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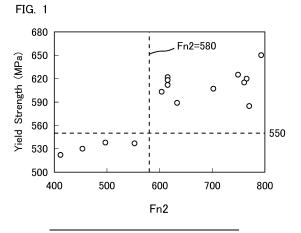
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#### (54) DUPLEX STAINLESS STEEL MATERIAL

(57) Provided is a duplex stainless steel material having high strength, excellent pitting resistance and excellent hot workability. The duplex stainless steel material according to the present disclosure has a chemical composition consisting of, in mass%, C: 0.030% or less, Si: 0.20 to 1.00%, Mn: 0.50 to 7.00%, P: 0.040% or less, S: 0.0100% or less, Al: 0.100% or less, Ni: 4.20 to 9.00%, Cr: 20.00 to 28.00%, Mo: 0.50 to 2.00%, Cu: 1.90 to

4.00%, N: 0.150 to 0.350%, V: 0.01 to 1.50%, and one or more types of element selected from the group consisting of Ca: 0.0001 to 0.0200% and Mg: 0.0001 to 0.0200%, with the balance being Fe and impurities, and satisfying Formulae (1) and (2) described in the description, a microstructure consisting of 35.0 to less than 50.0% of ferrite in volume ratio and austenite as the balance, and a yield strength of 550 MPa or more.



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#### Description

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#### **TECHNICAL FIELD**

[0001] The present disclosure relates to a duplex stainless steel material.

#### **BACKGROUND ART**

**[0002]** There are cases in which oil wells or gas wells (hereinafter, oil wells and gas wells are collectively referred to simply as "oil wells") become a corrosive environment containing a corrosive gas. Here, the corrosive gas means carbon dioxide gas and/or hydrogen sulfide gas. That is, steel materials for use in oil wells are required to have excellent corrosion resistance in a corrosive environment.

**[0003]** So far, as a method for improving the corrosion resistance of the steel material, there is known a method of increasing the content of chromium (Cr) and forming a passivation film mainly composed of Cr oxide on the surface of the steel material. Therefore, in an environment where excellent corrosion resistance is required, a duplex stainless steel material having an increased Cr content is used in some cases. On the other hand, a duplex stainless steel material having a duplex microstructure consisting of a ferrite phase and an austenite phase is excellent in corrosion resistance with respect to pitting and/or crevice corrosion (hereinafter, referred to as "pitting resistance") which is a problem in an aqueous solution containing chlorides.

**[0004]** In recent years, furthermore, deep wells below sea level are being actively developed. Therefore, there is a need to enhance the strength of duplex stainless steel materials. That is, there is a growing demand for a duplex stainless steel material that achieves both high strength and excellent pitting resistance in a compatible manner.

**[0005]** Japanese Patent Application Publication No. 05-132741 (Patent Literature 1), Japanese Patent Application Publication No. 09-195003 (Patent Literature 2), Japanese Patent Application Publication No. 2014-043616 (Patent Literature 3), and Japanese Patent Application Publication No. 2016-003377 (Patent Literature 4) each propose a duplex stainless steel that has high strength and excellent corrosion resistance.

[0006] The duplex stainless steel disclosed in Patent Literature 1 has a chemical composition consisting of, in weight%, C: 0.03% or less, Si: 1.0% or less, Mn: 1.5% or less, P: 0.040% or less, S: 0.008% or less, Sol. Al: 0.040% or less, Ni: 5.0 to 9.0%, Cr: 23.0 to 27.0%, Mo: 2.0 to 4.0%, W: more than 1.5 to 5.0%, and N: 0.24 to 0.32%, with the balance being Fe and unavoidable impurities, in which PREW (= Cr + 3.3(Mo + 0.5W) + 16N) is 40 or more. Patent Literature 1 discloses that this duplex stainless steel exhibits excellent corrosion resistance and high strength.

**[0007]** The duplex stainless steel disclosed in Patent Literature 2 consists of, in weight%, C: 0.12% or less, Si: 1% or less, Mn: 2% or less, Ni: 3 to 12%, Cr: 20 to 35%, Mo: 0.5 to 10%, W: more than 3 to 8%, Co: 0.01 to 2%, Cu: 0.1 to 5%, and N: 0.05 to 0.5%, with the balance being Fe and unavoidable impurities. Patent Literature 2 discloses that this duplex stainless steel has more excellent corrosion resistance, without lowering the strength.

[0008] The duplex stainless steel disclosed in Patent Literature 3 has a chemical composition consisting of, 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%, N: 0.24 to 0.40%, and Al: 0.03% or less, with the balance being Fe and impurities, in which a  $\sigma$  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 micro-structure of the steel, in a cross section in a thickness direction that is parallel to a rolling direction, when a straight line is drawn to be 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. Patent Literature 3 discloses that the strength of this duplex stainless steel can be enhanced without loss of corrosion resistance, and by combining the use of cold working with a high reduction rate, this duplex stainless steel exhibits excellent hydrogen embrittlement resistance characteristics.

[0009] The duplex stainless steel disclosed in Patent Literature 4 has a chemical composition consisting of, in mass%, C: 0.03% or less, Si: 0.2 to 1%, Mn: 0.5 to 2.0%, P: 0.040% or less, S: 0.010% or less, Sol. Al: 0.040% or less, Ni: 4 to less than 6%, Cr: 20 to less than 25%, Mo: 2.0 to 4.0%, N: 0.1 to 0.35%, O: 0.003% or less, V: 0.05 to 1.5%, Ca: 0.0005 to 0.02%, and B: 0.0005 to 0.02%, with the balance being Fe and impurities, and a metal microstructure composed of a duplex microstructure of a ferrite phase and an austenite phase, in which there is no precipitation of a sigma phase, a proportion of the ferrite phase in the metal microstructure is 50% or less in area ratio, and the number of oxides having a particle size of  $30~\mu\text{m}$  or more existing in a visual field of  $300~\text{mm}^2$  is 15 or less. Patent Literature 4 discloses that this duplex stainless steel is excellent in strength, pitting resistance, and low-temperature toughness.

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#### CITATION LIST

#### PATENT LITERATURE

#### 5 [0010]

Patent Literature 1: Japanese Patent Application Publication No. 05-132741
Patent Literature 2: Japanese Patent Application Publication No. 09-195003
Patent Literature 3: Japanese Patent Application Publication No. 2014-043616
Patent Literature 4: Japanese Patent Application Publication No. 2016-003377

#### SUMMARY OF INVENTION

#### **TECHNICAL PROBLEM**

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**[0011]** As described above, in recent years, there is a growing demand for a duplex stainless steel material that has higher strength than before and that exhibits excellent pitting resistance. Specifically, there is a growing demand for a duplex stainless steel material which has a yield strength of 550 MPa or more and exhibits excellent pitting resistance. Therefore, a duplex stainless seamless steel material which has a yield strength of 550 MPa or more and excellent pitting resistance may be obtained by a technique other than those disclosed in the aforementioned Patent Literatures 1 to 4.

**[0012]** A duplex stainless steel material is also sometimes subjected to hot rolling or hot working, such as hot extrusion, during production. Therefore, in addition to high strength and excellent pitting resistance, a duplex stainless steel material also needs to be excellent in hot workability. However, in the aforementioned Patent Literatures 1 to 4, hot workability has not been examined.

**[0013]** An objective of the present disclosure is to provide a duplex stainless steel material having a yield strength of 550 MPa or more, excellent pitting resistance and excellent hot workability.

#### SOLUTION TO PROBLEM

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[0014] A duplex stainless steel material according to the present disclosure has:

a chemical composition consisting of, in mass%,

C: 0.030% or less,

Si: 0.20 to 1.00%,

Mn: 0.50 to 7.00%,

P: 0.040% or less,

S: 0.0100% or less,

Al: 0.100% or less,

Ni: 4.20 to 9.00%,

Cr: 20.00 to 28.00%,

Mo: 0.50 to 2.00%,

Cu: 1.90 to 4.00%,

N: 0.150 to 0.350%,

45 V: 0.01 to 1.50%,

Nb: 0 to 0.100%,

Ta: 0 to 0.100%,

Ti: 0 to 0.100%,

Zr: 0 to 0.100%,

Hf: 0 to 0.100%,

B: 0 to 0.0200%, and

rare earth metal: 0 to 0.200%, and

one or more types of elements selected from the group consisting of

Ca: 0.0001 to 0.0200%, and

Mg: 0.0001 to 0.0200%,

with the balance being Fe and impurities, and

satisfying Formulae (1) and (2);

a microstructure consisting of 35.0 to less than 50.0% of ferrite in volume ratio and austenite as the balance; and

a yield strength of 550 MPa or more:

 $4.50 \le Mn + Cu \le 9.50$  (1)

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# $13 \times \text{Cr} - 19 \times \text{Ni} + 21 \times \text{Mo} - 17 \times \text{Cu} + 63 \times \text{Mn} + 8 \times \text{Si} + 984 \times \text{N} \ge 580 (2)$

where, a content in mass% of a corresponding element is substituted for each symbol of an element in Formulae (1) and (2).

