to 2.0%

[0067] Molybdenum (Mo) enhances the corrosion resistance of the steel pipe. Mo also dissolves in the steel and increases the strength of the steel pipe. If the content of Mo is less than 0.5%, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.
[0068] On the other hand, if the content of Mo is more than 2.0%, hot workability of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment.
[0069] Therefore, the content of Mo is 0.5 to 2.0%.
[0070] A preferable lower limit of the content of Mo is 0.6%, more preferably is 0.7%, and further preferably is 0.8%.
[0071] A preferable upper limit of the content of Mo is 1.9%, more preferably is 1.8%, further preferably is 1.7%, further preferably is 1.6%, and further preferably is 1.5%.

Cu: 1.5 to 3.0%

[0072] Copper (Cu) precipitates in the steel pipe and increases the strength of the steel pipe. If the content of Cu is less than 1.5%, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.
[0073] On the other hand, if the content of Cu is more than 3.0%, hot workability of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment.
[0074] Therefore, the content of Cu is 1.5 to 3.0%.
[0075] A preferable lower limit of the content of Cu is 1.6%, more preferably is 1.8%, and further preferably is 2.0%.
[0076] A preferable upper limit of the content of Cu is 2.9%, more preferably is 2.8%, and further preferably is 2.7%.

N: 0.15 to 0.30%

[0077] Nitrogen (N) dissolves in the steel pipe and increases the strength of the steel pipe. N also combines with Nb to form Nb carbo-nitrides, thereby increasing the strength of the steel pipe by precipitation strengthening. In addition, N stabilizes the austenitic structure of the steel pipe. If the content of N is less than 0.15%, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.
[0078] On the other hand, if the content of N is more than 0.30%, toughness and hot workability of the steel pipe will decrease even if the contents of other elements are within the range of the present embodiment.
[0079] Therefore, the content of N is 0.15 to 0.30%.
[0080] A preferable lower limit of the content of N is 0.16%, more preferably is 0.18%, and further preferably is 0.20%.
[0081] A preferable upper limit of the content of N is 0.29%, more preferably is 0.28%, further preferably is 0.27%, further preferably is 0.26%, and further preferably is 0.25%.

V: 0.01 to 0.50%

[0082] Vanadium (V) increases the strength of the steel pipe. If the content of V is less than 0.01%, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

[0083] On the other hand, if the content of V is more than 0.50%, even if the contents of other elements are within the range of the present embodiment, the strength of the steel pipe will be too high and the toughness and hot workability of the steel pipe will decrease.

[0084] Therefore, the content of V is 0.01 to 0.50%.

[0085] A preferable lower limit of the content of V is 0.02%, more preferably is 0.03%, further preferably is 0.05%, further preferably is 0.07%, and further preferably is 0.10%.

[0086] A preferable upper limit of the content of V is 0.48%, more preferably is 0.47%, further preferably is 0.45%, further preferably is 0.42%, and further preferably is 0.40%.

Nb: 0.030 to 0.300%

[0087] Niobium (Nb) forms carbo-nitrides and thereby increases the strength of the steel pipe. If the content of Nb is less than 0.030%, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

[0088] On the other hand, if the content of Nb is more than 0.300%, even if the contents of other elements are within the range of the present embodiment, the strength of the steel pipe will be too high and the toughness of the steel pipe will decrease.

[0089] Therefore, the content of Nb is 0.030 to 0.300%.

[0090] A preferable lower limit of the content of Nb is 0.031%, more preferably is 0.033%, further preferably is 0.035%, further preferably is 0.037%, and further preferably is 0.040%.

[0091] A preferable upper limit of the content of Nb is 0.294%, more preferably is 0.290%, further preferably is 0.280%, and further preferably is 0.250%.

Co: 0.10 to 0.50%

[0092] Cobalt (Co) forms a coating on the surface of the steel pipe and enhances the corrosion resistance of the steel pipe. Co also increases hardenability of the steel pipe and stabilizes the strength. If the content of Co is less than 0.10%, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

[0093] On the other hand, if the content of Co is more than 0.50%, the production cost will increase considerably even if the contents of other elements are within the range of the present embodiment.

[0094] Therefore, the content of Co is 0.10 to 0.50%.

[0095] A preferable lower limit of the content of Co is 0.11%, more preferably is 0.13%, and further preferably is 0.15%.

[0096] A preferable upper limit of the content of Co is 0.48%, more preferably is 0.45%, further preferably is 0.40%, and further preferably is 0.35%.

Sn: 0.001 to 0.050%

[0097] Tin (Sn) enhances the corrosion resistance of the steel pipe. If the content of Sn is less than 0.001%, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

[0098] On the other hand, if the content of Sn is more than 0.050%, even if the contents of other elements are within the range of the present embodiment, liquation cracking will occur at grain boundaries, which will decrease the hot workability of the steel pipe.

[0099] Therefore, the content of Sn is 0.001 to 0.050%.

[0100] A preferable lower limit of the content of Sn is 0.002%, more preferably is 0.003%, further preferably is 0.005%, further preferably is 0.006%, further preferably is 0.008%, and further preferably is 0.010%.

[0101] A preferable upper limit of the content of Sn is 0.048%, more preferably is 0.045%, further preferably is 0.043%, and further preferably is 0.040%.

[0102] The balance of the chemical composition of the duplex stainless steel pipe according to the present embodiment is Fe and impurities. Here, the term "impurities" with respect to the chemical composition refers to substances which are mixed in from ore or scrap as the raw material or from the production environment or the like when industrially producing the duplex stainless steel pipe, and which are permitted within a range that does not adversely affect the duplex stainless steel pipe according to the present embodiment.

[Regarding optional elements]

[0103] The chemical composition of the duplex stainless steel pipe described above may further contain, in lieu of a part of Fe, one or more types of element selected from the group consisting of Ta: 0 to 0.100%, Ti: 0 to 0.100%, Zr: 0 to 0.100%, Hf: 0 to 0.100%, W: 0 to 0.200%, Sb: 0 to 0.100%, Ca: 0 to 0.020%, Mg: 0 to 0.020%, B: 0 to 0.020%, and rare earth metal: 0 to 0.200%.
[0104] These optional elements are described hereunder.

[First group (Ta, Ti, Zr, Hf, and W)]

[0105] The duplex stainless steel pipe of the present embodiment may contain one or more types of element selected from the group consisting of Ta, Ti, Zr, Hf, and W in lieu of a part of Fe. Each of these elements is an optional element, and increases the strength of the steel pipe.

Ta: 0 to 0.100%

[0106] Tantalum (Ta) is an optional element, and does not have to be contained. That is, the content of Ta may be 0%.
[0107] When contained, that is, when the content of Ta is more than 0%, Ta forms carbo-nitrides and increases the strength of the steel pipe. If even a small amount of Ta is contained, the aforementioned advantageous effect will be obtained to a certain extent.
[0108] However, if the content of Ta is more than 0.100%, even if the contents of other elements are within the range of the present embodiment, the strength of the steel pipe will be too high and the toughness of the steel pipe will decrease.
[0109] Therefore, the content of Ta is 0 to 0.100%.
[0110] A preferable lower limit of the content of Ta is 0.001 %, more preferably is 0.002%, further preferably is 0.003%, further preferably is 0.005%, further preferably is 0.010%, and further preferably is 0.015%.
[0111] A preferable upper limit of the content of Ta is 0.080%, more preferably is 0.070%, further preferably is 0.060%, further preferably is 0.050%, and further preferably is 0.040%.

Ti: 0 to 0.100%

[0112] Titanium (Ti) is an optional element, and does not have to be contained. That is, the content of Ti may be 0%.
[0113] When contained, that is, when the content of Ti is more than 0%, Ti forms carbo-nitrides and increases the strength of the steel pipe. If even a small amount of Ti is contained, the aforementioned advantageous effect will be obtained to a certain extent.
[0114] However, if the content of Ti is more than 0.100%, even if the contents of other elements are within the range of the present embodiment, the strength of the steel pipe will be too high and the toughness of the steel pipe will decrease.
[0115] Therefore, the content of Ti is 0 to 0.100%.
[0116] A preferable lower limit of the content of Ti is 0.001%, more preferably is 0.002%, further preferably is 0.003%, further preferably is 0.005%, further preferably is 0.010%, and further preferably is 0.015%.
[0117] A preferable upper limit of the content of Ti is 0.098%, more preferably is 0.095%, further preferably is 0.090%, further preferably is 0.085%, further preferably is 0.080%, further preferably is 0.075%, and further preferably is 0.070%.

