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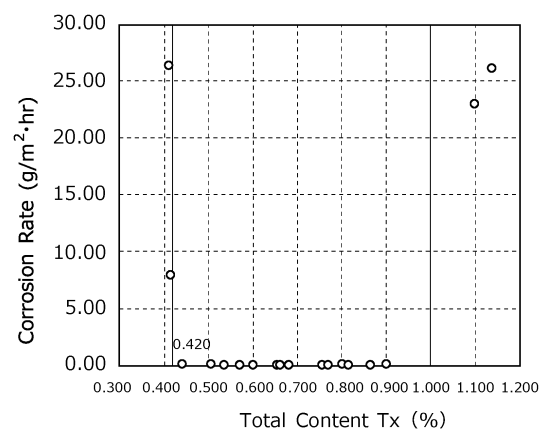
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(54) **ALLOY MATERIAL**

(57) An alloy material that has excellent intergranular corrosion resistance is provided. An alloy material according to the present disclosure has a chemical composition containing, in mass%, C: 0.005 to 0.020%, Si: 0.05 to 0.50%, Mn: 0.05 to 1.00%, P: 0.030% or less, S: 0.0100% or less, Cu: 1.5 to 3.0%, Ni: 35.0 to 50.0%, Cr: 20.0 to 30.0%, Mo: 2.5 to 4.0%, Co: 0.01 to 0.80%, W: 0.01 to 0.30%, Ca: 0.0050% or less, N: 0.001 to 0.015%, Al: 0.20% or less, B: 0.0030% or less, Sn: 0.050% or less, and Ti: 0.40 to 0.90%, with the balance being Fe and impurities, in which the total content of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%. The number density of fine nitrogen-containing precipitates at grain boundaries of the alloy material is 20/ μm or less.

FIG.1



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Description

TECHNICAL FIELD

5 **[0001]** The present disclosure relates to an alloy material.

BACKGROUND ART

10 **[0002]** Alloy materials are used in chemical plant equipment at oil refinery plants, petrochemical plants and the like. Examples of the respective apparatuses included in such chemical plant equipment include a vacuum distillation unit, a direct desulfurization unit, a catalytic reforming unit and the like. These apparatuses include a heating furnace pipe, a reactor, a tank, a heat exchanger, piping and the like. These apparatuses are welded structures that are formed by welding together materials.

15 **[0003]** These types of chemical plant equipment come into contact with process fluids including sulfides and/or chlorides. Therefore, the materials used in these types of equipment are exposed to corrosive environments that contain sulfides and/or chlorides. Consequently, the materials used in these types of equipment are required to have excellent corrosion resistance. For example, alloy materials which have a high content of Ni and a high content of Cr are used in these types of equipment.

20 **[0004]** As mentioned above, alloy materials that are used in chemical plant equipment are welded to form a part of a welded structure. When such welding is performed, a heat affected zone (HAZ) is formed in the alloy material. In the heat affected zone, intergranular corrosion is likely to occur due to sensitization. Therefore, alloy materials that are used in chemical plant equipment are required to have excellent intergranular corrosion resistance.

[0005] An alloy material that has excellent intergranular corrosion resistance is proposed in International Application Publication No. WO2017/168904 (Patent Literature 1).

25 **[0006]** The alloy material disclosed in Patent Literature 1 has a chemical composition consisting of, in mass%, C: 0.005 to 0.015%, Si: 0.05 to 0.50%, Mn: 0.05 to 1.5%, P: 0.030% or less, S: 0.020% or less, Cu: 1.0 to 5.0%, Ni: 30.0 to 45.0%, Cr: 18.0 to 30.0%, Mo: 2.0 to 4.5%, Ti: 0.5 to 2.0%, N: 0.001 to 0.015%, and Al: 0 to 0.50%, with the balance being Fe and impurities. An average grain size d (μm) satisfies Formula (1):

$$30 \quad d < 4.386 / (C_{\text{rel}} + 0.15) \quad (1)$$

where, C_{rel} in Formula (1) is defined by Formula (2):

$$35 \quad C_{\text{rel}} = C - 0.125\text{Ti} + 0.8571\text{N} \quad (2)$$

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

40 **[0007]** In the alloy material disclosed in Patent Literature 1, the relative amount of dissolved C (C_{rel}) and the average grain size d satisfy Formula (1). It is described in Patent Literature 1 that, by this means, the development of Cr-depleted zones can be suppressed and intergranular corrosion resistance can be increased.

CITATION LIST

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PATENT LITERATURE

[0008] Patent Literature 1: International Application Publication No. WO2017/168904

50 SUMMARY OF INVENTION

TECHNICAL PROBLEM

55 **[0009]** In the alloy material disclosed in Patent Literature 1, the intergranular corrosion resistance in a heat affected zone can be increased. However, the intergranular corrosion resistance in a heat affected zone may also be increased by means that is different from the means proposed in Patent Literature 1.

[0010] An objective of the present disclosure is to provide an alloy material in which, even when the alloy material is subjected to welding, excellent intergranular corrosion resistance is obtained in a heat affected zone.

SOLUTION TO PROBLEM

[0011] An alloy material according to the present disclosure is as follows.

[0012] An alloy material having a chemical composition consisting of, in mass%,

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C: 0.005 to 0.020%,

Si: 0.05 to 0.50%,

Mn: 0.05 to 1.00%,

P: 0.030% or less,

10 S: 0.0100% or less,

Cu: 1.5 to 3.0%,

Ni: 35.0 to 50.0%,

Cr: 20.0 to 30.0%,

Mo: 2.5 to 4.0%,

15 Co: 0.01 to 0.80%,

W: 0.01 to 0.30%,

Ca: 0.0050% or less,

N: 0.001 to 0.015%,

Al: 0.20% or less,

20 B: 0.0030% or less,

Sn: 0.050% or less,

Ti: 0.40 to 0.90%,

Nb: 0 to 0.150%,

V: 0 to 0.150%,

25 Zr: 0 to 0.150%,

Hf: 0 to 0.150%, and

Ta: 0 to 0.150%,

with the balance being Fe and impurities,

in which:

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a total content of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%, and

a number density of nitrogen-containing precipitates having a major axis of 10 to 100 nm at grain boundaries of the alloy material is 20/ μm or less.

35 ADVANTAGEOUS EFFECTS OF INVENTION

[0013] In the alloy material according to the present disclosure, even when the alloy material is subjected to welding, excellent intergranular corrosion resistance is obtained in a heat affected zone.

40 BRIEF DESCRIPTION OF DRAWINGS

[0014]

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[FIG. 1] FIG. 1 is a view illustrating the relation between a total content (%) of Ti, Nb, V, Zr, Hf, and Ta, and a corrosion rate ($\text{g}/\text{m}^2\cdot\text{hr}$) that is an index of intergranular corrosion resistance obtained by carrying out an intergranular corrosion test in accordance with ASTM A262 Practice C.

[FIG. 2] FIG. 2 is a view illustrating the relation between a number density ($1/\mu\text{m}$) of fine nitrogen-containing precipitates at grain boundaries, and a corrosion rate ($\text{g}/\text{m}^2\cdot\text{hr}$) that is an index of intergranular corrosion resistance obtained by carrying out an intergranular corrosion test in accordance with ASTM A262 Practice C.

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[FIG. 3] FIG. 3 is a view showing a TEM image of an alloy material whose chemical composition satisfies the requirements of the chemical composition of the present embodiment, and a diffraction pattern obtained by performing selected area electron diffraction on a fine precipitate indicated by an arrow in the TEM image.