#### ADVANTAGEOUS EFFECTS OF INVENTION

**[0015]** A duplex stainless steel material according to the present disclosure has a yield strength of 550 MPa or more, excellent pitting resistance and excellent hot workability.

#### BRIEF DESCRIPTION OF DRAWING

[0016] [FIG. 1] FIG. 1 is a view illustrating a relation between a value of Fn2 and a yield strength (MPa) of a steel material in the present Example.

#### DESCRIPTION OF EMBODIMENT

**[0017]** The present inventors conducted investigations and studies regarding a duplex stainless steel material having a yield strength of 550 MPa or more, excellent pitting resistance and excellent hot workability. As a result, the present inventors obtained the following findings.

[0018] First, the present inventors have considered that if a duplex stainless steel material has a chemical composition consisting of, in mass%, C: 0.030% or less, Si: 0.20 to 1.00%, Mn: 0.50 to 7.00%, P: 0.040% or less, S: 0.0100% or less, Al: 0.100% or less, Ni: 4.20 to 9.00%, Cr: 20.00 to 28.00%, Mo: 0.50 to 2.00%, Cu: 1.90 to 4.00%, N: 0.150 to 0.350%, V: 0.01 to 1.50%, Nb: 0 to 0.100%, Ta: 0 to 0.100%, Ti: 0 to 0.100%, Zr: 0 to 0.100%, Hf: 0 to 0.100%, B: 0 to 0.0200%, and rare earth metal: 0 to 0.200%, and one or more types of elements selected from the group consisting of Ca: 0.0001 to 0.0200% and Mg: 0.0001 to 0.0200%, with the balance being Fe and impurities, there is a possibility that a duplex stainless steel material having a yield strength of 550 MPa or more, excellent pitting resistance and excellent hot workability will be obtained.

[0019] As described above, a duplex stainless steel material has a characteristic of being excellent in pitting resistance. Here, the microstructure of the duplex stainless steel material having the aforementioned chemical composition consists of ferrite and austenite. Note that, as used herein, "consists of ferrite and austenite" means that the amount of any phase other than ferrite and austenite is negligibly small.

**[0020]** First, the present inventors found that, with respect to a duplex stainless steel material having the aforementioned chemical composition in which the microstructure consists of ferrite and austenite, the pitting resistance is increased by appropriately controlling the volume ratios of ferrite and austenite. Specifically, the present inventors found that the pitting resistance of the duplex stainless steel material is increased by making the volume ratio of ferrite 35.0 to less than 50.0%. Therefore, the microstructure of the duplex stainless steel material according to the present embodiment is a microstructure consisting of 35.0 to less than 50.0% of ferrite in volume ratio and austenite as the balance.

[0021] Thus, in the duplex stainless steel material according to the present embodiment having the chemical composition and microstructure described above, the volume ratio of austenite is equal to or more than the volume ratio of ferrite. On the other hand, the strength of austenite is lower than the strength of ferrite. That is, in the duplex stainless steel material having the aforementioned chemical composition and microstructure, because austenite, which has lower strength, is contained in a greater amount than ferrite, which has higher strength, the strength as a steel material overall is liable to be low. Therefore, the present inventors investigated various approaches for increasing the strength in a duplex stainless steel material having the aforementioned chemical composition and microstructure. As a result, the present inventors obtained the following findings.

**[0022]** As a chemical composition for increasing the yield strength of a duplex stainless steel material, first, the present inventors focused on manganese (Mn) and copper (Cu). Mn dissolves in a steel material and increases the yield strength of the steel material. Further, Cu precipitates as fine Cu precipitates in a steel material, and increases the yield strength of the steel material. That is, the present inventors considered that if the Mn content and Cu content are increased, the yield strength of the steel material will increase.

[0023] Here, it is defined that Fn1 = Mn+Cu. When Fn1 is increased, the yield strength of the steel material increases.

However, it was revealed that in a duplex stainless steel material having the aforementioned chemical composition and microstructure, if Fn1 is too high, although the yield strength of the steel material will increase, the hot workability of the steel material will decrease. Therefore, the duplex stainless steel material according to the present embodiment satisfies the following Formula (1). As a result, on the condition that the other requirements according to the present embodiment are satisfied, the duplex stainless steel material of the present embodiment can achieve both high yield strength and excellent hot workability in a compatible manner.

$$4.50 \le Mn + Cu \le 9.50$$
 (1)

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[0024] Where, a content in mass% of a corresponding element is substituted for each symbol of an element in Formula (1).

**[0025]** On the other hand, even in the case of a duplex stainless steel material that has the aforementioned chemical composition and microstructure and that satisfies Formula (1), there were some cases in which a yield strength of 550 MPa or more could not be consistently obtained. Therefore, next, the present inventors conducted detailed investigations and studies with regard to increasing the yield strength of a duplex stainless steel material having the aforementioned chemical composition and microstructure by a method other than a method that adjusts the aforementioned Fn1. As a result, the present inventors obtained the following findings.

[0026] As described above, in the duplex stainless steel material according to the present embodiment that contains a large amount of austenite, the yield strength of the steel material overall is liable to be low due to the characteristics of austenite. That is, if the strength of the austenite can be increased, the yield strength of the duplex stainless steel material can be increased. Specifically, as an approach for increasing the strength of austenite, the present inventors focused on the dissolved nitrogen (N) amount. N dissolves in the steel material and increases the strength of the steel material. That is, if N can be caused to selectively dissolve in austenite, the strength of austenite can be selectively increased, and as a result, there is a possibility of increasing the yield strength of the duplex stainless steel material.

[0027] Taking into consideration the above findings, the present inventors discovered that, with respect to a duplex

stainless steel material having the aforementioned chemical composition and microstructure and satisfying Formula (1), if the chemical composition is further caused to satisfy the following Formula (2), the yield strength of the duplex stainless steel material is increased.

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## $13 \times \text{Cr} - 19 \times \text{Ni} + 21 \times \text{Mo} - 17 \times \text{Cu} + 63 \times \text{Mn} + 8 \times \text{Si} + 984 \times \text{N} \ge 580 \text{ (2)}$

[0028] Where, a content in mass% of a corresponding element is substituted for each symbol of an element in Formula (2).

**[0029]** It is defined that  $Fn2 = 13 \times Cr - 19 \times Ni + 21 \times Mo - 17 \times Cu + 63 \times Mn + 8 \times Si + 984 \times N$ . FIG. 1 is a view illustrating a relation between a value of Fn2 and a yield strength (MPa) of steel materials in the present Example. FIG. 1 was created using the value of Fn2 and the yield strength (MPa) with respect to, among Examples that are described later, Examples having the aforementioned chemical composition and microstructure and satisfying Formula (1). Note that the yield strength was determined by a method to be described later.

**[0030]** Referring to FIG. 1, in the relation between Fn2 and the yield strength, an inflection point exists in the vicinity of Fn2 = 580. Further, it can be confirmed that when Fn2 is 580 or more, the yield strength markedly increases. Accordingly, the duplex stainless steel material according to the present embodiment has the aforementioned chemical composition, and a microstructure consisting of 35.0 to less than 50.0% of ferrite in volume ratio and austenite as the balance, in which Fn1 is 4.50 to 9.50, and furthermore Fn2 is 580 or more. As a result, the duplex stainless steel material according to the present embodiment had a high yield strength of 550 MPa or more, excellent pitting resistance, and excellent hot workability

**[0031]** The gist of the duplex stainless steel material according to the present embodiment which has been completed based on the above findings is as follows.

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[1] A duplex stainless steel material having:

a chemical composition consisting of, in mass%,

C: 0.030% or less.