Zr: 0 to 0.100%

[0118] Zirconium (Zr) is an optional element, and does not have to be contained. That is, the content of Zr may be 0%.
[0119] When contained, that is, when the content of Zr is more than 0%, Zr forms carbo-nitrides and increases the strength of the steel pipe. If even a small amount of Zr is contained, the aforementioned advantageous effect will be obtained to a certain extent.
[0120] However, if the content of Zr is more than 0.100%, even if the contents of other elements are within the range of the present embodiment, the strength of the steel pipe will be too high and the toughness of the steel pipe will decrease.
[0121] Therefore, the content of Zr is 0 to 0.100%.
[0122] A preferable lower limit of the content of Zr is 0.001%, more preferably is 0.002%, further preferably is 0.003%, further preferably is 0.005%, further preferably is 0.010%, and further preferably is 0.015%.
[0123] A preferable upper limit of the content of Zr is 0.090%, more preferably is 0.080%, further preferably is 0.070%, further preferably is 0.060%, and further preferably is 0.050%.

Hf: 0 to 0.100%

[0124] Hafnium (Hf) is an optional element, and does not have to be contained. That is, the content of Hf may be 0%.
[0125] When contained, that is, when the content of Hf is more than 0%, Hf forms carbo-nitrides and increases the strength of the steel pipe. If even a small amount of Hf is contained, the aforementioned advantageous effect will be obtained to a certain extent.
[0126] However, if the content of Hf is more than 0.100%, even if the contents of other elements are within the range of the present embodiment, the strength of the steel pipe will be too high and the toughness of the steel pipe will decrease.
[0127] Therefore, the content of Hf is 0 to 0.100%.
[0128] A preferable lower limit of the content of Hf is 0.001 %, more preferably is 0.002%, further preferably is 0.003%, further preferably is 0.005%, further preferably is 0.010%, and further preferably is 0.015%.
[0129] A preferable upper limit of the content of Hf is 0.095%, more preferably is 0.090%, further preferably is 0.085%, further preferably is 0.080%, further preferably is 0.070%, further preferably is 0.060%, and further preferably is 0.050%.

W: 0 to 0.200%

[0130] Tungsten (W) is an optional element, and does not have to be contained. That is, the content of W may be 0%.
[0131] When contained, that is, when the content of W is more than 0%, W forms carbo-nitrides and increases the strength of the steel pipe. If even a small amount of W is contained, the aforementioned advantageous effect will be obtained to a certain extent. However, if the content of W is more than 0.200%, even if the contents of other elements are within the range of the present embodiment, the strength of the steel pipe will be too high and the toughness of the steel pipe will decrease.
[0132] Therefore, the content of W is 0 to 0.200%.
[0133] A preferable lower limit of the content of W is 0.001%, more preferably is 0.003%, further preferably is 0.005%, further preferably is 0.010%, and further preferably is 0.015%.
[0134] A preferable upper limit of the content of W is 0.180%, more preferably is 0.150%, further preferably is 0.130%, further preferably is 0.100%, further preferably is 0.080%, and further preferably is 0.050%.

[Second group: Sb]

[0135] The chemical composition of the duplex stainless steel pipe of the present embodiment may further contain Sb in lieu of a part of Fe.
[0136] Sb: 0 to 0.100%
[0137] Antimony (Sb) is an optional element, and does not have to be contained. That is, the content of Sb may be 0%.
[0138] When contained, that is, when the content of Sb is more than 0%, Sb enhances the corrosion resistance of the steel pipe. If even a small amount of Sb is contained, the aforementioned advantageous effect will be obtained to a certain extent.
[0139] However, if the content of Sb is more than 0.100%, even if the contents of other elements are within the range of the present embodiment, the high-temperature ductility of the steel pipe will decrease and hot workability of the steel pipe will decrease.
[0140] Therefore, the content of Sb is 0 to 0.100%.
[0141] A preferable lower limit of the content of Sb is 0.001 %, more preferably is 0.003%, further preferably is 0.005%, further preferably is 0.010%, and further preferably is 0.015%.
[0142] A preferable upper limit of the content of Sb is 0.090%, more preferably is 0.085%, further preferably is 0.080%, further preferably is 0.070%, further preferably is 0.060%, and further preferably is 0.050%.

[Third group (Ca, Mg, B, and rare earth metal)]

[0143] The chemical composition of the duplex stainless steel pipe of the present embodiment may further contain, in lieu of a part of Fe, one or more types of element selected from the group consisting of Ca, Mg, B, and rare earth metal.
[0144] Each of these elements is an optional element, and increases hot workability of the steel pipe.

Ca: 0 to 0.020%

[0145] Calcium (Ca) is an optional element, and does not have to be contained. That is, the content of Ca may be 0%.
[0146] When contained, that is, when the content of Ca is more than 0%, Ca immobilizes S in the steel pipe as a sulfide and thereby increases hot workability of the steel pipe. If even a small amount of Ca is contained, the aforementioned advantageous effect will be obtained to a certain extent.

[0147] However, if the content of Ca is more than 0.020%, oxides in the steel pipe will coarsen. Consequently, even if the contents of other elements are within the range of the present embodiment, the toughness of the steel pipe will decrease.
[0148] Therefore, the content of Ca is 0 to 0.020%.
[0149] A preferable lower limit of the content of Ca is 0.001%, more preferably is 0.002%, further preferably is 0.003%, and further preferably is 0.005%.
[0150] A preferable upper limit of the content of Ca is 0.018%, more preferably is 0.016%, further preferably is 0.014%, further preferably is 0.012%, and further preferably is 0.010%.

Mg: 0 to 0.020%

[0151] Magnesium (Mg) is an optional element, and does not have to be contained. That is, the content of Mg may be 0%.
[0152] When contained, that is, when the content of Mg is more than 0%, Mg immobilizes S in the steel pipe as a sulfide and thereby increases hot workability of the steel pipe. If even a small amount of Mg is contained, the aforementioned advantageous effect will be obtained to a certain extent.
[0153] However, if the content of Mg is more than 0.020%, oxides in the steel pipe will coarsen. Consequently, even if the contents of other elements are within the range of the present embodiment, the toughness of the steel pipe will decrease.
[0154] Therefore, the content of Mg is 0 to 0.020%.
[0155] A preferable lower limit of the content of Mg is 0.001%, more preferably is 0.002%, further preferably is 0.003%, further preferably is 0.005%, and further preferably is 0.006%.
[0156] A preferable upper limit of the content of Mg is 0.018%, more preferably is 0.016%, and further preferably is 0.015%.

B: 0 to 0.020%

[0157] Boron (B) is an optional element, and does not have to be contained. That is, the content of B may be 0%.
[0158] When contained, that is, when the content of B is more than 0%, B suppresses segregation of S in the steel pipe to grain boundaries and thereby increases hot workability of the steel pipe. If even a small amount of B is contained, the aforementioned advantageous effect will be obtained to a certain extent.
[0159] However, if the content of B is more than 0.020%, boron nitride (BN) will be formed. Consequently, even if the contents of other elements are within the range of the present embodiment, the toughness of the steel pipe will decrease.
[0160] Therefore, the content of B is 0 to 0.020%.
[0161] A preferable lower limit of the content of B is 0.001%, more preferably is 0.002%, further preferably is 0.003%, and further preferably is 0.005%.
[0162] A preferable upper limit of the content of B is 0.018%, more preferably is 0.016%, further preferably is 0.014%, further preferably is 0.012%, and further preferably is 0.010%.

Rare earth metal: 0 to 0.200%

[0163] Rare earth metal (REM) is an optional element, and does not have to be contained. That is, the content of REM may be 0%.
[0164] When contained, that is, when the content of REM is more than 0%, REM immobilizes S in the steel pipe as a sulfide and thereby increases hot workability of the steel pipe. If even a small amount of REM is contained, the aforementioned advantageous effect will be obtained to a certain extent.
[0165] However, if the content of REM is more than 0.200%, oxides in the steel pipe will coarsen. Consequently, even if the contents of other elements are within the range of the present embodiment, the toughness of the steel pipe will decrease.
[0166] Therefore, the content of REM is 0 to 0.200%.
[0167] A preferable lower limit of the content of REM is 0.001%, more preferably is 0.005%, further preferably is 0.008%, further preferably is 0.010%, and further preferably is 0.020%.
[0168] A preferable upper limit of the content of REM is 0.180%, more preferably is 0.160%, further preferably is 0.140%, further preferably is 0.120%, further preferably is 0.100%, further preferably is 0.080%, further preferably is 0.060%, and further preferably is 0.050%.
[0169] Note that, in the present description the term "REM" means one or more elements selected from the group consisting of scandium (Sc) which is the element with atomic number 21, yttrium (Y) which is the element with atomic number 39, and the elements from lanthanum (La) with atomic number 57 to lutetium (Lu) with atomic number 71 that are lanthanoids. Further, in the present description, the term "content of REM" means the total content of these elements.