DESCRIPTION OF EMBODIMENT

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[0015] The present inventors conducted studies regarding an alloy material with which excellent intergranular corrosion resistance is obtained in a heat affected zone even when welding is performed. As a result, the present inventors obtained the following findings.

[0016] First, the present inventors conducted studies from the viewpoint of the chemical composition with regard to an alloy material which has excellent intergranular corrosion resistance even in a heat affected zone. As a result, the present inventors considered that if an alloy material has a chemical composition consisting of, in mass%, C: 0.005 to 0.020%, Si: 0.05 to 0.50%, Mn: 0.05 to 1.00%, P: 0.030% or less, S: 0.0100% or less, Cu: 1.5 to 3.0%, Ni: 35.0 to 50.0%, Cr: 20.0 to 30.0%, Mo: 2.5 to 4.0%, Co: 0.01 to 0.80%, W: 0.01 to 0.30%, Ca: 0.0050% or less, N: 0.001 to 0.015%, Al: 0.20% or less, B: 0.0030% or less, Sn: 0.050% or less, Ti: 0.40 to 0.90%, Nb: 0 to 0.150%, V: 0 to 0.150%, Zr: 0 to 0.150%, Hf: 0 to 0.150%, and Ta: 0 to 0.150%, with the balance being Fe and impurities, there is a possibility that excellent intergranular corrosion resistance will be obtained even in a heat affected zone in a case where the alloy material is subjected to welding.

[0017] Therefore, the present inventors prepared test specimens simulating a heat affected zone from alloy materials having the chemical composition described above. Specifically, the present inventors extracted test specimens from alloy materials having the chemical composition described above. The test specimens were subjected to a heat treatment that simulated welding. By the above method, test specimens which simulated a heat affected zone were prepared. Next, the intergranular corrosion resistance of the test specimens was investigated. As a result, it has been found that in some cases excellent intergranular corrosion resistance was not obtained in an alloy material satisfying the chemical composition described above.

[0018] Therefore, the present inventors conducted further studies. As a result, the present inventors obtained the following finding.

[0019] In the heat affected zone of an alloy material, during a heat treatment simulating welding, dissolved C combines with Cr to form Cr carbides. Consequently, dissolved Cr is depleted at the grain boundaries, and therefore Cr-depleted zones are formed at grain boundaries. In the heat affected zone of the alloy material, intergranular corrosion occurs due to the presence of such Cr-depleted zones.

[0020] Among the elements in the chemical composition described above, Ti, Nb, V, Zr, Hf, and Ta have high affinity with dissolved C. Therefore, these elements form carbides. The dissolved C in the alloy material is reduced by formation of the carbides. Consequently, it becomes difficult for Cr to form Cr carbides, and the formation of Cr-depleted zones at grain boundaries is suppressed.

[0021] Based on the above finding, the present inventors considered that the intergranular corrosion resistance can be increased by adjusting the total content of Ti, Nb, V, Zr, Hf, and Ta. The present inventors therefore conducted further studies to investigate the relation between a total content Tx (%) of Ti, Nb, V, Zr, Hf, and Ta and the intergranular corrosion resistance.

[0022] FIG. 1 is a view that illustrates, with respect to an alloy material having the chemical composition described above, the relation between the total content Tx (%) of Ti, Nb, V, Zr, Hf, and Ta, and a corrosion rate ($\text{g}/\text{m}^2 \cdot \text{hr}$) that is an index of intergranular corrosion resistance obtained by carrying out an intergranular corrosion test in accordance with ASTM A262 Practice C. FIG. 1 was created based on data obtained by tests described in Examples to be described later.

[0023] Referring to FIG. 1, when the total content Tx is within the range of 0.420 to 1.000%, even if the total content Tx increases, the corrosion rate is 0.20 $\text{g}/\text{m}^2 \cdot \text{hr}$ or less, and very excellent intergranular corrosion resistance is obtained.

[0024] On the other hand, when the total content Tx is less than 0.420%, the corrosion rate markedly increases as the total content Tx decreases. Accordingly, in FIG. 1, an inflection point exists in the vicinity of the total content Tx = 0.420%. In addition, when the total content Tx is more than 1.000%, the corrosion rate markedly increases as the total content Tx increases. Accordingly, in FIG. 1, an inflection point exists in the vicinity of the total content Tx = 1.000%.

[0025] Based on the above finding, the present inventors discovered that if the total content Tx of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%, the intergranular corrosion resistance will increase.

[0026] However, even when alloy materials satisfied the chemical composition described above, and furthermore, the total content Tx of Ti, Nb, V, Zr, Hf, and Ta was made to fall within the range of 0.420 to 1.000%, there were still some cases where the intergranular corrosion resistance was low. Therefore, the present inventors conducted studies regarding means for increasing the intergranular corrosion resistance from the viewpoint of the microstructure, and not just from the viewpoint of the chemical composition. As a result, the present inventors obtained the following finding.

[0027] In the chemical composition described above, N is contained to increase the strength. Among the elements Ti, Nb, V, Zr, Hf, and Ta which have high affinity with C, the elements Ti and Nb, in particular, also have high affinity with N. Therefore, Ti and Nb form nano-level-size nitrides or carbo-nitrides at grain boundaries. Hereunder, in the present description, nitrides and carbo-nitrides are also referred to as "nitrogen-containing precipitates".

[0028] Such kind of fine nitrogen-containing precipitates dissolve in a strongly oxidizing corrosive environment. Therefore, even in a case where there are no Cr-depleted zones present at grain boundaries, if a large number of fine nitrogen-containing precipitates are present at the grain boundaries, intergranular corrosion will occur due to dissolution of the nitrogen-containing precipitates, and the intergranular corrosion resistance will decrease.

[0029] Therefore, the present inventors considered that in an alloy material which has the chemical composition described above and in which the total content Tx of Ti, Nb, V, Zr, Hf, and Ta is within the range of 0.420 to 1.000%, if, furthermore, the number density of fine nitrogen-containing precipitates at the grain boundaries can be reduced, excellent intergranular corrosion resistance will be obtained even in a heat affected zone. Thus, the present inventors conducted

further studies regarding the relation between the number density of fine nitrogen-containing precipitates at grain boundaries and the intergranular corrosion resistance.

[0030] FIG. 2 is a view that illustrates, with respect to alloy materials which have the chemical composition described above and in which the total content of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%, the relation between the number density ($/\mu\text{m}$) of fine nitrogen-containing precipitates at grain boundaries, and a corrosion rate ($\text{g}/\text{m}^2\cdot\text{hr}$) that is an index of intergranular corrosion resistance obtained by carrying out an intergranular corrosion test in accordance with ASTM A262 Practice C. FIG. 2 was created based on data obtained by tests described in Examples to be described later.

[0031] Referring to FIG. 2, when the number density of fine nitrogen-containing precipitates at the grain boundaries is $20/\mu\text{m}$ or less, even if the number density increases, the corrosion rate is $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$ or less, and very excellent intergranular corrosion resistance is obtained. On the other hand, when the number density of fine nitrogen-containing precipitates at the grain boundaries is more than $20/\mu\text{m}$, the corrosion rate markedly increases as the number density increases. Therefore, in FIG. 2, an inflection point exists in the vicinity of the number density = $20/\mu\text{m}$.

[0032] Based on the above findings, the present inventors discovered that in an alloy material having the chemical composition described above and in which the total content Tx of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%, if the number density of fine nitrogen-containing precipitates at the grain boundaries is made $20/\mu\text{m}$ or less, excellent intergranular corrosion resistance is obtained even in a heat affected zone in a case where welding is performed.