Si: 0.20 to 1.00%,

Mn: 0.50 to 7.00%,

P: 0.040% or less,

S: 0.0100% or less,

Al: 0.100% or less,
Ni: 4.20 to 9.00%,
Cr: 20.00 to 28.00%,
Mo: 0.50 to 2.00%,
Cu: 1.90 to 4.00%,
N: 0.150 to 0.350%,
V: 0.01 to 1.50%,
Nb: 0 to 0.100%,
Ta: 0 to 0.100%,
Zr: 0 to 0.100%,
Hf: 0 to 0.100%,

rare earth metal: 0 to 0.200%, and

one or more types of elements selected from the group consisting of

Ca: 0.0001 to 0.0200%, and Mg: 0.0001 to 0.0200%,

B: 0 to 0.0200%, and

with the balance being Fe and impurities, and

satisfying Formulae (1) and (2);

a microstructure consisting of 35.0 to less than 50.0% of ferrite in volume ratio and austenite as the balance; and a yield strength of 550 MPa or more:

$$4.50 \le Mn + Cu \le 9.50 (1)$$

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# $13 \times \text{Cr} - 19 \times \text{Ni} + 21 \times \text{Mo} - 17 \times \text{Cu} + 63 \times \text{Mn} + 8 \times \text{Si} + 94 \times \text{N} \ge 580 (2)$

where, a content in mass% of a corresponding element is substituted for each symbol of an element in Formulae (1) and (2).

[2] The duplex stainless steel material according to [1], wherein

the chemical composition contains one or more types of elements selected from the group consisting of:

Nb: 0.001 to 0.100%, Ta: 0.001 to 0.100%, Ti: 0.001 to 0.100%, Zr: 0.001 to 0.100%, and Hf: 0.001 to 0.100%.

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[3] The duplex stainless steel material according to [1] or [2], wherein the chemical composition contains one or more types of elements selected from the group consisting of:

B: 0.0005 to 0.0200%, and rare earth metal: 0.001 to 0.200%.

**[0032]** Hereinafter, the duplex stainless steel material according to the present embodiment will be described in detail. Note that "%" concerning an element means mass% unless otherwise specified.

50 [Chemical composition]

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

55 C: 0.030% or less

**[0034]** Carbon (C) is unavoidably contained. That is, the lower limit of the C content is more than 0%. If the C content is too high, C will form Cr carbides at crystal grain boundaries and increase corrosion susceptibility at the grain boundaries

even if the contents of other elements are within the range of the present embodiment. As a result, the pitting resistance of the steel material will deteriorate. Therefore, the C content is 0.030% or less. An upper limit of the C content is preferably 0.028%, and more preferably 0.025%. The C content is preferably as low as possible. However, an extreme reduction of the C content will significantly increase the production cost. Therefore, when industrial manufacturing is taken into consideration, a lower limit of the C content is preferably 0.001%, and more preferably 0.005%.

Si: 0.20 to 1.00%

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**[0035]** Silicon (Si) deoxidizes steel. If the Si content is too low, the aforementioned effect cannot be sufficiently obtained even if the contents of other elements is within the range of the present embodiment. On the other hand, if the Si content is too high, the low-temperature toughness and hot workability of the steel material will deteriorate even if the contents of other elements are within the range of the present embodiment. Therefore, the Si content is 0.20 to 1.00%. A lower limit of the Si content is preferably 0.25%, and more preferably 0.30%. An upper limit of the Si content is preferably 0.80%, and more preferably 0.60%.

Mn: 0.50 to 7.00%

[0036] Manganese (Mn) deoxidizes steel and desulfurizes steel. Mn also dissolves in the steel material and increases the strength of the steel material. Furthermore, Mn enhances the hot workability of the steel material. If the Mn content is too low, the aforementioned effects cannot be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the Mn content is too high, Mn will segregate at grain boundaries together with impurities such as P and S, and the corrosion resistance of the steel material in a high-temperature environment will deteriorate even if the contents of other elements are within the range of the present embodiment. Therefore, the Mn content is 0.50 to 7.00%. A lower limit of the Mn content is preferably 0.75%, more preferably 0.90%, further preferably 1.75%, further preferably 2.00%, and further preferably 2.20%. An upper limit of the Mn content is preferably 6.50%, and more preferably 6.20%.

P: 0.040% or less

[0037] Phosphorus (P) is an impurity. That is, the lower limit of the P content is more than 0%. If the P content is too high, P will segregate at grain boundaries and the low-temperature toughness of the steel material will deteriorate even if the contents of other elements are within the range of the present embodiment. Therefore, the P content is 0.040% or less. An upper limit of the P content is preferably 0.035%, and more preferably 0.030%. The P content is preferably as low as possible. However, an extreme reduction of the P content will significantly increase the production cost. Therefore, when industrial manufacturing is taken into consideration, a lower limit of the P content is preferably 0.001%, and more preferably 0.003%.

S: 0.0100% or less

40 [0038] Sulfur (S) is an impurity. That is, the lower limit of the S content is more than 0%. If the S content is too high, S will segregate at grain boundaries and the low-temperature toughness and hot workability of the steel material will deteriorate even if the contents of other elements are within the range of the present embodiment. Therefore, the S content is 0.0100% or less. An upper limit of the S content is preferably 0.0085%, and more preferably 0.0030%. The S content is preferably as low as possible. However, an extreme reduction of the S content will significantly increase the refining cost in the steel making process. Therefore, when industrial manufacturing is taken into consideration, a lower limit of the S content is preferably 0.0001%, and more preferably 0.0002%.

Al: 0.100% or less

[0039] Aluminum (Al) is unavoidably contained. That is, a lower limit of the Al content is more than 0%. Al deoxidizes the steel. On the other hand, if the Al content is too high, coarse oxide-based inclusions are formed and low-temperature toughness of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Al content is 0.100% or less. A lower limit of the Al content is preferably 0.001%, more preferably 0.005%, and further preferably 0.010%. An upper limit of the Al content is preferably 0.090%, and more preferably 0.085%. Note that the Al content referred to in the present description means the content of "acid-soluble Al," that is, sol. Al.

Ni: 4.20 to 9.00%

[0040] Nickel (Ni) is an element that stabilizes the austenitic structure of a steel material. That is, Ni is an element necessary for obtaining a stable microstructure consisting of ferrite and austenite. Ni also enhances the corrosion resistance of the steel material in a high-temperature environment. If the Ni content is too low, the aforementioned effect cannot be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the Ni content is too high, the volume ratio of austenite becomes too high and the strength of the steel material decreases even if the content of other elements is within the range of the present embodiment. Therefore, the Ni content is 4.20 to 9.00%. A lower limit of the Ni content is preferably 4.30%, more preferably 4.35%, further preferably 4.40%, further preferably 4.50%, and further preferably 7.50%, further preferably 7.00%, and further preferably 6.75%.

Cr: 20.00 to 28.00%

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[0041] Chromium (Cr) enhances the corrosion resistance of the steel material in a high-temperature environment. Specifically, Cr forms a passivation film as an oxide on the surface of the steel material, and thereby increases the corrosion resistance of the steel material. Cr also increases the volume ratio of the ferritic structure of the steel material. By obtaining a sufficient ferritic structure, the corrosion resistance of the steel material is stabilized. If the Cr content is too low, the aforementioned effects cannot be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the Cr content is too high, the hot workability of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Cr content is 20.00 to 28.00%. A lower limit of the Cr content is preferably 20.50%, more preferably 21.00%, and further preferably 21.50%. An upper limit of the Cr content is preferably 27.50%, more preferably 27.00%, and further preferably 26.50%.

Mo: 0.50 to 2.00%

**[0042]** Molybdenum (Mo) enhances the corrosion resistance of the steel material in a high-temperature environment. If the Mo content is too low, the aforementioned effect cannot be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the Mo content is too high, hot workability of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Mo content is 0.50 to 2.00%. A lower limit of the Mo content is preferably 0.60%, more preferably 0.70%, and further preferably 0.80%. An upper limit of the Mo content is preferably less than 2.00%, more preferably 1.85%, and further preferably 1.50%.

Cu: 1.90 to 4.00%

[0043] Copper (Cu) increases the strength of the steel material by precipitation strengthening. Cu further enhances the corrosion resistance of the steel material in a high-temperature environment. If the Cu content is too low, the aforementioned effect cannot be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the Cu content is too high, hot workability of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Cu content is 1.90 to 4.00%. A lower limit of the Cu content is preferably 2.00%, more preferably more than 2.00%, further preferably 2.10%, further preferably 2.20%, and further preferably 2.50%. An upper limit of the Cu content is preferably 3.90%, more preferably 3.75%, and further preferably 3.50%.

N: 0.150 to 0.350%

**[0044]** Nitrogen (N) is an element that stabilizes the austenitic structure of a steel material. That is, N is an element necessary for obtaining a stable microstructure consisting of ferrite and austenite. N further enhances the corrosion resistance of the steel material. If the N content is too low, the aforementioned effect cannot be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the N content is too high, toughness and hot workability of the steel material will deteriorate even if the contents of other elements are within the range of the present embodiment. Therefore, the N content is 0.150 to 0.350%. A lower limit of the N content is preferably 0.170%, more preferably 0.180%, and further preferably 0.200%. An upper limit of the N content is preferably 0.340%, and more preferably 0.330%.