[(Feature 2) Regarding microstructure]

[0170] The microstructure of the duplex stainless steel pipe of the present embodiment is composed of, in volume ratio, ferrite in an amount of 35.0 to 65.0% and σ phase in an amount of 0 to less than 1.0%, with the balance being austenite. In the microstructure, structures other than ferrite, austenite, and σ phase are negligibly small. Specifically, the microstructure of the duplex stainless steel pipe according to the present embodiment may contain minute amounts of precipitates, inclusions and the like, in addition to ferrite and austenite. However, with respect to the chemical composition of the duplex stainless steel pipe according to the present embodiment, the volume ratios of precipitates and inclusions and the like are negligibly small as compared with the volume ratios of ferrite, austenite, and σ phase.

[0171] In the microstructure of the duplex stainless steel pipe of the present embodiment, the volume ratio of ferrite is 35.0 to 65.0%. If the volume ratio of ferrite is too low, the yield strength and/or corrosion resistance of the steel pipe may decrease in some cases. On the other hand, if the volume ratio of ferrite is too high, the toughness and/or hot workability of the steel pipe may decrease in some cases.

[0172] Therefore, in the microstructure of the duplex stainless steel pipe of the present embodiment, the volume ratio of ferrite is 35.0 to 65.0%.

[0173] A preferable lower limit of the volume ratio of ferrite is 36.0%, and more preferably is 37.0%.

[0174] A preferable upper limit of the volume ratio of ferrite is 64.0%, and more preferably is 63.0%.

[0175] In the microstructure of the duplex stainless steel pipe of the present embodiment, σ phase reduces corrosion resistance. Therefore, it is preferable that the volume ratio of σ phase is small. If the volume ratio of σ phase is 1.0% or more, the corrosion resistance of the duplex stainless steel pipe will decrease. Therefore, the volume ratio of σ phase is 0 to less than 1.0%.

[0176] A low volume ratio of σ phase is preferable, and most preferably the volume ratio of σ phase is 0%. However, if the volume ratio of σ phase is excessively lowered, the production cost will significantly increase. Therefore, a preferable lower limit of the volume ratio of σ phase is more than 0%, and more preferably is 0.1%.

[0177] The balance of the microstructure is austenite. When the microstructure is composed of, in volume ratio, ferrite in an amount of 35.0 to 65.0% and σ phase in an amount of 0 to less than 1.0%, with the balance being austenite, on the precondition that the other features, i.e. feature 1, feature 3, and feature 4, are satisfied, high strength and excellent corrosion resistance are obtained.

[Method for measuring ferrite volume ratio and σ-phase volume ratio]

[0178] The volume ratio of ferrite in the duplex stainless steel pipe can be determined by a method in accordance with ASTM E562 (2019).

[0179] Specifically, a test specimen for microstructure observation having an observation surface with dimensions of 5 mm in the pipe axis direction and 5 mm in the pipe circumferential direction is taken from a central portion of the wall thickness of the duplex stainless steel pipe. In the present description, the pipe circumferential direction of the steel pipe means the direction that is perpendicular to the pipe axis direction and the pipe diameter direction. Note that, the size of the test specimen is not particularly limited as long as the aforementioned observation surface is obtained.

[0180] The observation surface of the test specimen is mirror-polished. The mirror-polished observation surface is electrolytically etched in a 7% potassium hydroxide etching reagent to reveal the microstructure. The observation surface on which the microstructure has been revealed is observed in 10 visual fields using an optical microscope. The area of each visual field is set to 1.00 mm^2 (magnification of 100×). In each visual field, ferrite and austenite are identified based on contrast. In a case where the observation surface is electrolytically etched in a 7% potassium hydroxide etching reagent, a region in which the brightness is low corresponds to ferrite, and a region in which the brightness is high corresponds to austenite. Therefore, a person skilled in the art can easily identify ferrite and austenite based on contrast.

[0181] The area fraction of the identified ferrite is measured by a point counting method in accordance with ASTM E562 (2019). The arithmetic average value of the area fractions (10 area fractions in total) of ferrite obtained in the respective visual fields is defined as the volume ratio (%) of ferrite. A value to the first decimal place obtained by rounding off the second decimal place of the obtained numerical value is taken as the volume ratio (%) of ferrite.

[0182] The volume ratio of σ phase in the duplex stainless steel pipe is determined by the following method.

[0183] The aforementioned observation surface on which the microstructure has been revealed is observed in five visual fields using an optical microscope. The area of each visual field is set to 0.0625 mm^2 (magnification of 400×; 250 μm × 250 μm). In each visual field, σ phase is identified based on contrast. On the observation surface that has been electrolytically etched in a 7% potassium hydroxide etching reagent, σ phase can be identified as a black region with a lower brightness compared to other structures. Note that, in each visual field, element concentration analysis (EDS analysis) may be performed to identify σ phase. In the case of performing element concentration analysis, σ phase is identified by the following method. In each visual field, particles are identified based on contrast. The identified particles are subjected to EDS analysis. In the EDS analysis, the acceleration voltage is set to 20 kV, and the EDS analysis is conducted for quantification of N, Mo, Al, Si, P, S, Ca, Ti, Cr, Mn, Fe, Cu, and Nb as elements to be analyzed. Based on the EDS analysis result for each particle, if the content of Cr is 35.0% by mass or more and the content of Mo is 3.0% by mass or more in a particle, the relevant particle is identified as σ phase.

[0184] The area of the identified σ phase is determined. The area fraction (%) of σ phase is determined based on the total area of σ phase in the five visual fields and the total area of the five visual fields. The determined area fraction (%) of σ phase is regarded as the volume ratio (%) of σ phase. In the present embodiment, a value to the first decimal place obtained by rounding off the second decimal place of the obtained numerical value is taken as the volume ratio (%) of σ phase.

[(Feature 3) Regarding content of undissolved Nb and undissolved Nb/Al ratio]

[0185] In the duplex stainless steel pipe of the present embodiment, the content of undissolved Nb is 0.008% by mass or more, and an undissolved Nb/Al ratio that is a ratio of the content of undissolved Nb to the content of undissolved Al is 1.0 or more. These matters are described hereunder.

[Regarding content of undissolved Nb]

[0186] Undissolved Nb is Nb which does not dissolve in the base metal and is contained in precipitates. In the duplex stainless steel pipe of the present embodiment, a high yield strength of 655 MPa or more is obtained by sufficiently forming Nb carbo-nitrides in the steel pipe. When the content of undissolved Nb is less than 0.008% by mass, Nb carbo-nitrides are not sufficiently formed in the steel pipe. Consequently, sufficient yield strength cannot be obtained. Therefore, the content of undissolved Nb is 0.008% by mass or more.

[0187] A preferable lower limit of the content of undissolved Nb is, in percent by mass, 0.009%, more preferably is 0.010%, further preferably is 0.012%, further preferably is 0.015%, further preferably is 0.020%, and further preferably is 0.025%.

[0188] The upper limit of the content of undissolved Nb is not particularly limited. In the case of a chemical composition which satisfies feature 1, the upper limit of the content of undissolved Nb is for example, 0.300%, or for example is 0.250%.

[Regarding undissolved Nb/Al ratio]

[0189] The undissolved Nb/Al ratio which is a ratio of the content of undissolved Nb to the content of undissolved Al can be defined by the following equation.

Undissolved Nb/Al ratio = content of undissolved Nb (mass%)/content of undissolved Al (mass%)

[0190] The undissolved Nb/Al ratio is an index of the ratio of the formed amount of Nb carbo-nitrides in the steel pipe to the formed amount of Al nitrides in the steel pipe. As mentioned above, Nb carbo-nitrides in the steel pipe increase the strength of the steel pipe by precipitation strengthening. On the other hand, Al nitrides are coarse in comparison to Nb carbo-nitrides and do not contribute substantially to precipitation strengthening. Al nitrides also reduce the amount of dissolved N in the steel pipe and reduce the amount of dissolved N that is utilized for formation of Nb carbo-nitrides. Therefore, even if Nb carbo-nitrides form to a certain extent, if Al nitrides excessively form relative to the formed amount of Nb carbo-nitrides, a sufficient amount of dissolved N and a sufficient formed amount of Nb carbo-nitrides will not be obtained in the steel pipe. Consequently, in some cases sufficient strength will not be obtained in the duplex stainless steel pipe.