[0033] The alloy material according to the present embodiment, which has been completed based on the above findings, is as follows.

[0034]

[1] An alloy material having a chemical composition consisting of, in mass%,

C: 0.005 to 0.020%,

Si: 0.05 to 0.50%,

Mn: 0.05 to 1.00%,

P: 0.030% or less,

S: 0.0100% or less,

Cu: 1.5 to 3.0%,

Ni: 35.0 to 50.0%,

Cr: 20.0 to 30.0%,

Mo: 2.5 to 4.0%,

Co: 0.01 to 0.80%,

W: 0.01 to 0.30%,

Ca: 0.0050% or less,

N: 0.001 to 0.015%,

Al: 0.20% or less,

B: 0.0030% or less,

Sn: 0.050% or less,

Ti: 0.40 to 0.90%,

Nb: 0 to 0.150%,

V: 0 to 0.150%,

Zr: 0 to 0.150%,

Hf: 0 to 0.150%, and

Ta: 0 to 0.150%,

with the balance being Fe and impurities,

in which:

a total content of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%, and

a number density of nitrogen-containing precipitates having a major axis of 10 to 100 nm at grain boundaries of the alloy material is $20/\mu\text{m}$ or less.

[2] The alloy material according to [1], in which the chemical composition contains one or more elements selected from a group consisting of:

Nb: 0.001 to 0.150%,

V: 0.001 to 0.150%,

Zr: 0.001 to 0.150%,

Hf: 0.001 to 0.150%, and

Ta: 0.001 to 0.150%.

[3] The alloy material according to [1] or [2], in which:
the alloy material is an alloy pipe.

5 [0035] Hereunder, the alloy material of the present embodiment is described in detail. Note that, the symbol "%" in relation to elements means "mass percent" unless otherwise stated.

[Features of alloy material of present embodiment]

10 [0036] The alloy material of the present embodiment satisfies the following Feature 1 to Feature 3.

(Feature 1)

15 [0037] The chemical composition consists of, in mass%, C: 0.005 to 0.020%, Si: 0.05 to 0.50%, Mn: 0.05 to 1.00%, P: 0.030% or less, S: 0.0100% or less, Cu: 1.5 to 3.0%, Ni: 35.0 to 50.0%, Cr: 20.0 to 30.0%, Mo: 2.5 to 4.0%, Co: 0.01 to 0.80%, W: 0.01 to 0.30%, Ca: 0.0050% or less, N: 0.001 to 0.015%, Al: 0.20% or less, B: 0.0030% or less, Sn: 0.050% or less, Ti: 0.40 to 0.90%, Nb: 0 to 0.150%, V: 0 to 0.150%, Zr: 0 to 0.150%, Hf: 0 to 0.150%, and Ta: 0 to 0.150%, with the balance being Fe and impurities.

20 (Feature 2)

[0038] The total content of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%.

25 (Feature 3)

[0039] The number density of nitrogen-containing precipitates having a major axis of 10 to 100 nm at grain boundaries of the alloy material is 20/ μm or less.

30 [0040] Hereunder, Feature 1 to Feature 3 are described.

[(Feature 1) Regarding chemical composition]

[0041] The chemical composition of the alloy material of the present embodiment contains the following elements.

35 C: 0.005 to 0.020%

[0042] Carbon (C) increases the strength of the alloy material. If the content of C is less than 0.005%, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

40 [0043] On the other hand, if the content of C is more than 0.020%, C will form $M_{23}C_6$ -type Cr carbides at grain boundaries. In such case, Cr-depleted zones will form at the grain boundaries. Consequently, the intergranular corrosion resistance of the alloy material will decrease even if the contents of other elements are within the range of the present embodiment.

[0044] Therefore, the content of C is to be 0.005 to 0.020%.

45 [0045] A preferable lower limit of the content of C is 0.006%, more preferably is 0.007%, and further preferably is 0.008%.

[0046] A preferable upper limit of the content of C is 0.019%, more preferably is 0.017%, further preferably is 0.015%, and further preferably is 0.013%.

50 Si: 0.05 to 0.50%

[0047] Silicon (Si) deoxidizes the alloy in the steel production process. If the content of Si is less than 0.05%, the aforementioned advantageous effect will not be sufficiently obtained.

55 [0048] On the other hand, if the content of Si is more than 0.50%, even if the contents of other elements are within the range of the present embodiment, inclusions will excessively form and the corrosion resistance of the alloy material will decrease.

[0049] Therefore, the content of Si is to be 0.05 to 0.50%.

[0050] A preferable lower limit of the content of Si is 0.08%, more preferably is 0.12%, and further preferably is 0.15%.

[0051] A preferable upper limit of the content of Si is 0.45%, more preferably is 0.40%, further preferably is 0.38%, and

further preferably is 0.35%.

Mn: 0.05 to 1.00%

5 **[0052]** Manganese (Mn) deoxidizes the alloy. In addition, Mn is an austenite forming element, and stabilizes austenite in the alloy material. If the content of Mn is too low, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

[0053] On the other hand, if the content of Mn is more than 1.00%, even if the contents of other elements are within the range of the present embodiment, inclusions will excessively form and the corrosion resistance of the alloy material will decrease.

10 **[0054]** Therefore, the content of Mn is to be 0.05 to 1.00%.

[0055] A preferable lower limit of the content of Mn is 0.10%, more preferably is 0.20%, further preferably is 0.30%, and further preferably is 0.40%.

15 **[0056]** A preferable upper limit of the content of Mn is 0.90%, more preferably is 0.85%, further preferably is 0.80%, and further preferably is 0.70%.

P: 0.030% or less

20 **[0057]** Phosphorus (P) is an impurity which is unavoidably contained. That is, the content of P is more than 0%. P segregates to grain boundaries. Therefore, if the content of P is too high, the intergranular corrosion resistance of the alloy material will decrease even if the contents of other elements are within the range of the present embodiment.

[0058] Therefore, the content of P is to be 0.030% or less.

25 **[0059]** The content of P is preferably as low as possible. However, excessively reducing 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%.

[0060] A preferable upper limit of the content of P is 0.028%, more preferably is 0.025%, further preferably is 0.023%, and further preferably is 0.020%.

S: 0.0100% or less

30 **[0061]** Sulfur (S) is an impurity which is unavoidably contained. That is, the content of S is more than 0%. S segregates to grain boundaries. Therefore, if the content of S is too high, the intergranular corrosion resistance of the alloy material will decrease even if the contents of other elements are within the range of the present embodiment.

[0062] Therefore, the content of S is to be 0.0100% or less.

35 **[0063]** The content of S is preferably as low as possible. However, excessively reducing 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 0.0001%, and more preferably is 0.0002%.

[0064] A preferable upper limit of the content of S is 0.0050%, more preferably is 0.0040%, further preferably is 0.0030%, further preferably is 0.0020%, and further preferably is 0.0010%.

40 Cu: 1.5 to 3.0%

45 **[0065]** Copper (Cu) increases the corrosion resistance of the alloy material in environments containing non-oxidizing acids and chlorides. If the content of Cu is less than 1.5%, the aforementioned advantageous effect will not be sufficiently obtained.

[0066] On the other hand, if the content of Cu is more than 3.0%, the hot workability of the alloy material will decrease even if the contents of other elements are within the range of the present embodiment.

[0067] Therefore, the content of Cu is to be 1.5 to 3.0%.