V: 0.01 to 1.50%

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[0045] Vanadium (V) forms a carbonitride and increases the strength of the steel material. If the V content is too low, the aforementioned effect cannot be sufficiently obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the V content is too high, the strength of the steel material will be too high and the toughness of the steel material will deteriorate even if the contents of other elements are within the range of the present embodiment. Therefore, the V content is 0.01 to 1.50%. A lower limit of the V content is preferably 0.02%, more preferably 0.03%, and further preferably 0.05%. An upper limit of the V content is preferably 1.20%, and more preferably 1.00%.

**[0046]** The chemical composition of the duplex stainless steel material according to the present embodiment contains one or more types of elements selected from the group consisting of Ca and Mg. That is, the chemical composition of the duplex stainless steel material according to the present embodiment may contain at least one of Ca and Mg, or may contain both Ca and Mg. In other words, either one of Ca and Mg need not be contained. In short, the content of either one of Ca and Mg may be 0%. Each of these elements improves the hot workability of the steel material.

Ca: 0.0001 to 0.0200%

[0047] Calcium (Ca) immobilizes S in the steel material as sulfide to make it harmless, and thereby improves the hot workability of the steel material. On the other hand, if the Ca content is too high, even if the contents of other elements are within the range of the present embodiment, oxides in the steel material coarsen and the toughness of the steel material deteriorates. Therefore, when contained, the Ca content is 0.0001 to 0.0200%. A preferable lower limit of the Ca content for more effectively obtaining the aforementioned effect is 0.0003%, more preferably 0.0005%, further preferably 0.0008%, and further preferably 0.0010%. An upper limit of the Ca content is preferably 0.0180%, and more preferably 0.0150%.

Mg: 0.0001 to 0.0200%

**[0048]** Magnesium (Mg) immobilizes S in the steel material as sulfide to make it harmless, and thereby improves the hot workability of the steel material. On the other hand, if the Mg content is too high, even if the contents of other elements are within the range of the present embodiment, oxides in the steel material coarsen and the toughness of the steel material deteriorates. Therefore, when contained, the Mg content is 0.0001 to 0.0200%. A preferable lower limit of the Mg content for more effectively obtaining the aforementioned effect is 0.0003%, more preferably 0.0005%, further preferably 0.0008%, and further preferably 0.0100%. An upper limit of the Mg content is preferably 0.0180%, and more preferably 0.0150%.

**[0049]** The balance of the chemical composition of the duplex stainless steel material according to the present embodiment is Fe and impurities. Here, impurities in a chemical composition means those which are mixed from ores and scraps as the raw material or from the production environment when industrially producing the duplex stainless steel material, and which are permitted within a range not adversely affecting the duplex stainless steel material of the present embodiment.

**[0050]** Note that various elements may be mentioned as examples of impurities. The impurities may be one type of element only, or may be two or more types of elements. The impurities are, for example, Co, W, Sb and Sn. There may be a case where these elements are contained, for example, as impurities having the following contents:

Co: 0.30% or less, W: 0.30% or less, Sb: 0.30% or less, and Sn: 0.30% or less.

<sup>45</sup> [Optional elements]

**[0051]** The chemical composition of the duplex stainless steel material described above may further contain one or more types of elements selected from the group consisting of Nb, Ta, Ti, Zr, and Hf in lieu of a part of Fe. All of these elements are optional elements and increase the strength of the steel material.

Nb: 0 to 0.100%

[0052] Niobium (Nb) is an optional element and does not have to be contained. That is, the Nb content may be 0%. When contained, Nb forms a carbonitride and increases the strength of the steel material. If even a small amount of Nb is contained, the aforementioned effect can be obtained to some extent. However, if the Nb content is too high, the strength of the steel material becomes too high and the toughness of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Nb content is 0 to 0.100%. A lower limit of the Nb content is preferably more than 0%, more preferably 0.001%, further preferably 0.002%. An upper limit

of the Nb content is preferably 0.080%, and more preferably 0.070%.

Ta: 0 to 0.100%

[0053] Tantalum (Ta) is an optional element and does not have to be contained. That is, the Ta content may be 0%. When contained, Ta forms a carbonitride and increases the strength of the steel material. If even a small amount of Ta is contained, the aforementioned effect can be obtained to some extent. However, if the Ta content is too high, the strength of the steel material becomes too high and the toughness of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Ta content is 0 to 0.100%. A lower limit of the Ta content is preferably more than 0%, more preferably 0.001%, further preferably 0.002%, and further preferably 0.003%. An upper limit of the Ta content is preferably 0.080%, and more preferably 0.070%.

Ti: 0 to 0.100%

[0054] Titanium (Ti) is an optional element and does not have to be contained. That is, the Ti content may be 0%. When contained, Ti forms a carbonitride and increases the strength of the steel material. If even a small amount of Ti is contained, the aforementioned effect can be obtained to some extent. However, if the Ti content is too high, the strength of the steel material becomes too high and the toughness of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Ti content is 0 to 0.100%. A lower limit of the Ti content is preferably more than 0%, more preferably 0.001%, further preferably 0.002%. An upper limit of the Ti content is preferably 0.080%, and more preferably 0.070%.

Zr: 0 to 0.100%

[0055] Zirconium (Zr) is an optional element and does not have to be contained. That is, the Zr content may be 0%. When contained, Zr forms a carbonitride and increases the strength of the steel material. If even a small amount of Zr is contained, the aforementioned effect can be obtained to some extent. However, if the Zr content is too high, the strength of the steel material becomes too high and the toughness of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Zr content is 0 to 0.100%. A lower limit of the Zr content is preferably more than 0%, more preferably 0.001%, further preferably 0.002%, and further preferably 0.003%. An upper limit of the Zr content is preferably 0.080%, and more preferably 0.070%.

Hf: 0 to 0.100%

[0056] Hafnium (Hf) is an optional element and does not have to be contained. That is, the Hf content may be 0%. When contained, Hf forms a carbonitride and increases the strength of the steel material. If even a small amount of Hf is contained, the aforementioned effect can be obtained to some extent. However, if the Hf content is too high, the strength of the steel material becomes too high and the toughness of the steel material deteriorates even if the contents of other elements are within the range of the present embodiment. Therefore, the Hf content is 0 to 0.100%. A lower limit of the Hf content is preferably more than 0%, more preferably 0.001%, further preferably 0.002%. An upper limit of the Hf content is preferably 0.080%, and more preferably 0.070%.

**[0057]** The chemical composition of the duplex stainless steel material described above may further contain one or more types of elements selected from the group consisting of B and rare earth metal, in place of part of Fe. All of these elements are optional elements and enhance the hot workability of the steel material.

B: 0 to 0.0200%

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**[0058]** Boron (B) is an optional element and does not have to be contained. That is, the B content may be 0%. When contained, B suppresses segregation of S at grain boundaries in the steel material and enhances the hot-workability of the steel material. If even a small amount of B is contained, the aforementioned effect can be obtained to some extent. However, if the B content is too high, boron nitride (BN) is produced, thereby deteriorating the low-temperature toughness of the steel material even if the contents of other elements are within the range of the present embodiment. Therefore, the B content is 0 to 0.0200%. A lower limit of the B content is preferably more than 0%, more preferably 0.0005%, further preferably 0.0010%, further preferably 0.0015%, and further preferably 0.0020%. An upper limit of the B content is preferably 0.0180%, more preferably 0.0150%, and further preferably 0.0100%.

Rare earth metal: 0 to 0.200%

**[0059]** Rare earth metal (REM) is an optional element and does not have to be contained. That is, the REM content may be 0%. When contained, REM immobilizes S in the steel material as sulfide to make it harmless, and thus improves the hot-workability of the steel material. If even a small amount of REM is contained, the aforementioned effect can be obtained to some extent. However, if the REM content is too high, the oxide in the steel material becomes coarse, thereby deteriorating the toughness of the steel material even if the contents of other elements are within the range of the present embodiment. Therefore, the REM content is 0 to 0.200%. A lower limit of the REM content is preferably more than 0%, more preferably 0.005%, and further preferably 0.010%. An upper limit of the REM content is preferably 0.180%, more preferably 0.150%, further preferably 0.120%, and further preferably 0.100%.

**[0060]** Note that REM in this description is Scandium (Sc) of atomic number 21, Yttrium (Y) of atomic number 39, and one or more types of elements selected from the group consisting of lanthanum (La) of atomic number 57 to lutetium (Lu) of atomic number 71, which are called lanthanoids. Moreover, the REM content in the present description is the total content of these elements.