[0191] In a duplex stainless steel pipe that satisfies feature 1 and feature 2, if the content of undissolved Nb is 0.008% or more and the undissolved Nb/Al ratio is 1.0 or more, a sufficient formed amount of Nb carbo-nitrides and a sufficient dissolved N amount can be secured in the steel pipe. As a result, the yield strength of the duplex stainless steel pipe can be raised to 655 MPa or more.

[0192] A preferable lower limit of the undissolved Nb/Al ratio is 1.1, more preferably is 1.2, further preferably is 1.5, further preferably is 2.0, further preferably is 2.5, and further preferably is 3.0.

[0193] The upper limit of the undissolved Nb/Al ratio is not particularly limited. In the case of a chemical composition which satisfies feature 1, the upper limit of the undissolved Nb/Al ratio is for example, 70.0, or for example, 65.0.

[Method for measuring content of undissolved Nb and undissolved Nb/Al ratio]

[0194] The content of undissolved Nb and the undissolved Nb/Al ratio are determined by the following method.

[0195] A cylindrical test specimen having a diameter of 8 mm and a length of 50 mm is taken from the duplex stainless steel pipe. Specifically, a cylindrical test specimen that has the central portion of the wall thickness of the steel pipe as the central axis thereof is prepared. The axial direction of the cylindrical test specimen is to be the pipe axis direction of the steel pipe.

[0196] The cylindrical test specimen is subjected to constant current electrolysis using a 10% AA-based solution (a solution containing, in volume fraction, 10% acetylacetone, 1% tetramethylammonium chloride, and 89% methanol solution).

[0197] First, pre-electrolysis is performed to remove deposits (surface scale and impurities) from the surface of the cylindrical test specimen. In the pre-electrolysis, a region from the surface of the scale to a position at a depth of approximately 100 μm is electrolyzed at normal temperature (25°C) with a current of 1000 mA. After the pre-electrolysis, the cylindrical test specimen is immersed in an alcohol solution. The cylindrical test specimen immersed in the alcohol solution is subjected to ultrasonic cleaning to remove deposits from the surface of the cylindrical test specimen. The mass of the cylindrical test specimen from which the deposits have been removed, that is, the mass of the cylindrical test specimen before constant current electrolysis is measured.

[0198] Next, the cylindrical test specimen is subjected to constant current electrolysis. Specifically, a new 10% AA-based solution is prepared. Then, using the new 10% AA-based solution, electrolysis in which the current density is maintained at 20 mA/cm^2 is performed at normal temperature. After the constant current electrolysis, the cylindrical test specimen is immersed in an alcohol solution and then the cylindrical test specimen is subjected to ultrasonic cleaning to remove deposits on the surface of the cylindrical test specimen. The mass of the cylindrical test specimen from which the deposits have been removed is measured, and the measured value is taken as the mass of the cylindrical test specimen after constant current electrolysis.

[0199] The 10% AA-based solution used in the constant current electrolysis, and the alcohol solution used in the ultrasonic cleaning thereafter are suction filtered through a filter with a mesh size of 0.2 μm to extract residue.

[0200] The extracted residue is subjected to chemical elemental analysis. Specifically, the residue is dissolved in acid to obtain a solution. The solution is subjected to chemical elemental analysis using ICP-AES to perform quantitative analysis of Nb and Al. Based on the Nb mass and Al mass obtained by the quantitative analysis, and the difference in the mass of the cylindrical test specimen between before and after the constant current electrolysis, the content of Nb (mass%) in the residue and the content of Al (mass%) in the residue are determined. The determined content of Nb in the residue is taken as the content of undissolved Nb (mass%). The determined content of Al in the residue is taken as the content of undissolved Al (mass%). The undissolved Nb/Al ratio is determined based on the content of undissolved Nb and the content of undissolved Al.

[(Feature 4) Regarding yield strength]

[0201] The yield strength of the duplex stainless steel pipe according to the present embodiment is 655 MPa or more (95 ksi or more). The duplex stainless steel pipe of the present embodiment satisfies feature 1 to feature 3. As a result, excellent corrosion resistance is obtained, and a high yield strength of 655 MPa or more is also obtained.

[0202] A preferable lower limit of the yield strength of the duplex stainless steel pipe according to the present embodiment is 660 MPa or more, more preferably is 665 MPa, further preferably is 670 MPa, and further preferably is 675 MPa.

[0203] Although not particularly limited, the upper limit of the yield strength of the duplex stainless steel pipe according to the present embodiment is, for example, 800 MPa.

[Method for measuring yield strength]

[0204] The yield strength of the duplex stainless steel pipe of the present embodiment is determined by conducting a tensile test by a method in accordance with ASTM E8/E8M (2022).

[0205] Specifically, an arc-shaped test specimen is taken from the duplex stainless steel pipe of the present embodiment. For example, the arc-shaped test specimen has a thickness that is the same as the wall thickness of the steel pipe, and has a width of 25.4 mm and a gage length of 50.8 mm. The longitudinal direction of the arc-shaped test specimen is to be parallel to the pipe axis direction of the steel pipe.

[0206] A tensile test is carried out at normal temperature (25°C) in air using the arc-shaped test specimen. In the present embodiment, the 0.2% offset proof stress obtained by the tensile test is defined as the yield strength (MPa). In the present embodiment, an integer obtained by rounding off the first decimal place of the obtained numerical value is adopted as the yield strength (MPa).

[Advantageous effects of duplex stainless steel pipe of present embodiment]

[0207] The duplex stainless steel pipe of the present embodiment satisfies feature 1 to feature 4. Therefore, in the duplex stainless steel pipe of the present embodiment, a high yield strength of 655 MPa or more (95 ksi or more) is obtained, and in addition, excellent corrosion resistance is obtained.

[Regarding corrosion resistance]

[0208] In the present embodiment, the corrosion resistance of the duplex stainless steel pipe is evaluated by the following method.

[Corrosion resistance evaluation method]

[0209] A test specimen for a four-point bending test is taken from the duplex stainless steel pipe of the present embodiment. The size of the test specimen is, for example, 2 mm in thickness × 10 mm in width × 75 mm in length. The test specimen is prepared from the central portion of the wall thickness of the steel pipe. In this case, the longitudinal direction of the test specimen is to be parallel to the pipe axis direction of the steel pipe.

[0210] A 20% by mass sodium chloride aqueous solution adjusted to pH 4.0 is used as the test solution. In accordance with ASTM G39-99 (2021), stress corresponding to 90% of the actual yield stress is applied to the test specimen by four-point bending. The test specimen to which stress has been applied is enclosed in an autoclave together with the test jig. The test solution is poured into the autoclave so as to leave a vapor phase portion, and this is adopted as a test bath. After the test bath is degassed, a gaseous mixture of H_2S gas at 0.2 bar and CO_2 gas at 30 bar is charged under pressurization into the autoclave, and the test bath is stirred to cause the gaseous mixture to saturate. After sealing the autoclave, the test bath is stirred for 720 hours at 90°C.

[0211] In the present embodiment, after 720 hours elapse in the test environment described above, observation using a magnifying glass with a magnification of 10× is performed to check for the presence or absence of a crack. If the occurrence of a crack is suspected as a result of the observation with the magnifying glass, observation using an optical microscope with a magnification of 100× is further performed to confirm the presence or absence of a crack. If a crack is not confirmed, it is evaluated that "excellent corrosion resistance is obtained".

[Shape of duplex stainless steel pipe]

[0212] The duplex stainless steel pipe of the present embodiment may be a welded tube or may be a seamless steel pipe. Preferably, the duplex stainless steel pipe according to the present embodiment is a seamless steel pipe.

[Production method]

[0213] One example of a method for producing the duplex stainless steel pipe of the present embodiment composed as described above will now be described. Note that, a method for producing the duplex stainless steel pipe according to the present embodiment is not limited to the production method described hereunder.

[0214] A method for producing the duplex stainless steel pipe of the present embodiment includes the following steps.