[0068] A preferable lower limit of the content of Cu is 1.6%, and more preferably is 1.7%.

50 **[0069]** A preferable upper limit of the content of Cu is 2.5%, more preferably is 2.3%, further preferably is 2.1%, and further preferably is 2.0%.

Ni: 35.0 to 50.0%

55 **[0070]** Nickel (Ni) is an austenite forming element, and stabilizes the austenite in the alloy material. In addition, Ni increases the intergranular corrosion resistance of the alloy material. If the content of Ni is less than 35.0%, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

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[0071] On the other hand, if the content of Ni is more than 50.0%, the intergranular corrosion resistance of the alloy material will decrease even if the contents of other elements are within the range of the present embodiment. Furthermore, if the content of Ni is more than 50.0%, the production cost will significantly increase.

[0072] Therefore, the content of Ni is to be 35.0 to 50.0%.

[0073] A preferable lower limit of the content of Ni is 36.0%, more preferably is 37.0%, and further preferably is 38.0%.

[0074] A preferable upper limit of the content of Ni is 48.0%, more preferably is 46.0%, and further preferably is 44.0%.

Cr: 20.0 to 30.0%

[0075] Chromium (Cr) increases the intergranular corrosion resistance of the alloy material. If the content of Cr is less than 20.0%, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

[0076] On the other hand, if the content of Cr is more than 30.0%, even if the contents of other elements are within the range of the present embodiment, intermetallic compounds typified by the σ phase will form. In such case, the intergranular corrosion resistance of the alloy material will decrease.

[0077] Therefore, the content of Cr is to be 20.0 to 30.0%.

[0078] A preferable lower limit of the content of Cr is 20.3%, more preferably is 20.5%, further preferably is 20.8%, and further preferably is 21.0%.

[0079] A preferable upper limit of the content of Cr is 29.0%, more preferably is 28.5%, further preferably is 28.0%, and further preferably is 27.5%.

Mo: 2.5 to 4.0%

[0080] Molybdenum (Mo) increases the corrosion resistance of the alloy material.

[0081] If the content of Mo is less than 2.5%, the aforementioned advantageous effect will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

[0082] On the other hand, if the content of Mo is more than 4.0%, even if the contents of other elements are within the range of the present embodiment, intermetallic compounds typified by the σ phase will form. In such case, the intergranular corrosion resistance of the alloy material will decrease.

[0083] Therefore, the content of Mo is to be 2.5 to 4.0%.

[0084] A preferable lower limit of the content of Mo is 2.6%, more preferably is 2.7%, and further preferably is 2.8%.

[0085] A preferable upper limit of the content of Mo is 3.9%, more preferably is 3.8%, and further preferably is 3.7%.

Co: 0.01 to 0.80%

[0086] Cobalt (Co) increases the corrosion resistance of the alloy material. If the content of Co 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.

[0087] On the other hand, if the content of Co is more than 0.80%, the production cost will rise even if the contents of other elements are within the range of the present embodiment.

[0088] Therefore, the content of Co is to be 0.01 to 0.80%.

[0089] A preferable lower limit of the content of Co is 0.03%, more preferably is 0.05%, further preferably is 0.10%, and further preferably is 0.20%.

[0090] A preferable upper limit of the content of Co is 0.75%, more preferably is 0.70%, and further preferably is 0.65%.

W: 0.01 to 0.30%

[0091] Tungsten (W) increases the corrosion resistance of the alloy material. If the content of W 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.

[0092] On the other hand, if the content of W is more than 0.30%, the hot workability of the alloy material will decrease even if the contents of other elements are within the range of the present embodiment.

[0093] Therefore, the content of W is to be 0.01 to 0.30%.

[0094] A preferable lower limit of the content of W is 0.02%, and more preferably is 0.03%.

[0095] A preferable upper limit of the content of W is 0.25%, more preferably is 0.20%, further preferably is 0.15%, and further preferably is 0.12%.

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Ca: 0.0050% or less

5 **[0096]** Calcium (Ca) is unavoidably contained. In other words, the content of Ca is more than 0%. Ca immobilizes S in the alloy material as a sulfide to thereby make the S harmless. By this means, Ca increases the hot workability and the weldability of the alloy material. If even a small amount of Ca is contained, the aforementioned advantageous effect will be obtained to a certain extent.

[0097] However, if the content of Ca is more than 0.0050%, even if the contents of other elements are within the range of the present embodiment, coarse oxides will form in the alloy material. In such case, the hot workability of the alloy material will decrease.

10 **[0098]** Therefore, the content of Ca is to be 0.0050% or less.

[0099] A preferable lower limit of the content of Ca is 0.0001%, more preferably is 0.0005%, further preferably is 0.0010%, and further preferably is 0.0015%.

[0100] A preferable upper limit of the content of Ca is 0.0045%, more preferably is 0.0040%, further preferably is 0.0035%, and further preferably is 0.0030%.

15 N: 0.001 to 0.015%

[0101] Nitrogen (N) dissolves in the alloy material and thereby increases the strength of the alloy material. If the content of N 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.

20 **[0102]** On the other hand, if the content of N is more than 0.015%, nitrides will excessively form at grain boundaries. In such case, the intergranular corrosion resistance of the alloy material will decrease.

[0103] Therefore, the content of N is to be 0.001 to 0.015%.

[0104] A preferable lower limit of the content of N is 0.002%, and more preferably is 0.003%.

25 **[0105]** A preferable upper limit of the content of N is 0.012%, more preferably is 0.010%, and further preferably is 0.009%.

Al: 0.20% or less

30 **[0106]** Aluminum (Al) is unavoidably contained. In other words, the content of Al is more than 0%. Al deoxidizes the alloy. If even a small amount of Al is contained, the aforementioned advantageous effect will be obtained to a certain extent.

[0107] However, if the content of Al is more than 0.20%, oxide-based inclusions will excessively form even if the contents of other elements are within the range of the present embodiment. In such case, the corrosion resistance of the alloy material will decrease.

35 **[0108]** Therefore, the content of Al is to be 0.20% or less.

[0109] A preferable lower limit of the content of Al is 0.01%, more preferably is 0.02%, and further preferably is 0.03%.

[0110] A preferable upper limit of the content of Al is 0.18%, more preferably is 0.16%, further preferably is 0.14%, and further preferably is 0.12%.

40 B: 0.0030% or less

[0111] Boron (B) is unavoidably contained. In other words, the content of B is more than 0%. B segregates to grain boundaries and strengthens the grain boundaries and increases the hot workability of the alloy material. If even a small amount of B is contained, the aforementioned advantageous effect will be obtained to a certain extent.

45 **[0112]** However, if the content of B is more than 0.0030%, even if the contents of other elements are within the range of the present embodiment, B will excessively segregate to the grain boundaries. In such case, the hot workability of the alloy material will decrease.

[0113] Therefore, the content of B is to be 0.0030% or less.

[0114] A preferable lower limit of the content of B is 0.0001%, and more preferably is 0.0002%.

50 **[0115]** A preferable upper limit of the content of B is 0.0025%, more preferably is 0.0020%, further preferably is 0.0018%, and further preferably is 0.0016%.

Sn: 0.050% or less

55 **[0116]** The content of tin (Sn) is more than 0%. Sn increases the corrosion resistance of the alloy material. If even a small amount of Sn is contained, the aforementioned advantageous effect will be obtained to a certain extent.

[0117] However, if the content of Sn is more than 0.050%, the hot workability of the alloy material will decrease even if the contents of other elements are within the range of the present embodiment.