[Regarding Formula (1)]

**[0061]** The chemical composition of the duplex stainless steel material according to the present embodiment also satisfies the following Formula (1).

 $4.50 \le Mn + Cu \le 9.50$  (1)

[0062] Where, a content in mass% of a corresponding element is substituted for each symbol of an element in Formula (1).

[0063] Fn1 (= Mn+Cu) is an index relating to the strength and the hot workability of the duplex stainless steel material. If Fn1 is too low, even if the other components are within the range of the present embodiment, a yield strength of 550 MPa or more cannot be obtained. On the other hand, if Fn1 is too high, even if the other components are within the range of the present embodiment, the hot workability of the duplex stainless steel material will deteriorate. Therefore, in the chemical composition of the duplex stainless steel material according to the present embodiment, Fn1 is 4.50 to 9.50. As a result, on the condition that the other requirements of the present embodiment are satisfied, the duplex stainless steel material can achieve both yield strength and hot workability in a compatible manner.

**[0064]** A lower limit of Fn1 is preferably 4.55, more preferably 4.60, further preferably 4.70, and further preferably 5.00. An upper limit of Fn1 is preferably 9.20, more preferably 9.00, further preferably 8.70, and further preferably 8.50.

[Regarding Formula (2)]

**[0065]** The chemical composition of the duplex stainless steel material according to the present embodiment also satisfies the following Formula (2).

 $13 \times \text{Cr} - 19 \times \text{Ni} + 21 \times \text{Mo} - 17 \times \text{Cu} + 63 \times \text{Mn} + 8 \times \text{Si} + 984 \times \text{N} \ge 580 \text{ (2)}$ 

[0066] Where, a content in mass% of a corresponding element is substituted for each symbol of an element in Formula

[0067] Fn2 (= 13×Cr-19×Ni+21×Mo-17×Cu+63×Mn+8×Si+984×N) is an index indicating a distribution state of N in the ferrite and the austenite. If Fn2 is too low, even if the other components are within the range of the present embodiment, a large proportion of N will be distributed in the ferrite, and the amount of dissolved N in the austenite will decrease. Consequently, the yield strength of the duplex stainless steel material will decrease. Therefore, in the chemical composition of the duplex stainless steel material according to the present embodiment, Fn2 is 580 or more. As a result, on the condition that the other requirements of the present embodiment are satisfied, the amount of dissolved N in the austenite increases, and the yield strength of the duplex stainless steel material can be increased to 550 MPa or more. [0068] A lower limit of Fn2 is preferably 590, more preferably 600, and further preferably 610. An upper limit of Fn2 is not particularly limited. However, in the range of the chemical composition described above, the upper limit of Fn2 is practically 1087.

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#### [Micro structure]

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**[0069]** The microstructure of the duplex stainless steel material according to the present embodiment consists of, in volume ratio, 35.0 to less than 50.0% of ferrite, and austenite as the balance. As used herein, "consists of ferrite, and austenite as the balance" means that the amount of any phase other than ferrite and the austenite is negligibly small. For example, in the chemical composition of the duplex stainless steel material according to the present embodiment, volume ratios of precipitates and inclusions are negligibly small as compared with volume ratios of ferrite and austenite. That is, the microstructure of the duplex stainless according to the present embodiment may contain minute amounts of precipitates, inclusions, etc., in addition to ferrite and austenite.

**[0070]** Further, in the microstructure of the duplex stainless steel material according to the present embodiment, the volume ratio of ferrite is 35.0 to less than 50.0%. If the volume ratio of ferrite is too low, the strength and/or corrosion resistance of the steel material may deteriorate. On the other hand, if the volume ratio of ferrite is too high, the corrosion resistance of the steel material deteriorates. Further, if the volume ratio of ferrite is too high, the low-temperature toughness and/or the hot workability of the steel material may deteriorate. Therefore, in the microstructure of the duplex stainless steel material according to the present embodiment, the volume ratio of ferrite is 35.0 to less than 50.0%.

**[0071]** A lower limit of the volume ratio of ferrite is preferably 35.5%, and more preferably 36.5%. An upper limit of the volume ratio of ferrite is preferably 48.0%, more preferably 47.0%, and further preferably 45.0%.

[0072] In the present embodiment, the volume ratio of ferrite in the duplex stainless steel material can be determined by a method conforming to ASTM E562 (2011). A test specimen for microstructure observation is prepared from an arbitrary location in the duplex stainless steel material according to the present embodiment. Here, the arbitrary location from which the test specimen is prepared is not particularly limited. For example, the test specimen is prepared from a center portion in a thickness direction of the steel material. An observation surface at which to carry out the microstructure observation is not particularly limited. For example, a cross section perpendicular to a rolling direction of the duplex stainless steel material is adopted as the observation surface. Note that the size of the test specimen is not particularly limited, and it suffices that an observation surface of 5 mm  $\times$  5 mm can be obtained.

**[0073]** The observation surface of the test specimen taken is mirror-polished. The mirror-polished observation surface is electrolytically etched in a 7% potassium hydroxide etching solution to reveal the microstructure. The observation surface on which the microstructure has been revealed is observed in 10 fields of view using an optical microscope. The visual field area is not particularly limited, and, for example, is 1.00 mm<sup>2</sup> (at a magnification of 100 times). In each field of view, ferrite is identified from contrast. The area ratios of the identified ferrite are measured by a point counting method conforming to ASTM E562 (2011). In the present embodiment, an arithmetic average value of the area ratios of ferrite obtained in the 10 fields of view is defined as the volume ratio (%) of ferrite.

[Yield strength of duplex stainless steel material]

**[0074]** The yield strength of the duplex stainless steel material according to the present embodiment is 550 MPa or more. By having the chemical composition and microstructure described above, the duplex stainless steel material according to the present embodiment exhibits excellent pitting resistance and excellent hot workability, even when the yield strength is 550 MPa or more.

**[0075]** A lower limit of the yield strength of the duplex stainless steel material according to the present embodiment is preferably 560 MPa, and more preferably 570 MPa. Note that an upper limit of the yield strength of the duplex stainless steel material according to the present embodiment is not particularly limited. The upper limit of the yield strength of the duplex stainless steel material according to the present embodiment is, for example, 700 MPa. The upper limit of the yield strength may be 690 MPa, may be 680 MPa, or may be 670 MPa.

[0076] The yield strength of the duplex stainless steel material according to the present embodiment can be determined by the following method. Specifically, a tensile test is performed by a method conforming to ASTM E8/E8M (2013). A round bar test specimen is prepared from the steel material according to the present embodiment. If the steel material is a steel plate, the round bar test specimen is prepared from a center portion of the thickness. If the steel material is a steel pipe, the round bar test specimen is prepared from a center portion of the wall thickness. The size of the round bar test specimen is, for example, as follows: a parallel portion diameter is 6 mm and a parallel portion length is 30 mm. Note that an axial direction of the round bar test specimen is parallel with the rolling direction of the steel material. The tensile test is carried out in the atmosphere at room temperature (25°C) using the prepared round bar test specimen, and the obtained 0.2% offset proof stress is defined as the yield strength (MPa).

<sup>55</sup> [Pitting resistance of duplex stainless steel material]

**[0077]** By having the aforementioned chemical composition and the aforementioned microstructure, the duplex stainless steel material according to the present embodiment exhibits excellent pitting resistance. In the present embodiment,

excellent pitting resistance is defined as follows.

[0078] Specifically, the duplex stainless steel material according to the present embodiment is subjected to a corrosion test in accordance with "Method E" specified in ASTM G48 (2015). A test specimen for the corrosion test is prepared from the steel material according to the present embodiment. If the steel material is a steel plate, the test specimen is prepared from a center portion of the thickness. If the steel material is a steel pipe, the test specimen is prepared from a center portion of the wall thickness. The size of the test specimen is, for example, as follows: a thickness of 3 mm, a width of 25 mm, and a length of 50 mm. A longitudinal direction of the test specimen is parallel with the rolling direction of the steel material.

**[0079]** A solution of 6%FeCl<sub>3</sub> + 1%HCl is adopted as the test solution. The test specimen is immersed in the test solution so that the solution volume to specimen area ratio is 5 mL/cm<sup>2</sup> or more. The temperature at the start of the test is set to 20°C, and the temperature of the test solution is increased by 5°C every 24 hours. The temperature when pitting occurs on the test specimen is defined as the critical pitting temperature (CPT). If the obtained CPT is 25°C or more, it is determined that the duplex stainless steel material exhibits excellent pitting resistance.