(Step 1) Starting material preparation step
(Step 2) Hot working step
(Step 3) Solution treatment step
(Step 4) Straightening step
(Step 5) Aging heat treatment step
Each step is described hereunder.

[(Step 1) Starting material preparation step]

[0215] In the starting material preparation step, a starting material having a chemical composition that satisfies feature 1 is prepared. The starting material may be prepared by producing the starting material, or may be prepared by purchasing the starting material from a third party. That is, a method for preparing the starting material is not particularly limited.

[0216] In the case of producing the starting material, for example, the starting material is produced by the following method. A molten steel having the chemical composition described above is produced. A cast piece (a slab, a bloom, or a billet) is produced by a continuous casting process using the molten steel. An ingot may also be produced by an ingot-making process using the molten steel. As required, a slab, a bloom, or an ingot may be subjected to blooming to produce a billet. The starting material is produced by the above process.

[(Step 2) Hot working step]

[0217] In the hot working step, the starting material prepared in the aforementioned starting material preparation step is subjected to hot working to produce a hollow shell. The hot working may be hot forging, may be hot extrusion, or may be hot rolling. The hot working method is not particularly limited, and it suffices to use a well-known method.

[0218] As the hot working method, for example, hot extrusion such as the Ugine-Sejournet process or the Ehrhardt push bench process may be performed, or piercing-rolling according to the Mannesmann process, which is one type of hot rolling, may be performed. Note that, hot working may be performed only one time or may be performed multiple times. For example, after performing the aforementioned piercing-rolling on the starting material, the aforementioned hot extrusion may be performed. For example, in addition, after performing the aforementioned piercing-rolling on the starting material, elongating, which is one type of hot rolling, may be performed. That is, in the hot working step, hot working is performed by a well-known method to produce a hollow shell. Note that, the heating temperature during hot working is, for example, 1000 to 1280°.

[(Step 3) Solution treatment step]

[0219] In the solution treatment step, a solution treatment is performed on the hollow shell after the hot working step. Specifically, the hollow shell is loaded into a heat treatment furnace to heat the hollow shell. Then, after being held at a desired temperature (solution treatment temperature), the hollow shell is rapidly cooled. In the solution treatment, the following conditions are satisfied.

(Condition 1)

[0220] An average heating rate HR1 from 700 to 900°C when heating the hollow shell is to be 0.25°C/sec or more.

(Condition 2)

[0221] A solution treatment temperature T1 is to be within the range of 980 to 1 100°C.

[0222] Each condition is described hereunder.

(Regarding Condition 1)

[0223] During heating in the solution treatment, Al nitrides are easily formed in the temperature range of 700 to 900°C. By making the residence time in the temperature range of 700 to 900°C as short as possible, formation of Al nitrides in the hollow shell is suppressed, and as a result, the undissolved Nb/Al ratio in the produced hollow shell increases. If the average heating rate HR1 from 700 to 900°C is 0.25°C/sec or more, the undissolved Nb/Al ratio in the produced hollow shell can be sufficiently increased. The upper limit of the average heating rate HR1 is, for example, 0.60°C/sec.

(Regarding Condition 2)

[0224] The solution treatment temperature T1 influences the ferrite volume ratio in the microstructure of the steel pipe. If the solution treatment temperature T1 is too low, in some cases the ferrite volume ratio in the duplex stainless steel pipe will be less than 35.0% and the strength and/or corrosion resistance of the produced duplex stainless steel pipe will decrease. On the other hand, if the solution treatment temperature T1 is too high, in some cases the volume ratio of ferrite in the duplex stainless steel pipe after the solution treatment will be 65.0% or more and the corrosion resistance of the steel pipe will, on the contrary, decrease. If the solution treatment temperature T1 is 980 to 1100°C, the ferrite volume ratio of the duplex stainless steel pipe will be in an appropriate range.

[0225] Note that, a holding time t1 at the solution treatment temperature T1 is, for example, 10 to 180 minutes. Here, the term "solution treatment temperature T1" means the temperature (°C) of the heat treatment furnace for performing the solution treatment. The phrase "holding time t1 at the solution treatment temperature T1" means the time (mins) for which the hollow shell is held at the solution treatment temperature.

[(Step 4) Straightening step]

[0226] In the straightening step, the hollow shell subjected to the aforementioned solution treatment step is subjected to straightening at normal temperature. Imparting strain to the hollow shell by straightening causes a sufficient amount of Nb carbo-nitrides to be formed in the aging heat treatment step that is the next step.

[0227] FIG. 1 is a schematic diagram of a rotary straightener that is one example of a straightening machine. Referring to

FIG. 1, the rotary straightener includes a plurality of stands ST1 to STn (n is a natural number of 3 or more). In FIG. 1, the rotary straightener has four stands. However, the number of stands is not particularly limited as long as the number of stands is three or more. For example, straightening may be performed using three stands, or straightening may be performed using five or more stands. Each stand includes a pair of skew rolls. The stands are arranged in one row along a pass line PL along which the hollow shell passes. Among the plurality of stands, the skew rolls of the stands other than a stand ST2 are arranged on the pass line PL, and the skew rolls of the stand ST2 are arranged at a position that deviates from the pass line PL.

[0228] FIG. 2 is a front view of the straightening machine illustrated in FIG. 1. The view on the left side of FIG. 2 is a cross-sectional view perpendicular to the axial direction of the hollow shell before performing straightening. The view on the right side of FIG. 2 is a front view of a stand that has a smallest roll gap DB. Crush straightening is performed as the straightening according to the present embodiment. The term "crush straightening" means straightening in which the hollow shell is subjected to rolling reduction to deform the hollow shell into an elliptical shape. Referring to FIG. 2, the roll draft with respect to the hollow shell at the stand that has the smallest roll gap DB is defined as a crush amount δc (mm). The crush amount δc can be calculated by subtracting the roll gap DB at the stand that has the smallest roll gap DB from the outer diameter DA of the hollow shell before straightening.

[0229] In the straightening step, the following condition is satisfied.

(Condition 3)

[0230] The crush amount δc is to be 3 mm or more.

(Regarding Condition 3)

[0231] If the crush amount δc in the straightening is too small, strain will not be introduced sufficiently into the hollow shell before the aging heat treatment. Consequently, a sufficient amount of Nb carbo-nitrides will not form in the aging heat treatment step that is the next step. If the crush amount δc is 3 mm or more, strain will be introduced sufficiently into the hollow shell. As a result, in the duplex stainless steel pipe after the aging heat treatment step, a sufficient amount of Nb carbo-nitrides will be formed and a sufficient content of undissolved Nb will be obtained. Note that, the upper limit of the crush amount is, for example, 8 mm.

[(Step 5) Aging heat treatment step]

[0232] In the aging heat treatment step, the hollow shell is subjected to an aging heat treatment. In the aging heat treatment step of the present embodiment, when the aging heat treatment is performed, a sufficient amount of Nb carbo-nitrides is formed while suppressing the formation of σ phase. The aging heat treatment satisfies the following conditions.

(Condition 4)

[0233] An aging heat treatment temperature T2 satisfies the following Formula (A).

$$T2 < 700 - (0.5Cr + 0.3Mn + 3Mo + 1.5Si + 8Nb - Ni - 0.6Cu - 4Co - 10Sn)^2 \quad (A)$$

[0234] Where, the content of the corresponding element in percent by mass in the duplex stainless steel pipe is substituted for each symbol of an element in Formula (A).

(Condition 5)

[0235] A holding time t2 at the aging heat treatment temperature T2 satisfies the following Formula (B).

$$t2 > (1/60) \times 10^{(3200/(T2+273.15)-3Nb)} \quad (B)$$

[0236] Where, the aging heat treatment temperature T2 (°C) is substituted for T2 in Formula (B), and the content of Nb in percent by mass in the duplex stainless steel pipe is substituted for Nb in Formula (B).

[0237] Each condition is described hereunder.

(Regarding Condition 4)

[0238] FnA is defined as follows.

$$FnA = 700 - (0.5Cr + 0.3Mn + 3Mo + 1.5Si + 8Nb + Ni - 0.6Cu - 4Co - 10Sn)^2$$

[0239] FnA means the lower limit of a temperature (°C) that promotes formation of σ phase. In FnA, the elements Cr, Mn, Mo, Si, and Nb promote formation of σ phase. On the other hand, the elements Ni, Cu, Co, and Sn suppress formation of σ phase. If the aging heat treatment temperature T2 is equal to or higher than FnA, formation of σ phase will be promoted in the hollow shell during the aging heat treatment. As a result, the volume ratio of σ phase will be excessively high in the produced duplex stainless steel pipe. If the aging heat treatment temperature T2 is less than FnA, formation of σ phase will be sufficiently suppressed in the hollow shell during the aging heat treatment. As a result, the volume ratio of σ phase will be sufficiently reduced in the produced duplex stainless steel pipe.