[0118] Therefore, the content of Sn is to be 0.050% or less.

[0119] A preferable lower limit of the content of Sn is 0.001%, and more preferably is 0.002%.

[0120] A preferable upper limit of the content of Sn is 0.040%, more preferably is 0.030%, further preferably is 0.020%, and further preferably is 0.015%.

5

Ti: 0.40 to 0.90%

[0121] Titanium (Ti) combines with C to form Ti carbides, and thereby immobilizes C. In this way, Ti suppresses formation of Cr carbides that are formed by dissolved C combining with Cr. Consequently, it is difficult for Cr-depleted zones to form at grain boundaries. As a result, the intergranular corrosion resistance of the alloy material increases. In addition, Ti combines with C and/or N to form Ti carbides, Ti nitrides, or Ti carbo-nitrides, which increases the strength of the alloy material.

10

[0122] If the content of Ti is less than 0.40%, the aforementioned advantageous effects will not be sufficiently obtained even if the contents of other elements are within the range of the present embodiment.

15

[0123] On the other hand, if the content of Ti is more than 0.90%, even if the contents of other elements are within the range of the present embodiment, Ti nitrides and/or Ti carbo-nitrides will excessively form at grain boundaries. In such case, the intergranular corrosion resistance of the alloy material will decrease.

[0124] Therefore, the content of Ti is to be 0.40 to 0.90%.

[0125] A preferable lower limit of the content of Ti is 0.41%, more preferably is 0.43%, and further preferably is 0.45%.

20

[0126] A preferable upper limit of the content of Ti is 0.85%, more preferably is 0.80%, further preferably is 0.75%, and further preferably is 0.70%.

[0127] The balance of the chemical composition of the alloy material according to the present embodiment is Fe and impurities. Here, the term "impurities" means substances which are mixed in from ore and scrap used as the raw material or from the production environment or the like when industrially producing the alloy material, and which are not intentionally contained but are permitted within a range that does not have a marked adverse effect on the operational advantages of the alloy material according to the present embodiment.

25

[Regarding optional elements]

30

[0128] The chemical composition of the alloy of the present embodiment may further contain one or more elements selected from the group consisting of the following elements:

Nb: 0 to 0.150%,

V: 0 to 0.150%,

35

Zr: 0 to 0.150%,

Hf: 0 to 0.150%, and

Ta: 0 to 0.150%.

[0129] Each of these elements is an optional element. Each of these elements combines with dissolved C to form carbides, and thereby increases the intergranular corrosion resistance of the alloy material.

40

[0130] Hereunder, each element is described.

Nb: 0 to 0.150%

45

[0131] Niobium (Nb) is an optional element, and does not have to be contained. In other words, the content of Nb may be 0%. When contained, Nb combines with C to form Nb carbides, and thereby immobilizes C. In this way, Nb can suppress the formation of Cr-depleted zones at grain boundaries, and thus the intergranular corrosion resistance of the alloy material increases. In addition, Nb combines with C and/or N to form Nb carbides, Nb nitrides, or Nb carbo-nitrides, and thereby increases the strength of the alloy material. If even a small amount of Nb is contained, the aforementioned advantageous effects will be obtained to a certain extent.

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[0132] However, if the content of Nb is more than 0.150%, Nb nitrides and/or Nb carbo-nitrides will excessively form at grain boundaries even if the contents of other elements are within the range of the present embodiment. In such case, the intergranular corrosion resistance of the alloy material will decrease.

[0133] Therefore, the content of Nb is to be 0 to 0.150%.

55

[0134] A preferable lower limit of the content of Nb is 0.001%, more preferably is 0.002%, and further preferably is 0.005%.

[0135] A preferable upper limit of the content of Nb is 0.140%, more preferably is 0.130%, further preferably is 0.100%, further preferably is 0.070%, further preferably is 0.050%, and further preferably is 0.040%.

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V: 0 to 0.150%

[0136] Vanadium (V) is an optional element, and does not have to be contained. In other words, the content of V may be 0%. When contained, V combines with C to form V carbides, and thereby immobilizes C. In this way, V can suppress the formation of Cr-depleted zones at grain boundaries, and thus the intergranular corrosion resistance of the alloy material increases. In addition, V combines with C and/or N to form V carbides, V nitrides, or V carbo-nitrides, and thereby increases the strength of the alloy material. If even a small amount of V is contained, the aforementioned advantageous effects will be obtained to a certain extent.

[0137] However, if the content of V is more than 0.150%, the strength of the alloy material will become excessively high even if the contents of other elements are within the range of the present embodiment. In such case, the hot workability of the alloy material will decrease. In addition, if the content of V is more than 0.150%, V carbides and/or V carbo-nitrides will excessively form at grain boundaries. In such case, the intergranular corrosion resistance of the alloy material will decrease.

[0138] Therefore, the content of V is to be 0 to 0.150%.

[0139] A preferable lower limit of the content of V is 0.001%, more preferably is 0.002%, and further preferably is 0.005%.

[0140] A preferable upper limit of the content of V is 0.140%, more preferably is 0.130%, further preferably is 0.100%, further preferably is 0.070%, further preferably is 0.050%, and further preferably is 0.040%.

Zr: 0 to 0.150%

[0141] Zirconium (Zr) is an optional element, and does not have to be contained. In other words, the content of Zr may be 0%. When contained, Zr combines with C to form Zr carbides, and thereby immobilizes C. In this way, Zr can suppress the formation of Cr-depleted zones at grain boundaries, and thus the intergranular corrosion resistance of the alloy material increases. In addition, Zr combines with C and/or N to form Zr carbides, Zr nitrides, or Zr carbo-nitrides, and thereby increases the strength of the alloy material. If even a small amount of Zr is contained, the aforementioned advantageous effects will be obtained to a certain extent.

[0142] However, if the content of Zr is more than 0.150%, the strength of the alloy material will become excessively high even if the contents of other elements are within the range of the present embodiment. In such case, the hot workability of the alloy material will decrease.

[0143] Therefore, the content of Zr is to be 0 to 0.150%.

[0144] A preferable lower limit of the content of Zr is 0.001%, more preferably is 0.002%, further preferably is 0.005%, and further preferably is 0.010%.

[0145] A preferable upper limit of the content of Zr is 0.140%, more preferably is 0.130%, and further preferably is 0.120%.

Hf: 0 to 0.150%

[0146] Hafnium (Hf) is an optional element, and does not have to be contained. In other words, the content of Hf may be 0%. When contained, Hf combines with C to form Hf carbides, and thereby immobilizes C. In this way, Hf can suppress the formation of Cr-depleted zones at grain boundaries, and thus the intergranular corrosion resistance of the alloy material increases. In addition, Hf combines with C and/or N to form Hf carbides, Hf nitrides, or Hf carbo-nitrides, and thereby increases the strength of the alloy material. If even a small amount of Hf is contained, the aforementioned advantageous effects will be obtained to a certain extent.

[0147] However, if the content of Hf is more than 0.150%, the strength of the alloy material will become excessively high even if the contents of other elements are within the range of the present embodiment. In such case, the hot workability of the alloy material will decrease.

[0148] Therefore, the content of Hf is to be 0 to 0.150%.

[0149] A preferable lower limit of the content of Hf is 0.001%, more preferably is 0.002%, further preferably is 0.005%, and further preferably is 0.010%.

[0150] A preferable upper limit of the content of Hf is 0.140%, more preferably is 0.130%, and further preferably is 0.120%.