15 [Hot workability of duplex stainless steel material]

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**[0080]** By having the aforementioned chemical composition and the aforementioned microstructure, the duplex stainless steel material according to the present embodiment exhibits excellent hot workability. In the present embodiment, the excellent hot workability is defined as follows.

**[0081]** Specifically, the duplex stainless steel material according to the present embodiment is subjected to a hot workability test (Gleeble test). A test specimen for the Gleeble test is prepared from the steel material according to the present embodiment. If the steel material is a steel plate, the test specimen is prepared from a center portion of the thickness. If the steel material is a steel pipe, the test specimen is prepared from a center portion of the wall thickness. The test specimen is, for example, a round bar test specimen having a diameter of 10 mm and a length of 130 mm. A longitudinal direction of the test specimen is parallel with the rolling direction of the steel material.

**[0082]** The test specimen heated to 1000°C is subjected to a tensile test at a strain rate of 10s<sup>-1</sup> to cause the test specimen to break. A reduction value (%) is determined based on the broken test specimen. If the obtained reduction value is 40% or more, it is determined that the duplex stainless steel material exhibits the excellent hot workability.

30 [Shape of duplex stainless steel material]

[0083] The shape of the duplex stainless steel material according to the present embodiment is not particularly limited. The duplex stainless steel material, for example, may be a steel pipe, may be a steel plate, may be a steel bar, or may be a wire rod. Preferably the duplex stainless steel material according to the present embodiment is a seamless steel pipe. In a case where the duplex stainless steel material according to the present embodiment is a seamless steel pipe, even if the wall thickness is 5 mm or more, the duplex stainless steel material has a yield strength of 550 MPa or more, excellent pitting resistance, and excellent hot workability.

[Method for producing duplex stainless steel material]

**[0084]** A method for producing a steel pipe will be described as one example of a method for producing the duplex stainless steel material according to the present embodiment which has the above-described configuration. Note that the method for producing the duplex stainless steel material according to the present embodiment is not limited to the production method described below.

**[0085]** An example of the method for producing the duplex stainless steel material according to the present embodiment includes a starting material preparation step, a hot working step, and a solution treatment step. Hereinafter, each production step will be described in detail.

[Starting material preparation step]

**[0086]** In the starting material preparation step, a starting material having the above-described chemical composition is prepared. The starting material may be prepared by producing it, or may be prepared by purchasing it from a third party. That is, the method for preparing the starting material is not particularly limited.

**[0087]** When the starting material is produced, the production is performed by, for example, the following method. A molten steel having the above-described chemical composition is produced. By using the molten steel, a cast piece (a slab, a bloom, or a billet) is produced by a continuous casting method. A steel ingot may be produced by an ingot-making method by using the molten steel. If desired, a slab, a bloom or an ingot may be subjected to blooming to produce a billet. The starting material is produced by the step described above.

### [Hot working step]

**[0088]** In the hot working step, the starting material prepared by the above-described preparation step is subjected to hot working to produce a steel material. The hot working may be hot forging, may be hot extrusion, or may be hot rolling. A method for performing hot working is not particularly limited, and a well-known method may be used.

**[0089]** If the steel material is a steel pipe, for example, the steel material may be subjected to hot working by the Ugine-Sejournet process or the Ehrhardt push bench process (that is, hot extrusion). If the steel material is a steel pipe, for example, the steel material may be subjected to piercing-rolling (that is, hot rolling) according to the Mannesmann process. 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

#### [Solution treatment step]

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[0090] In the solution treatment step, the steel material produced by the aforementioned hot working step is subjected to a solution treatment. A method for performing the solution treatment is not particularly limited, and a well-known method may be used. For example, the steel material is charged into a heat treatment furnace, and after being held at a predetermined temperature, is quenched. Note that, in the case of performing a solution treatment by charging the steel material into a heat treatment furnace, holding the steel material at a predetermined temperature, and thereafter quenching the steel material, the temperature at which the solution treatment is performed (solution treatment temperature) means the temperature (°C) of the heat treatment furnace for performing the solution treatment. Similarly, the holding time at the solution treatment temperature (solution treatment time) means a time from when the starting material is charged into the inside of the heat treatment furnace for performing the solution treatment until the starting material is taken out from the heat treatment furnace.

[0091] Preferably, the solution treatment temperature in the solution treatment step of the present embodiment is set to 900 to 1200°C. If the solution treatment temperature is too low, precipitates (for example, a  $\sigma$  phase that is an intermetallic compound or the like) may remain in the steel material after the solution treatment. In this case, the pitting resistance of the steel material deteriorates. Furthermore, if the solution treatment temperature is too low, in some cases the volume ratio of ferrite in the steel material after the solution treatment will be less than 35.0%, and the strength and/or corrosion resistance of the steel material may deteriorate. On the other hand, if the solution treatment temperature is too high, in some cases the volume ratio of ferrite in the steel material after the solution treatment will be 50.0% or more, and the pitting resistance of the steel material may deteriorate. Furthermore, in this case, the low-temperature toughness and hot workability of the steel material may deteriorate.

**[0092]** Therefore, when performing the solution treatment by charging the steel material into a heat treatment furnace, holding the steel material at a predetermined temperature, and thereafter performing quenching, the solution treatment temperature is preferably set within the range of 900 to 1200°C. A lower limit of the solution treatment temperature is more preferably 920°C, and further preferably 940°C. An upper limit of the solution treatment temperature is more preferably 1180°C, and further preferably 1160°C.

**[0093]** When performing the solution treatment by charging the steel material into a heat treatment furnace, holding the steel material at a predetermined temperature, and thereafter performing quenching, the solution treatment time is not particularly limited, and may be in accordance with a well-known condition. The solution treatment time is, for example, 5 to 180 minutes. The quenching method is, for example, water cooling.

**[0094]** Note that, as necessary, the steel material on which the solution treatment was performed may be subjected to a pickling treatment. In this case, the pickling treatment may be performed by a well-known method and is not particularly limited. Further, if the steel material on which the solution treatment was performed is subjected to cold working, the strength of the steel material will be too high and the toughness of the steel material will deteriorate. Therefore, it is preferable not to subject the duplex stainless steel material according to the present embodiment to cold working.

**[0095]** Through the steps described above, the duplex stainless steel material according to the present embodiment can be produced. Note that the method for producing the duplex stainless steel material described above is one example, and the duplex stainless steel material may be produced by another method. Hereunder, the present invention is described in more detail by way of Examples.

#### **EXAMPLES**

[0096] Molten steels having the chemical compositions shown in Table 1 were melted using a 50 kg vacuum furnace, and ingots were produced by an ingot casting method. Note that the symbol"-" in Table 1 means that the content of the corresponding element was at an impurity level. Further, Fn1 and Fn2 that were determined based on the chemical composition described in Table 1 and the definitions described above are shown in Table 2.