(Regarding Condition 5)

[0240] FnB is defined as follows.

$$FnB = (1/60) \times 10^{(3200/(T2+273.15)-3Nb)}$$

[0241] FnB means the lower limit of the holding time (mins) required for formation of a sufficient amount of Nb carbo-nitrides. Because the content of Nb in the steel pipe significantly influences formation of Nb carbo-nitrides, Nb is included in FnB. If the holding time t2 at the aging heat treatment temperature T2 is equal to or less than FnB, a sufficient amount of Nb carbo-nitrides will not be formed in the produced duplex stainless steel pipe. Consequently, a sufficient content of undissolved Nb will not be obtained. If the holding time t2 is longer than FnB, a sufficient amount of Nb carbo-nitrides will be formed in the produced duplex stainless steel pipe. Therefore, a sufficient content of undissolved Nb will be obtained.

[Other steps]

[0242] The production method of the present embodiment may also include other production steps in addition to the production steps described above. For example, the duplex stainless steel pipe after the aging heat treatment step may be subjected to a pickling treatment step. In such case, the pickling treatment step is not particularly limited, and it suffices to perform the pickling treatment step according to a well-known method. Note that, in the production method of the present embodiment a cold rolling step needs not to be performed at a timing that is after the hot working step and is before the solution treatment step. Even if the cold rolling step is omitted, a duplex stainless steel pipe having sufficient strength will be obtained.

[0243] The duplex stainless steel pipe of the present embodiment can be produced by performing the steps described above. Note that, the method for producing the duplex stainless steel pipe described above is one example, and the duplex stainless steel pipe of the present embodiment may also be produced by another method. Hereunder, the duplex stainless steel pipe of the present embodiment is described in further detail by way of examples.

EXAMPLES

[0244] Duplex stainless steel pipes that were seamless steel pipes having the chemical compositions shown in Table 1A and Table 1B were produced.

[Table 1A]

[0245]

TABLE 1A

Steel Symbol	Chemical Composition (unit is mass%; balance is Fe and impurities)												
	C	Si	Mn	P	S	Al	Ni	Cr	Mo	Cu	N	v	Nb
A	0.028	0.91	2.2	0.001	0.017	0.036	5.3	25.2	1.1	2.6	0.22	0.06	0.051
B	0.017	0.35	0.5	0.005	0.017	0.050	4.5	27.7	0.6	3.0	0.20	0.31	0.111

(continued)

Steel Symbol	Chemical Composition (unit is mass%; balance is Fe and impurities)												
	C	Si	Mn	P	S	Al	Ni	Cr	Mo	Cu	N	v	Nb
C	0.030	0.43	4.8	0.001	0.017	0.052	7.3	25.6	0.5	1.8	0.28	0.30	0.033
D	0.006	0.32	5.5	0.010	0.020	0.007	8.6	21.4	0.7	2.1	0.24	0.35	0.059
E	0.009	0.57	2.4	0.031	0.011	0.012	5.8	29.6	0.7	2.5	0.21	0.47	0.284
F	0.028	0.86	5.4	0.019	0.016	0.053	6.7	23.9	1.9	2.7	0.30	0.28	0.198
G	0.027	0.78	4.1	0.004	0.012	0.055	7.9	25.7	2.0	2.4	0.29	0.28	0.141
H	0.028	0.68	1.2	0.027	0.005	0.070	7.1	27.7	1.7	2.9	0.27	0.07	0.294
I	0.028	0.66	2.5	0.030	0.014	0.075	7.8	21.5	1.5	2.5	0.20	0.46	0.155
J	0.010	0.62	4.5	0.021	0.003	0.070	5.6	24.8	0.9	1.7	0.27	0.36	0.041
K	0.003	0.35	1.5	0.036	0.007	0.092	7.2	23.7	2.0	2.5	0.15	0.08	0.244
L	0.029	0.28	5.5	0.029	0.012	0.076	4.5	24.0	1.8	2.1	0.26	0.46	0.121
M	0.017	0.22	6.2	0.032	0.006	0.034	5.0	27.3	0.8	2.0	0.21	0.32	0.185
N	0.007	0.88	1.6	0.016	0.003	0.085	8.4	23.6	0.7	2.7	0.16	0.23	0.138
O	0.026	0.82	1.1	0.012	0.003	0.034	7.4	21.4	0.9	2.2	0.26	0.43	0.232
P	0.001	0.22	2.2	0.025	0.002	0.052	7.5	25.3	0.9	1.6	0.24	0.26	0.264
Q	0.010	0.65	6.3	0.025	0.001	0.062	8.0	20.2	1.2	2.3	0.30	0.03	0.051
R	0.003	0.62	4.1	0.024	0.017	0.020	8.5	22.0	0.8	2.9	0.21	0.13	0.461
S	0.025	0.56	4.1	0.019	0.009	0.023	7.1	25.1	1.7	1.9	0.24	0.37	0.011
T	0.014	0.63	0.6	0.023	0.001	0.045	6.8	22.8	1.9	1.7	0.16	0.07	0.063

[Table 1B]

[0246]

TABLE 1B

Steel Symbol	Chemical Composition (unit is mass%; balance is Fe and impurities)											
	Co	Sn	Ta	Ti	Zr	Hf	w	Sb	Ca	Mg	B	REM
A	0.23	0.032	-	-	-	-	-	-	-	-	-	-
B	0.29	0.007	0.034	-	-	-	-	-	-	-	-	-
C	0.17	0.046	-	0.079	-	-	-	-	-	-	-	-
D	0.45	0.006	-	-	0.056	-	-	-	-	-	-	-
E	0.19	0.029	-	-	-	0.043	-	-	-	-	-	-
F	0.20	0.033	-	-	-	-	0.048	-	-	-	-	-
G	0.13	0.044	-	-	-	-	-	0.023	-	-	-	-
H	0.36	0.014	-	-	-	-	-	-	0.018	-	-	-
I	0.25	0.036	-	-	-	-	-	-	-	0.014	-	-
J	0.38	0.021	-	-	-	-	-	-	-	-	0.010	-
K	0.10	0.025	-	-	-	-	-	-	-	-	-	0.042
L	0.22	0.028	0.045	-	-	-	-	0.048	-	-	-	-
M	0.45	0.047	-	0.098	-	-	-	-	0.010	-	-	-
N	0.28	0.050	-	-	0.073	-	-	-	-	0.006	-	-

(continued)

Steel Symbol	Chemical Composition (unit is mass%; balance is Fe and impurities)											
	Co	Sn	Ta	Ti	Zr	Hf	w	Sb	Ca	Mg	B	REM
O	0.17	0.045	-	-	-	0.092	-	-	-	-	0.009	-
P	0.33	0.032	-	-	-	-	0.130	-	-	-	-	0.008
Q	0.38	0.032	-	-	-	-	-	0.084	0.011	-	-	-
R	0.49	0.047	-	-	-	-	-	-	-	-	-	-
S	0.22	0.042	-	-	-	-	-	-	-	-	-	-
T	0.11	0.003	-	-	-	-	0.190	-	-	-	0.018	0.187

[0247] Specifically, molten steels were melted using a 50 kg vacuum furnace. The molten steels were used to produce ingots by an ingot-making process. Note that, the symbol "-" in Table 1B means that the content of the corresponding element was at an impurity level. For example, the symbol "-" means that the content of Ta, the content of Ti, the content of Zr, the content of Hf, the content of W, the content of Sb, the content of Ca, the content of Mg, the content of B, and the content of REM of steel A were each 0% when rounded off to the third decimal place.

[0248] Each ingot was subjected to hot working (hot extrusion) to produce a hollow shell. The heating temperature during the hot working was in the range of 1000 to 1280°C. The hollow shell of each test number on which hot working had been performed was then subjected to a solution treatment. In the solution treatment, the average heating rate HR1 (°C/sec) from 700 to 900°C, the solution treatment temperature T1 (°C), and the holding time t1 (mins) at the solution treatment temperature T1 were as shown in Table 2.