Ta: 0 to 0.150%

[0151] Tantalum (Ta) is an optional element, and does not have to be contained. In other words, the content of Ta may be 0%. When contained, Ta combines with C to form Ta carbides, and thereby immobilizes C. In this way, Ta can suppress the formation of Cr-depleted zones at grain boundaries, and thus the intergranular corrosion resistance of the alloy material increases. In addition, Ta combines with C and/or N to form Ta carbides, Ta nitrides, or Ta carbo-nitrides, and thereby

increases the strength of the alloy material. If even a small amount of Ta is contained, the aforementioned advantageous effects will be obtained to a certain extent.

[0152] However, if the content of Ta is more than 0.150%, the strength of the alloy material will become excessively high even if the contents of other elements are within the range of the present embodiment. In such case, the hot workability of the alloy material will decrease.

[0153] Therefore, the content of Ta is to be 0 to 0.150%.

[0154] A preferable lower limit of the content of Ta is 0.001%, more preferably is 0.002%, further preferably is 0.005%, and further preferably is 0.010%.

[0155] A preferable upper limit of the content of Ta is 0.140%, more preferably is 0.130%, and further preferably is 0.120%.

[(Feature 2) Regarding total content Tx of Ti, Nb, V, Zr, Hf, and Ta]

[0156] In the alloy material of the present embodiment, the total content Tx of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%.

[0157] As described above, each of Ti, Nb, V, Zr, Hf, and Ta combines with C to form carbides, and thereby immobilizes C. In this way, these elements suppress the formation of Cr carbides which are formed by dissolved C combining with Cr. Therefore, it is difficult for Cr-depleted zones to form at the grain boundaries. As a result, the intergranular corrosion resistance of the alloy material increases.

[0158] As illustrated in FIG. 1, even if an alloy material satisfies Feature 1, if the total content Tx of one or more elements selected from the group consisting of Ti, Nb, V, Zr, Hf, and Ta is less than 0.420%, excellent intergranular corrosion resistance will not be obtained even if the contents of other elements are within the range of the present embodiment. On the other hand, if the total content Tx is more than 1.000%, nitrides and/or carbo-nitrides will excessively form at the grain boundaries even if the contents of other elements are within the range of the present embodiment. In such case, as illustrated in FIG. 1, the intergranular corrosion resistance of the alloy material will decrease.

[0159] When the total content Tx of one or more elements selected from the group consisting of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%, as illustrated in FIG. 1, the intergranular corrosion resistance of the alloy material markedly increases.

[0160] A preferable lower limit of the total content Tx is 0.425%, more preferably is 0.440%, further preferably is 0.460%, further preferably is 0.480%, and further preferably is 0.500%.

[0161] A preferable upper limit of the total content Tx is 0.950%, more preferably is 0.920%, further preferably is 0.900%, further preferably is 0.880%, further preferably is 0.850%, further preferably is 0.830%, and further preferably is 0.800%.

[(Feature 3) Regarding number density ($/\mu\text{m}$) of fine nitrogen-containing precipitates at grain boundaries]

[0162] In the alloy material of the present embodiment, in addition, the number density of nitrogen-containing precipitates having a major axis of 10 to 100 nm at the grain boundaries is $20/\mu\text{m}$ or less.

[0163] Here, the term "nitrogen-containing precipitates" means precipitates that contain N. That is, the nitrogen-containing precipitates are nitrides and/or carbo-nitrides. Further, nitrogen-containing precipitates having a major axis of 10 to 100 nm are referred to as "fine nitrogen-containing precipitates".

[0164] When an alloy material is used in a strongly oxidizing corrosive environment, in some cases fine nitrogen-containing precipitates that are present at grain boundaries dissolve. If the fine nitrogen-containing precipitates dissolve, the intergranular corrosion resistance of the alloy material will decrease. Therefore, it is preferable for the number density of fine nitrogen-containing precipitates at grain boundaries to be low.

[0165] The number of fine nitrogen-containing precipitates per $1\mu\text{m}$ of grain boundary is defined as the number density of fine nitrogen-containing precipitates ($/\mu\text{m}$). If the number density of fine nitrogen-containing precipitates is more than $20/\mu\text{m}$, even if the alloy material satisfies Feature 1 and Feature 2, sufficient intergranular corrosion resistance will not be obtained. If the number density of fine nitrogen-containing precipitates is $20/\mu\text{m}$ or less, as illustrated in FIG. 2, excellent intergranular corrosion resistance will be obtained.

[Method for determining number density of fine nitrogen-containing precipitates]

[0166] The number density of fine nitrogen-containing precipitates at grain boundaries can be determined by the following method.

[0167] First, a test specimen is taken from the alloy material.

[0168] In the case of the alloy material being an alloy plate, a microstructure observation specimen is taken from a $t/4$ portion that is the observation target region. Here, the term " $t/4$ portion" refers to, when the plate thickness is taken as " t (mm)", a portion that is at a depth of $t/4$ from the surface of the alloy plate. In the case of the alloy material being an alloy pipe, a microstructure observation specimen is taken from a central portion of the wall thickness that is the observation target region. In the case of the alloy material being an alloy bar, a microstructure observation specimen is taken from an $R/2$

portion that is the observation target region. Here, the term "R/2 portion" refers to the central portion of a radius R in a cross section perpendicular to the rolling direction of the alloy bar. The size of the microstructure observation specimen is not particularly limited.

5 [0169] The surface of the microstructure observation specimen is mirror-polished, and thereafter the microstructure observation specimen is immersed for 10 minutes in a 3% nital etching reagent to etch the surface. The etched surface is then covered with a carbon deposited film. The microstructure observation specimen whose surface is covered with the deposited film is immersed for 20 minutes in a 5% nital etching reagent. The deposited film is thereby peeled off from the immersed microstructure observation specimen. The deposited film that peeled off from the microstructure observation specimen is cleaned with ethanol, and thereafter is scooped up with a sheet mesh and dried.

10 [0170] The deposited film (replica film) is observed using a transmission electron microscope (TEM). Specifically, an arbitrary position is specified on the deposited film, and the specified position is observed at an observation magnification of 50,000× with an acceleration voltage of 200 kV. Note that, although not particularly limited, the size of the observation visual field is, for example, 2.0 μm × 2.0 μm.

15 [0171] In a bright field image of the observation visual field, grain boundaries of the alloy material can be easily identified based on the contrast. Precipitates which are present on grain boundaries can also be easily identified based on the contrast. Therefore, precipitates that are present on the grain boundaries are identified. The major axis of each identified precipitate is measured. Here, the term "major axis" means the maximum length (nm) of a line segment connecting two points at the interface between the precipitate and the parent phase. Among the precipitates on the grain boundaries, those precipitates which have a major axis of 10 to 100 nm are identified. Hereinafter, a precipitate which has a major axis of 20 10 to 100 nm is referred to as a "fine precipitate". Note that, the major axis of a precipitate can be determined by performing image analysis of an observation image in TEM observation.

[0172] FIG. 3 is a view showing a TEM image of an alloy material satisfying Feature 1 and Feature 2, and a diffraction pattern obtained by performing selected area electron diffraction on a fine precipitate indicated by an arrow in the TEM image. In a case where selected area electron diffraction is performed on fine precipitates identified in an alloy material satisfying Feature 1 and Feature 2, almost all of the diffraction patterns are identified as the MX type (nitride or carbonytride) as illustrated in FIG. 3. That is, almost no precipitates other than fine nitrogen-containing precipitates are included among the identified fine precipitates. Therefore, the identified fine precipitates are regarded as fine nitrogen-containing precipitates.