	[Table 1]	
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FABLE 1

		REM	1	-	-		-	-	-	-	0.012	1	-	1	0.010	1	-	-	-	-		-	-	-
		В		-	-	1	-	-	0.0020	0.0019	0.0020	0.0020	0.0019	-	0.0021	0.0021	-	-	-	-	0.0023	0.0021	-	0.0020
		Hf	1	1	-	ı	-	0.001	-	-	1	-	0.002		-	-	-	-	-		ı	-	-	-
		Zr	1	1	1	ı	0.001	ı	ı	1	1	ı	0.003	ı	ı	1	ı	ı	0.001	ı	ı	1	1	-
		Ι	1	1	1	ı	1	0.001	1	1	1	0.002	-	1	1	1	-	-	1	1	ı	1	1	0.003
	es)	Та	ı	ı	1	ı	0.003	1	1	ı	1	ı	0.003	ı	1	ı	•	-	0.001	ı	ı	ı	1	1
	Fe and impurities)	qN	1	1	1	ı	1	1	1	1	1	0.002	-	1	0.002	0.002	-	-	1	1	0.002	1	-	-
	Fe and	Mg		0.0019	0.0023	ı	1	0.0023	ı	1	0.0020	ı	-	ı		0.0023	0.0022	1	0.0023	ı	ı	1	0.0022	-
TABLE 1	ice being	Са	0.0022	-	0.0027	0.0022	0.0020	-	0.0020	0.0022	0.0027	0.0020	0.0022	0.0020	0.0023	0.0027	0.0020	0.0023	0.0020	0.0020	0.0023	0.0017	0.0022	0.0021
	e balar	>	0.10	0.11	60.0	0.10	0.11	0.11	0.10	0.10	60.0	0.10	0.10	0.10	60.0	0.11	0.05	0.05	0.05	0.05	0.05	0.11	0.12	0.10
	ss%, th	z	0.216	0.218	0.228	0.199	0.242	0.203	0.233	0.216	0.228	0.233	0.216	0.231	0.194	0.187	0.159	0.187	0.159	0.159	0.187	0.205	0.238	0.053
Ľ	(in ma	Cu	3.20	3.62	3.19	3.20	3.20	2.99	2.50	3.20	3.19	2.21	3.20	2.78	3.80	2.52	3.40	3.97	3.89	2.29	2.44	2.13	2.46	2.44
	osition	Мо	66.0	1.12	66.0	96.0	1.02	66.0	66.0	66.0	1.48	66.0	66.0	1.57	1.13	86.0	66.0	1.10	66.0	66.0	1.10	0.89	1.14	0.98
	al comp	C	25.20	26.21	25.17	22.25	25.01	25.11	25.13	25.20	25.17	25.13	25.20	27.88	27.64	25.00	23.25	25.00	23.25	23.25	25.00	22.62	18.47	24.56
	Chemic	Ē	4.81	5.29	4.82	5.00	4.91	4.82	4.80	4.81	4.82	4.80	4.81	4.59	5.73	5.98	4.83	5.03	4.83	4.83	5.03	3.04	5.38	5.57
		A	0.080	0.075	0.081	0.075	0.070	0.081	0.077	0.080	0.081	0.077	0.080	0.029	0.040	0.075	0.012	0.014	0.012	0.012	0.014	0.023	0.031	0.033
		S	0.0005	0.0005	0.0005	0.0003	0.0002	0.0002	0.0005	0.0005	0.0005	0.0005	0.0005	0.0003	0.0005	0.0004	0.0002	0.0002	0.0002	0.0002	0.0002	0.0005	0.0004	0.0002
		Ъ	0.020	0.019	0.019	0.019	0.020	0.020	0.019	0.020	0.019	0.019	0.020	0.016	0.017	0.019	0.023	0.021	0.023	0.023	0.021	0.016	0.021	0.016
		Mn	3.10	4.45	90.3	4.32	5.58	3.09	5.05	3.10	90.3	5.05	3.10	1.61	06.9	2.78	2.59	0.65	2.05	1.01	0.97	2.53	3.64	2.22
		Si	0.52	0.56	0.52	0.54	0.53	99.0	0.51	0.52	0.52	0.51	0.52	0.52	0.49	0.51	0.50	0.52	09.0	0.50	0.52	0.44	0.54	0.50
		0	0.015	0.013	0.015	0.014	0.015	0.016	0.015	0.015	0.015	0.015	0.015	0.015	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.015	0.014	0.015
	S. C.		∢	В	C	۵	Ш	Щ	Э	I	_	ſ	¥	Τ	M	z	0	Ь	Ø	8	S	T	n	>

[Table 2]

## [0098]

5 TABLE 2

	Test Number	Steel	Fn1	Fn2	Solution treatment temperature (°C)	Ferrite volume ratio (%)	YS (MPa)	CPT (°C)	Hot workability test
10	1	Α	6.30	615	980	46.4	622	30	E
	2	В	8.07	702	1000	45.7	607	35	E
	3	С	8.25	749	1050	48.5	625	35	Е
	4 D		7.52	633	1050	44.8	589	30	Е
15	5	Е	8.78	793	950	48.3	650	30	Е
	6	F	6.08	604	1000	45.0	603	35	Е
	7	G	7.55	765	980	46.1	620	30	Е
20	8	Н	6.30	615	980	46.4	618	30	E
	9	I	8.25	760	1000	47.6	615	35	E
	10	J	7.26	770	1050	43.8	585	35	E
0.5	11	K	6.30	615	1050	46.7	612	35	E
25	12	L	4.39	594	980	48.9	531	30	Е
	13	М	10.70	839	1050	43.5	642	35	NA
	14	N	5.30	552	1000	36.8	537	30	E
30	15	0	5.99	497	1050	38.8	538	35	E
	16	Р	4.62	414	1000	39.1	522	30	E
	17	Q	5.94	455	1000	38.4	530	35	E
35	18	R	3.30	416	1050	39.9	524	40	Е
35	19	S	3.41	460	1070	36.0	513	40	E
	20	T	4.66	584	1050	58.0	594	20	Е
	21	U	6.10	587	1050	38.9	588	20	Е
40	22	V	4.66	389	1000	38.6	518	30	Е
	23	G	7.55	765	750	33.0	640	20	E

[0099] The ingot of each Test Number was heated to 1200°C, and subjected to hot forging and hot working to produce a steel plate having a thickness of 10 mm. The steel plate of each Test Number was subjected to a solution treatment in which the steel plate was held for 15 minutes at the solution treatment temperature described in Table 2. The steel plates of the respective Test Numbers that had been subjected to the solution treatment were water-cooled.

## [Evaluation tests]

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**[0100]** The steel plates of the respective Test Numbers that had been subjected to the aforementioned solution treatment were subjected to microstructure observation, a tensile test, a corrosion test, and a hot workability test which are described below.

# [Microstructure observation]

**[0101]** The steel plate of each Test Number was subjected to microstructure observation by the above-described method conforming to ASTM E562 (2011) to determine the ferrite volume ratio (%). Note that, in the present Example,

a test specimen for microstructure observation was prepared from the center portion of the thickness of the steel plate of each Test Number, and a cross section perpendicular to the rolling direction was adopted as the observation surface. Further, the microstructure of the steel plate of each Test Number was a microstructure consisting of ferrite and austenite. Table 2 shows the ferrite volume ratios (%) determined for the steel plate of each Test Number.

[Tensile test]

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**[0102]** A tensile test was carried out on the steel plate of each Test Number by the above-described method conforming to ASTM E8/E8M (2013) to determine yield strength (MPa). In the present Example, the round bar test specimen for the tensile test was prepared from the center portion of the thickness of the steel plate of each Test Number, and the axial direction of the round bar test specimen was parallel to the rolling direction. The 0.2% offset proof stress obtained in the tensile test was defined as the yield strength (MPa). Table 2 shows the yield strength determined for the steel plate of each Test Number as "YS (MPa)".

## 15 [Corrosion test]

**[0103]** A corrosion test was carried out on the steel plate of each Test Number by the above-described method conforming to ASTM G48 (2015) Method E to evaluate pitting resistance. In the present Example, the test specimen for the corrosion test was prepared from the center portion of the thickness of the steel plate of each Test Number. The size of the test specimen was as follows: a thickness of 3 mm, a width of 25 mm, and a length of 50 mm, and the longitudinal direction of the test specimen was parallel with the rolling direction.

**[0104]** The test specimen of each Test Number was immersed in a test solution (6%FeCl<sub>3</sub> + 1%HCl) at 20°C so that the solution volume to specimen area ratio was 5 mL/cm<sup>2</sup> or more. Every 24 hours from the time at which the test specimen was immersed in the test solution, the temperature of the test solution was increased by 5°C, and whether or not pitting had occurred was confirmed with the naked eyes. The temperature when pitting occurred was defined as the CPT (°C). The CPT (°C) obtained in the corrosion test for the steel plate of each Test Number is shown in Table 2.

[Hot workability test]

- [0105] A hot workability test (Gleeble test) was carried out on the steel plate of each Test Number to evaluate hot workability. Specifically, a round bar test specimen having a diameter of 10 mm and a length of 130 mm was prepared from the steel plate of each Test Number. The round bar test specimen was prepared from the center portion of the thickness of the steel plate of each Test Number. Note that the longitudinal direction of the round bar test specimen was parallel with the rolling direction.
- [0106] After heating the round bar test specimen of each Test Number to 1000°C, a tensile test was carried out at a strain rate of 10s-1 to cause the round bar test specimen of each Test Number to break. A reduction value (%) was determined based on the broken round bar test specimen of each Test Number. If the obtained reduction value was 40% or more, it was determined that the steel plate of the relevant Test Number exhibited excellent hot workability ("E" (Excellent) in Table 2). On the other hand, if the obtained reduction value was less than 40%, it was determined that the steel plate of the relevant Test Number did not exhibit excellent hot workability ("NA" (Not Acceptable) in Table 2). The evaluation result of the hot workability test for the steel plate of each Test Number is shown in Table 2.