[Table 2]

[0249]

TABLE 2

Test Number	Steel Symbol	Solution Treatment			Straightening	Aging Heat Treatment			
		Average Heating Rate HR1 (°C/sec)	Solution Treatment Temperature T1 (°C)	Holding Time t1 (mins)	Crush Amount δc (mm)	FnA(°C)	FnB (mins)	Aging Heat Treatment Temperature T2 (°C)	Holding Time t2 (mins)
1	A	0.37	1000	20	3	595	60	590	65
2	B	0.49	990	20	3	606	36	600	55
3	C	0.31	1050	30	3	649	42	640	50
4	D	0.34	1060	30	3	686	25	680	30
5	E	0.59	1010	20	3	546	25	520	30
6	F	0.56	1080	20	4	539	39	535	45
7	G	0.57	1060	40	5	554	82	505	90
8	H	0.27	1090	20	3	550	25	515	60
9	I	0.28	1060	20	4	643	36	570	45
10	J	0.34	1080	20	5	612	61	595	70
11	K	0.43	1020	20	5	569	30	530	35
12	L	0.45	1030	100	3	517	94	505	120
13	M	0.51	1040	20	6	573	64	500	80
14	N	0.29	1040	20	6	673	22	630	30
15	O	0.46	1030	20	3	651	23	560	30
16	P	0.39	1060	20	6	630	21	550	30
17	Q	0.33	1060	20	6	667	41	630	50
18	T	0.30	1000	30	4	591	93	540	100
19	R	0.36	1060	20	6	657	2	640	10
20	S	0.43	1080	130	6	595	133	540	180
21	A	0.38	1000	20	6	595	31	660	40
22	L	0.31	1030	20	6	517	56	550	70

(continued)

Test Number	Steel Symbol	Solution Treatment			Straightening	Aging Heat Treatment			
		Average Heating Rate HR1 (°C/sec)	Solution Treatment Temperature T1 (°C)	Holding Time t1 (mins)	Crush Amount δc (mm)	FnA(°C)	FnB (mins)	Aging Heat Treatment Temperature T2 (°C)	Holding Time t2 (mins)
23	A	0.39	1000	20	4	595	161	500	70
24	L	0.27	1030	20	4	517	94	505	40
25	A	0.14	1000	20	5	595	73	570	75
26	C	0.19	1050	30	5	649	42	640	60
27	A	0.26	1000	20	2	595	73	570	75
28	C	0.30	1050	30	1	649	42	640	50

[0250] The hollow shell after the solution treatment was subjected to straightening using a rotary straightener equipped with three stands. The crush amount δc (mm) during straightening was as shown in Table 2. An aging heat treatment was performed on the hollow shell after the straightening. The aging heat treatment temperature T2 (°C) and the holding time t2 (mins) in the aging heat treatment were as shown in Table 2. Note that, FnA (°C) and FnB (mins) of each test number are also shown in Table 2. A duplex stainless steel pipe of each test number was produced by the above production process.

[Evaluation tests]

[0251] The duplex stainless steel pipe of each test number was subjected to the following evaluation tests.

(Test 1) Test to measure ferrite volume ratio and σ-phase volume ratio
(Test 2) Test to measure content of undissolved Nb and undissolved Nb/Al ratio
(Test 3) Yield strength measurement test
(Test 4) Corrosion resistance test
Hereunder, each test is described.

[(Test 1) Test to measure ferrite volume ratio and σ-phase volume ratio]

[0252] The ferrite volume ratio (%) and the σ-phase volume ratio (%) of the duplex stainless steel pipe of each test number were determined in accordance with the method described above in the section [Method for measuring ferrite volume ratio and σ-phase volume ratio]. The determined ferrite volume ratio (%) and σ-phase volume ratio (%) are shown in Table 3.

[Table 3]

[0253]

TABLE 3

Test Number	Steel Symbol	Microstructure					YS (MPa)	Corrosion Resistance	Remarks
		Ferrite Volume Ratio (%)	σ-Phase Volume Ratio (%)	Content of Undissolved Nb (mass%)	Content of Undissolved Al (mass%)	Undissolved Nb/Al Ratio			
1	A	43.1	0.1	0.031	0.005	6.2	683	NO SSC	Inventive Example
2	B	44.4	0.0	0.070	0.010	7.0	718	NO SSC	Inventive Example
3	C	59.4	0.0	0.012	0.010	1.2	670	NO SSC	Inventive Example
4	D	56.6	0.0	0.041	0.001	41.0	697	NO SSC	Inventive Example
5	E	48.3	0.0	0.211	0.005	42.2	738	NO SSC	Inventive Example
6	F	39.8	0.4	0.135	0.011	12.3	711	NO SSC	Inventive Example
7	G	35.7	0.8	0.118	0.011	10.7	690	NO SSC	Inventive Example
8	H	61.0	0.3	0.217	0.035	6.2	752	NO SSC	Inventive Example
9	I	59.4	0.2	0.109	0.038	2.9	711	NO SSC	Inventive Example
10	J	51.3	0.0	0.024	0.014	1.7	704	NO SSC	Inventive Example
11	K	49.0	0.1	0.171	0.013	13.2	745	NO SSC	Inventive Example
12	L	44.7	0.2	0.084	0.010	8.4	697	NO SSC	Inventive Example
13	M	63.5	0.0	0.091	0.017	5.4	676	NO SSC	Inventive Example
14	N	39.0	0.0	0.083	0.043	1.9	718	NO SSC	Inventive Example
15	O	60.5	0.0	0.076	0.004	19.0	684	NO SSC	Inventive Example
16	P	64.6	0.0	0.204	0.013	15.7	759	NO SSC	Inventive Example
17	Q	50.0	0.1	0.041	0.016	2.6	669	NO SSC	Inventive Example
18	T	49.9	0.1	0.029	0.019	1.5	703	NO SSC	Inventive Example
19	R	47.7	0.0	0.313	0.004	78.3	835	SSC	Comparative Example
20	s	39.4	0.0	0.002	0.002	1.0	614	NO SSC	Comparative Example
21	A	42.1	4.2	0.038	0.005	7.6	752	SSC	Comparative Example
22	L	43.1	3.0	0.084	0.019	4.4	766	SSC	Comparative Example

(continued)

Test Number	Steel Symbol	Microstructure					YS (MPa)	Corrosion Resistance	Remarks
		Ferrite Volume Ratio (%)	σ-Phase Volume Ratio (%)	Content of Undissolved Nb (mass%)	Content of Undissolved Al (mass%)	Undissolved Nb/Al Ratio			
23	A	42.4	0.1	0.005	0.005	1.0	621	NO SSC	Comparative Example
24	L	46.0	0.1	0.003	0.002	1.5	615	NO SSC	Comparative Example
25	A	42.3	0.1	0.018	0.021	0.9	625	NO SSC	Comparative Example
26	C	58.6	0.1	0.021	0.033	0.6	631	NO SSC	Comparative Example
27	A	40.9	0.1	0.011	0.018	0.6	629	NO SSC	Comparative Example
28	C	58.9	0.1	0.009	0.013	0.7	640	NO SSC	Comparative Example

[(Test 2) Test to measure content of undissolved Nb and undissolved Nb/Al ratio]

[0254] The content of undissolved Nb (mass%) and the undissolved Nb/Al ratio of the duplex stainless steel pipe of each test number were determined in accordance with the method described above in the section [Method for measuring content of undissolved Nb and undissolved Nb/Al ratio]. The determined content of undissolved Nb (mass%), content of undissolved Al (mass%), and undissolved Nb/Al ratio are shown in Table 3.

[(Test 3) Yield strength measurement test]

[0255] The yield strength (MPa) of the duplex stainless steel pipe of each test number was determined in accordance with the method described above in the section [Method for measuring yield strength]. Note that, each arc-shaped test specimen had a thickness that was the same as the wall thickness of the steel pipe, had a width of 25.4 mm, and had a gage length of 50.8 mm. The determined yield strength (MPa) is shown in the column "YS (MPa)" in Table 3.

[(Test 4) Corrosion resistance test]

[0256] The corrosion resistance of the duplex stainless steel pipe of each test number was evaluated in accordance with the method described above in the section [Corrosion resistance evaluation method]. Note that, the size of the test specimen was 2 mm in thickness $\times$ 10 mm in width $\times$ 75 mm in length. For test specimens in which a crack was not confirmed after 720 hours elapsed, it was determined that excellent corrosion resistance was obtained. The test numbers in which excellent corrosion resistance was obtained are indicated by the description "NO SSC" in the column "Corrosion Resistance" in Table 3. On the other hand, for test specimens in which a crack was confirmed after 720 hours elapsed, it was determined that excellent corrosion resistance was not obtained. The test numbers in which excellent corrosion resistance was not obtained are indicated by the description "SSC" in the column "Corrosion Resistance" in Table 3.