25 [0173] The number of fine nitrogen-containing precipitates which are present on the grain boundaries within the observation visual field is counted. In addition, the total length (μm) of the grain boundaries within the observation visual field is measured. The number density (/μm) of fine nitrogen-containing precipitates at the grain boundaries is then determined based on the obtained number of fine nitrogen-containing precipitates and the total length of the grain boundaries. In the present embodiment, a value obtained by rounding off the tenths place of the obtained numerical value is adopted as the number density of fine nitrogen-containing precipitates.

30 [Regarding advantageous effect of alloy material of present embodiment]

35 [0174] As described above, the alloy material of the present embodiment satisfies Feature 1 to Feature 3. Therefore, the alloy material of the present embodiment has excellent intergranular corrosion resistance in a strongly oxidizing corrosive environment. Here, intergranular corrosion resistance is evaluated by the following method.

[Method for evaluating intergranular corrosion resistance]

40 [0175] A test specimen having a thickness of 5 mm, a width of 10 mm, and a length of 50 mm is taken from the alloy material. The longitudinal direction of the test specimen is to be made parallel to the rolling direction of the alloy material. In order to obtain a test specimen which simulates a heat affected zone, the test specimen is subjected to a sensitization treatment. Specifically, the test specimen is held at 700°C for 60 minutes. After the holding time elapses, the test specimen is allowed to cool. By performing the above sensitization treatment, a test specimen that simulates a heat affected zone is prepared.

45 [0176] The surface of the prepared test specimen is finished by polishing with wet 600 grit emery paper, degreased with acetone, and dried. The test specimen is subjected to an intergranular corrosion test in accordance with ASTM A262 Practice C. Specifically, a test bath that is boiled 65% nitric acid is prepared. The test specimen is immersed in the test bath for 48 hours. After the 48 hours pass, the test specimen is taken out from the test bath. The corrosion rate (g/m²·hr) is determined based on the change in the mass of the test specimen between before and after the test, and the surface area of the test specimen before the test. This operation is repeated five times, and the corrosion rate (g/m²·hr) for each of the five times is determined. If the arithmetic average value of the obtained five corrosion rates is 0.20 g/m²·hr or less, it is determined that the alloy material is excellent in intergranular corrosion resistance.

[Regarding microstructure of alloy material of present embodiment]

5 [0177] The microstructure of the alloy material of the present embodiment is composed of austenite. However, this excludes precipitates and inclusions.

[Shape of alloy material]

10 [0178] The shape of the alloy material according to the present embodiment is not particularly limited. The alloy material may be an alloy plate, may be an alloy pipe, or may be an alloy bar. In a case where the alloy material is an alloy pipe, preferably the alloy material is a seamless alloy pipe.

[Uses of alloy material]

15 [0179] The uses of the alloy material of the present embodiment are not particularly limited. For example, the alloy material of the present embodiment is particularly suitable for use in a corrosive environment. The alloy material of the present embodiment can be used, for example, in equipment relating to the petroleum industry, the gas industry, the petrochemical industry, and the chemical industry. In particular, the alloy material according to the present embodiment is suitable for use in primary processing equipment for petroleum and gas, and equipment of chemical plants and the like.

20 [Method for producing alloy material]

[0180] A method for producing the alloy material of the present embodiment that satisfies Feature 1 to Feature 3 will now be described.

25 [0181] The production method described hereunder is one example of a method for producing the alloy material of the present embodiment. Therefore, an alloy material that satisfies Feature 1 to Feature 3 may also be produced by a production method other than the production method described hereunder. However, the production method described hereunder is a preferable example of a method for producing the alloy material of the present embodiment.

30 [0182] A method for producing the alloy material of the present embodiment includes the following processes. However, the cold working process in Process 3 is an optional process. In other words, the cold working process in Process 3 does not have to be performed.

- (Process 1) Preparation process
- (Process 2) Hot working process
- (Process 3) Cold working process
- 35 (Process 4) Heat treatment process

[0183] Each process is described hereunder.

40 [(Process 1) Preparation process]

[0184] In the preparation process, a starting material having a chemical composition according to Feature 1 that is described above is prepared. The starting material may be supplied by a third party or may be produced. The starting material may be an ingot, or may be a slab, a bloom, or a billet.

45 [0185] In the case of producing the starting material, the starting material is produced by the following method. An alloy in a liquid state (molten metal) that has the chemical composition described above is produced. The produced molten metal is used to produce an ingot by an ingot-making process. The produced molten metal may also be used to produce a slab, a bloom, or a billet by a continuous casting process. Hot working may be performed on the produced ingot, slab, or bloom to produce a billet. For example, hot forging or blooming may be performed on the ingot or bloom to produce a cylindrical billet, and the billet may be used as the starting material. In such case, although not particularly limited, the temperature of the starting material immediately before the start of the hot forging is, for example, 1000 to 1300°C. The method for cooling the starting material after hot forging is not particularly limited.

50 [(Process 2) Hot working process]

55 [0186] In the hot working process, hot working is performed on the starting material prepared in the preparation process to produce an intermediate alloy material. The intermediate alloy material, for example, may be an alloy pipe, may be an alloy plate, or may be an alloy bar.

[0187] In the case of the intermediate alloy material being an alloy pipe, the following working is performed in the hot

working process. First, a cylindrical starting material is prepared. A through-hole is formed along the central axis in the cylindrical starting material by machining. The cylindrical starting material in which the through-hole has been formed is heated. The heated cylindrical starting material is then subjected to a hot-extrusion process, which is typified by the Ugine-Sejournet process, to produce an intermediate alloy material (alloy pipe). A hot hollow forging process may be performed instead of the hot extrusion process.

[0188] Further, instead of the hot extrusion process, an alloy pipe may be produced by performing piercing-rolling according to the Mannesmann process. In such case, the cylindrical starting material is heated. The heated cylindrical starting material is then pierced and rolled using a piercing machine. In the case of performing piercing-rolling, although not particularly limited, the piercing ratio is, for example, 1.0 to 4.0. The cylindrical starting material subjected to piercing and rolling is further subjected to hot rolling with a mandrel mill, a stretch reducing mill, a sizing mill or the like to produce a hollow blank (alloy pipe). The heating temperature of the starting material in the hot working process is, for example, 1000 to 1300°C. Although not particularly limited, the cumulative reduction of area in the hot working process is, for example, 20 to 80%. In the case of producing an alloy pipe by hot working, preferably the temperature (finishing temperature) of the hollow blank immediately after completing the hot working is 800°C or more.

[0189] In the case of the intermediate alloy material being an alloy plate, one or a plurality of rolling mills equipped with a pair of work rolls is used in the hot working process, for example. The starting material such as a slab is heated. The heated starting material is subjected to hot working to produce an alloy plate. The hot working is, for example, hot forging or hot rolling. The heating temperature of the starting material before hot working is, for example, 1000 to 1300°C.

[0190] In the case of the intermediate alloy material being an alloy bar, a continuous mill equipped with a plurality of roll stands arranged in a row is used in the hot working process. Each roll stand has a pair of rolls in which grooves are formed. The heated cylindrical starting material is subjected to hot rolling using the continuous mill to produce an alloy bar. The heating temperature of the cylindrical starting material before hot rolling is, for example, 1000 to 1300°C.