#### [Evaluation Results]

- [0107] Referring to Table 1 and Table 2, in the steel plates of Test Numbers 1 to 11, the chemical composition was appropriate, Fn1 was in the range of 4.50 to 9.50, and Fn2 was 580 or more. In addition, the production method performed with respect to the steel plates of Test Numbers 1 to 11 was a preferable production method described in the present description. As a result, the steel plates of Test Numbers 1 to 11 had a micro structure in which the volume ratio of ferrite was 35.0 to less than 50.0%, with austenite as the balance. In addition, the yield strength of the steel plates of Test Numbers 1 to 11 was 550 MPa or more. Further, for the steel plates of Test Numbers 1 to 11, the CPT was 25°C or more and excellent pitting resistance was exhibited. Furthermore, the steel plates of Test Numbers 1 to 11 exhibited excellent hot workability in the hot workability test.
  - **[0108]** On the other hand, in the steel plate of Test Number 12, Fn1 was less than 4.50. As a result, the yield strength of the steel plate of Test Number 12 was less than 550 MPa and the desired yield strength was not obtained.
- [0109] In the steel plate of Test Number 13, Fn1 was more than 9.50. As a result, the steel plate of Test Number 13 did not exhibit excellent hot workability in the hot workability test.
  - **[0110]** In the steel plates of Test Numbers 14 to 17, Fn2 was less than 580. As a result, the yield strength of the steel plates of Test Numbers 14 to 17 was less than 550 MPa and the desired yield strength was not obtained.

**[0111]** In the steel plates of Test Numbers 18 and 19, Fn1 was 4.50 or less. Further, in the steel plates of Test Numbers 18 and 19, Fn2 was less than 580. As a result, the yield strength of the steel plates of Test Numbers 18 and 19 was less than 550 MPa and the desired yield strength was not obtained.

**[0112]** In the steel plate of Test Number 20, the Ni content was too low. Consequently, the volume ratio of ferrite in the steel plate of Test Number 20 was 50.0% or more. As a result, for the steel plate of Test Number 20, the CPT was less than 25°C and excellent pitting resistance was not exhibited.

**[0113]** In the steel plate of Test Number 21, the Cr content was too low. As a result, for the steel plate of Test Number 21, the CPT was less than 25°C and excellent pitting resistance was not exhibited.

**[0114]** In the steel plate of Test Number 22, the N content was too low. Furthermore, in the steel plate of Test Number 22, Fn2 was less than 580. As a result, the yield strength of the steel plate of Test Number 22 was less than 550 MPa and the desired yield strength was not obtained.

**[0115]** In the steel plate of Test Number 23, the solution treatment temperature in the production process was too low. Consequently, the volume ratio of ferrite in the steel plate of Test Number 23 was less than 35.0%. As a result, for the steel plate of Test Number 23, the CPT was less than 25°C and excellent pitting resistance was not exhibited.

**[0116]** The embodiment of the present disclosure has been described so far. However, the embodiment described above is merely an example for carrying out the present disclosure. Therefore, the present disclosure is not limited to the above-described embodiment, and can be implemented by appropriately modifying the above-described embodiment within a range not departing from the spirit thereof.

Claims

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1. A duplex stainless steel material comprising:

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25 a chemical composition consisting of, in mass%, C: 0.030% or less, Si: 0.20 to 1.00%, Mn: 0.50 to 7.00%, P: 0.040% or less, S: 0.0100% or less, AI: 0.100% or less,
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Ni: 4.20 to 9.00%, Cr: 20.00 to 28.00%, Mo: 0.50 to 2.00%, Cu: 1.90 to 4.00%,

N: 0.150 to 0.350%, V: 0.01 to 1.50%, Nb: 0 to 0.100%,

Ta: 0 to 0.100%, Ti: 0 to 0.100%,

Zr: 0 to 0.100%, Hf: 0 to 0.100%,

B: 0 to 0.0200%, and

rare earth metal: 0 to 0.200%, and

one or more types of elements selected from the group consisting of:

Ca: 0.0001 to 0.0200%, and Mg: 0.0001 to 0.0200%,

with the balance being Fe and impurities,

and satisfying Formulae (1) and (2);

a microstructure consisting of 35.0 to less than 50.0% of ferrite in volume ratio and austenite as the balance; and

a yield strength of 550 MPa or more:

 $4.50 \le Mn + Cu \le 9.50 (1)$ 

# $13 \times \text{Cr} - 19 \times \text{Ni} + 21 \times \text{Mo} - 17 \times \text{Cu} + 63 \times \text{Mn} + 8 \times \text{Si} + 984 \times \text{N} \ge 580 \text{ (2)}$

where, a content in mass% of a corresponding element is substituted for each symbol of an element in Formulae (1) and (2).

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

Nb: 0.001 to 0.100%, Ta: 0.001 to 0.100%, Ti: 0.001 to 0.100%, Zr: 0.001 to 0.100%, and Hf: 0.001 to 0.100%.

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

B: 0.0005 to 0.0200%, and rare earth metal: 0.001 to 0.200%.

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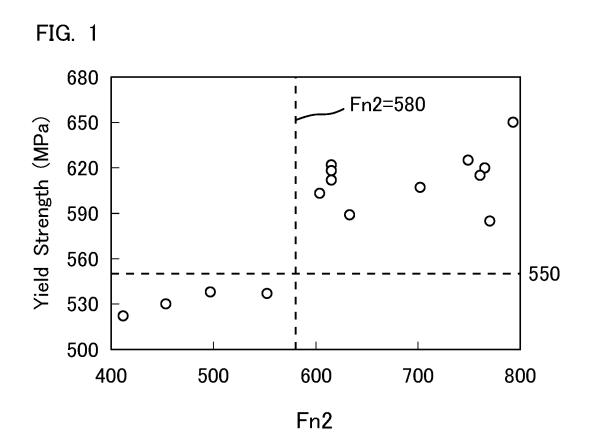
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#### INTERNATIONAL SEARCH REPORT International application No. 5 PCT/JP2020/031050 A. CLASSIFICATION OF SUBJECT MATTER C21D 9/08(2006.01)i; C22C 38/00(2006.01)i; C22C 38/58(2006.01)i FI: C22C38/00 302H; C22C38/58; C21D9/08 E According to International Patent Classification (IPC) or to both national classification and IPC 10 FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C21D9/08; C22C38/00; C22C38/58 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 15 Published unexamined utility model applications of Japan 1971-2020 Registered utility model specifications of Japan 1996-2020 Published registered utility model applications of Japan 1994-2020 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 C. DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Α WO 2012/111536 A1 (SUMITOMO METAL INDUSTRIES, 1 - 3LTD.) 23 August 2012 (2012-08-23) entire text 25 Α JP 2012-197509 A (NIPPON STEEL & SUMIKIN STAINLESS 1 - 3STEEL CORPORATION) 18 October 2012 (2012-10-18) entire text WO 2013/035588 A1 (NIPPON STEEL & SUMITOMO METAL 1 - 3Α CORPORATION) 14 March 2013 (2013-03-14) entire 30 WO 2012/111537 A1 (SUMITOMO METAL INDUSTRIES, Α 1 - 3LTD.) 23 August 2012 (2012-08-23) entire text 35 40 Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: later document published after the international filing date or priority date and not in conflict with the application but cited to understand document defining the general state of the art which is not considered the principle or theory underlying the invention earlier application or patent but published on or after the international 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 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) 45 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 referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than document member of the same patent family the priority date claimed Date of the actual completion of the international search Date of mailing of the international search report 50 19 October 2020 (19.10.2020) 02 November 2020 (02.11.2020) Name and mailing address of the ISA/ Authorized officer Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan Telephone No.

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		IONAL SEARCH REPOR	T International ap	pplication No.
5	Information	on on patent family members	PCT/JP	2020/031050
	Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
10	WO 2012/111536 A1	23 Aug. 2012	US 2013/0312880 A1 entire text EP 2677054 A1 entire text	
15	JP 2012-197509 A	18 Oct. 2012	CN 103370436 A entire text US 2013/0343948 A1 entire text WO 2012/121380 A1 entire text EP 2684973 A1	
20			entire text KR 10-2013-0123434 A entire text CN 103562424 A entire text	
25	WO 2013/035588 A1	14 Mar. 2013	US 2014/0212322 A1 entire text EP 2754726 A1 entire text CN 103781931 A entire text	
30	WO 2012/111537 A1	23 Aug. 2012	US 2013/0315776 A1 entire text EP 2677056 A1 entire text CN 103370435 A entire text	
35				
40				
45				
50				
55	Form PCT/ISA/210 (patent family an	nex) (January 2015)		

#### REFERENCES CITED IN THE DESCRIPTION

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## Patent documents cited in the description

- JP 5132741 A [0005] [0010]
- JP 9195003 A **[0005] [0010]**

- JP 2014043616 A [0005] [0010]
- JP 2016003377 A [0005] [0010]