[Evaluations results]

[0257] Referring to Table 1A, Table 1B, Table 2, and Table 3, the duplex stainless steel pipes of Test Nos. 1 to 18 satisfied feature 1 to feature 4. Therefore, in these seamless steel pipes, a high yield strength of 655 MPa or more was obtained. In addition, excellent corrosion resistance was obtained. In other words, in the duplex stainless steel pipes of Test Nos. 1 to 18, a high yield strength of 655 MPa or more and excellent corrosion resistance were both achieved.

[0258] On the other hand, in Test No. 19, the content of Nb was too high. Consequently, excellent corrosion resistance was not obtained.

[0259] In Test No. 20, the content of Nb was too low. Consequently, the content of undissolved Nb was too low. As a result, the yield strength was less than 655 MPa, which was low.

[0260] In Test Nos. 21 and 22, in the aging heat treatment, the aging heat treatment temperature T2 was equal to or higher than FnA, and thus Formula (A) was not satisfied. Consequently, the σ-phase volume ratio was 1.0% or more, which was high. As a result, excellent corrosion resistance was not obtained.

[0261] In Test Nos. 23 and 24, in the aging heat treatment, the holding time t2 at the aging heat treatment temperature T2 was shorter than FnB, and thus Formula (B) was not satisfied. Consequently, the content of undissolved Nb was too low. As a result, the yield strength was less than 655 MPa, which was low.

[0262] In Test Nos. 25 and 26, in the solution treatment, the average heating rate HR1 from 700 to 900°C was too slow. Consequently, the undissolved Nb/Al ratio was low. As a result, the yield strength was less than 655 MPa, which was low.

[0263] In Test Nos. 27 and 28, in the straightening, the crush amount δc was too small. Consequently, the undissolved Nb/Al ratio was low. As a result, the yield strength was less than 655 MPa, which was low.

[0264] 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 embodiment described above, and can be implemented by appropriately modifying the above-described embodiment within a range that does not depart from the gist thereof.

Claims

1. A duplex stainless steel pipe that has a chemical composition consisting of, in mass%,

C: 0.030% or less,
Si: 0.20 to 1.00%,
Mn: 0.5 to 7.0%,

P: 0.040% or less,
S: 0.020% or less,
Al: 0.100% or less,
Ni: 4.0 to 9.0%,
Cr: 20.0 to 30.0%,
Mo: 0.5 to 2.0%,
Cu: 1.5 to 3.0%,
N: 0.15 to 0.30%,
V: 0.01 to 0.50%,
Nb: 0.030 to 0.300%,
Co: 0.10 to 0.50%,
Sn: 0.001 to 0.050%,
Ta: 0 to 0.100%,
Ti: 0 to 0.100%,
Zr: 0 to 0.100%,
Hf: 0 to 0.100%,
W: 0 to 0.200%,
Sb: 0 to 0.100%,
Ca: 0 to 0.020%,
Mg: 0 to 0.020%,
B: 0 to 0.020%, and
rare earth metal: 0 to 0.200%,
with the balance being Fe and impurities, and
has a microstructure that is composed of, in volume ratio, ferrite in an amount of 35.0 to 65.0% and σ phase in an amount of 0 to less than 1.0%, with the balance being austenite; wherein
a content of undissolved Nb is 0.008% by mass or more, and a ratio of the content of undissolved Nb to a content of undissolved Al is 1.0 or more, and
a yield strength is 655 MPa or more.

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

Ta: 0.001 to 0.100%,
Ti: 0.001 to 0.100%,
Zr: 0.001 to 0.100%,
Hf: 0.001 to 0.100%,
W: 0.001 to 0.200%,
Sb: 0.001 to 0.100%,
Ca: 0.001 to 0.020%,
Mg: 0.001 to 0.020%,
B: 0.001 to 0.020%, and
rare earth metal: 0.001 to 0.200%.

FIG. 1

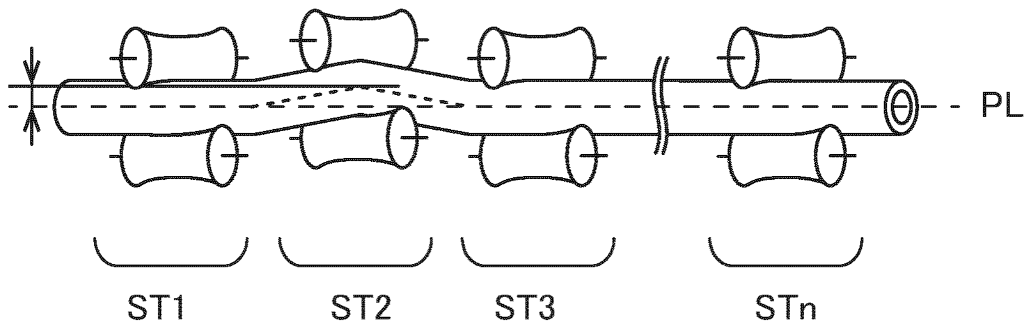
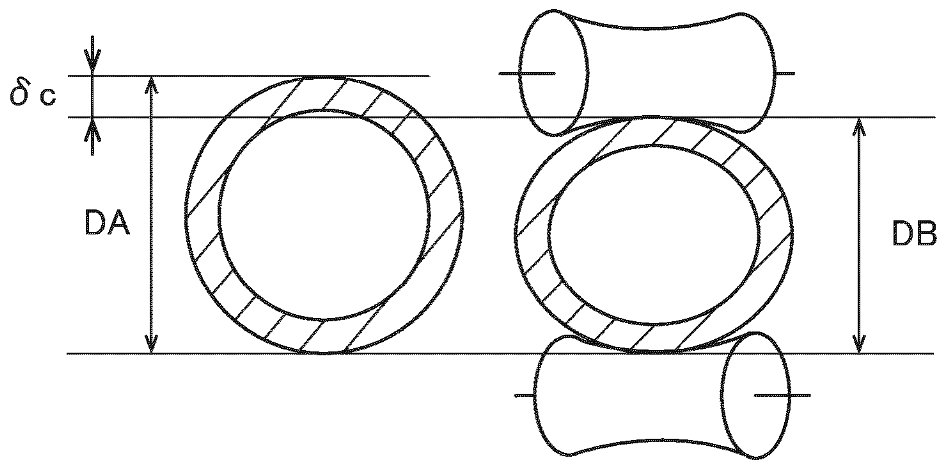


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No. **PCT/JP2024/010269**

A. CLASSIFICATION OF SUBJECT MATTER

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

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00; C21D8/10; C21D9/08; 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 1971-2024
Registered utility model specifications of Japan 1996-2024
Published registered utility model applications of Japan 1994-2024

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 7173411 B1 (JFE STEEL CORPORATION) 16 November 2022 (2022-11-16) entire text	1, 2
A	JP 2021-167446 A (NIPPON STEEL CORPORATION) 21 October 2021 (2021-10-21) entire text	1, 2
A	JP 7239085 B1 (NIPPON STEEL CORPORATION) 14 March 2023 (2023-03-14) entire text	1, 2
A	JP 6981573 B1 (JFE STEEL CORPORATION) 15 December 2021 (2021-12-15) entire text	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
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 June 2024	**18 June 2024**

Name and mailing address of the ISA/JP	Authorized officer
Japan Patent Office (ISA/JP) **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/010269

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 7173411 B1	16 November 2022	EP 4282990 A1 entire text CN 116917523 A AR 125543 A1 AU 2022240057 A1 CA 3208799 A1 BR 112023017868 A2 MX 2023010534 A WO 2022/196196 A1	
JP 2021-167446 A	21 October 2021	(Family: none)	
JP 7239085 B1	14 March 2023	WO 2023/058631 A1 AR 127220 A CA 3231469 A1	
JP 6981573 B1	15 December 2021	US 2023/0090536 A1 entire text WO 2021/171836 A1 EP 4086016 A1 CN 115151670 A BR 112022016509 A2 MX 2022010352 A	

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2018193591 A **[0005] [0009]**
- WO 2012121232 A **[0005] [0009]**