[(Process 3) Cold working process]

[0191] A cold working process is performed as necessary. In other words, a cold working process does not have to be performed. In the case of performing a cold working process, cold working is performed on the intermediate alloy material after the intermediate alloy material has been subjected to a pickling treatment. In the case of the intermediate alloy material being an alloy pipe or an alloy bar, the cold working is, for example, cold drawing. In the case of the intermediate alloy material being an alloy plate, the cold working is, for example, cold rolling. Performing the cold working process allows the development of recrystallization and the formation of uniform grains to occur. Although not particularly limited, the reduction of area in the cold working process is, for example, 10 to 90%.

[(Process 4) Heat treatment process]

[0192] In the heat treatment process, the intermediate alloy material after the hot working process or after the cold working process is subjected to a heat treatment. A heat treatment temperature T (°C) is 900 to 1150°C. A holding time t (mins) at the heat treatment temperature T is 3 to 30 minutes. After the holding time t elapses, the intermediate alloy material is rapidly cooled.

[0193] In addition, in the heat treatment process of Process 4, the following Condition 1 is satisfied. (Condition 1)

$$75/(4Z) \leq \Sigma A \leq 32260Z \quad (1)$$

where, ΣA in Formula (1) is defined by Formula (2), and Z in Formula (1) is defined by Formula (3).

$$\Sigma A = (t/60) \times (\exp(40000/(T + 273)))/10^{10} \quad (2)$$

$$Z = 60C/(1.6Ti + 5Nb + 100N) \quad (3)$$

[0194] In Formula (2), the heat treatment temperature (°C) is substituted for T , and the holding time (mins) at the heat treatment temperature T is substituted for t .

[0195] In Formula (3), the content in percent by mass of a corresponding element in the chemical composition of the alloy material is substituted for each symbol of an element.

[0196] Formula (1) is a condition for reducing the number density of fine nitrogen-containing precipitates at the grain boundaries of the alloy material after production. ΣA defined by Formula (2) is an index of the amount of fine nitrogen-

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containing precipitates that precipitate within the range of the aforementioned heat treatment temperature T and holding time t. Further, Z defined by Formula (3) is an index relating to the formation of fine nitrogen-containing precipitates with respect to the chemical composition.

5 **[0197]** On the precondition that the heat treatment temperature T (°C) is within the range of 900 to 1150°C and the holding time t (mins) is within the range of 3 to 30 minutes, if the chemical composition (contents of C, Ti, Nb, and N) of the intermediate alloy material that is the object of the heat treatment, the heat treatment temperature T, and the holding time t each satisfy Formula (1), the number density of fine nitrogen-containing precipitates at the grain boundaries in the alloy material after the heat treatment process will decrease to 20/μm or less. Therefore, in the heat treatment process, the heat treatment temperature T (°C) and the holding time t (mins) are adjusted to satisfy Formula (1).

10 **[0198]** The alloy material of the present embodiment can be produced by the processes described above. The production method described above is one example of a method for producing the alloy material of the present embodiment. Therefore, a method for producing the alloy material of the present embodiment is not limited to the above production method. As long as Feature 1 to Feature 3 are satisfied, a method for producing the alloy material is not limited to the production method described above.

15 **EXAMPLES**

[0199] The advantageous effect of the alloy material of the present embodiment is described more specifically hereunder by way of examples. The conditions adopted in the following examples are one example of conditions adopted for confirming the feasibility and advantageous effect of the alloy material of the present embodiment. Accordingly, the alloy material of the present embodiment is not limited to this one example of conditions.

[Production of alloy materials]

25 **[0200]** Ingots having the chemical compositions shown in Table 1-1 and Table 1-2 were produced. Each ingot was formed in a cylindrical shape with an outer diameter of 120 mm, and the mass of each ingot was 30 kg.

[Table 1-1]

30 **[0201]**

TABLE 1-1

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Co	w
1	0.008	0.30	0.41	0.014	0.0031	1.6	37.1	23.5	2.8	0.05	0.02
2	0.006	0.15	0.38	0.026	0.0022	2.3	40.5	26.5	2.6	0.12	0.01
3	0.012	0.38	0.59	0.025	0.0006	2.4	37.2	24.4	3.3	0.02	0.15
4	0.016	0.42	0.24	0.019	0.0012	1.8	41.3	21.7	2.8	0.11	0.12
5	0.010	0.23	0.81	0.010	0.0010	2.7	39.7	22.2	2.9	0.20	0.18
6	0.008	0.33	0.69	0.008	0.0009	1.6	48.4	26.5	3.2	0.08	0.04
7	0.009	0.41	0.16	0.022	0.0018	1.7	37.7	21.1	2.8	0.02	0.02
8	0.011	0.34	0.61	0.019	0.0033	2.5	41.5	25.6	3.0	0.56	0.08
9	0.014	0.29	0.77	0.018	0.0016	2.4	38.8	28.8	3.0	0.17	0.07
10	0.008	0.15	0.60	0.016	0.0023	1.8	39.5	20.5	2.9	0.40	0.01
11	0.006	0.26	0.75	0.008	0.0012	1.7	40.2	20.9	3.0	0.62	0.06
12	0.018	0.21	0.98	0.026	0.0008	2.2	38.2	22.8	3.5	0.62	0.08
13	0.013	0.34	0.66	0.019	0.0002	1.9	39.0	22.2	3.4	0.06	0.01
14	0.010	0.28	0.50	0.016	0.0022	2.0	45.0	27.3	3.2	0.50	0.10
15	0.023	0.30	0.33	0.025	0.0011	1.8	40.0	26.0	3.1	0.02	0.12
16	0.008	0.11	0.65	0.011	0.0008	2.9	32.0	20.8	3.2	0.02	0.05

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(continued)

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)											
	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Co	w	
5	17	0.011	0.25	0.82	0.009	0.0015	1.9	53.0	22.2	3.2	0.15	0.04
	18	0.012	0.38	0.15	0.015	0.0018	2.2	39.2	19.3	2.6	0.01	0.02
	19	0.008	0.41	0.44	0.012	0.0009	1.6	40.6	34.0	3.2	0.12	0.06
10	20	0.008	0.12	0.35	0.015	0.0005	1.8	44.6	20.4	4.8	0.25	0.07
	21	0.012	0.42	0.88	0.025	0.0002	2.2	39.2	22.3	3.1	0.12	0.01
	22	0.017	0.32	0.64	0.022	0.0016	2.1	39.2	27.1	3.2	0.11	0.11
	23	0.006	0.19	0.57	0.015	0.0011	2.8	41.0	20.9	3.0	0.28	0.02
15	24	0.009	0.45	0.84	0.013	0.0022	1.6	48.3	24.4	3.7	0.03	0.24
	25	0.009	0.33	0.63	0.026	0.0013	1.8	38.1	21.8	2.6	0.42	0.05
	26	0.019	0.47	0.11	0.010	0.0008	2.4	45.9	26.9	3.8	0.67	0.24
20	27	0.003	0.08	0.68	0.023	0.0003	1.5	44.2	22.5	3.2	0.02	0.68
	28	0.018	0.26	0.65	0.016	0.0002	1.7	40.2	20.9	3.0	0.62	0.07
	29	0.009	0.48	0.96	0.025	0.0011	2.3	37.7	20.5	2.7	0.25	0.13
	30	0.013	0.34	0.66	0.019	0.0002	1.9	39.0	22.2	3.4	0.06	0.01
25	31	0.010	0.27	0.22	0.014	0.0001	1.5	40.5	26.3	3.2	0.19	0.07

[Table 1-2]

[0202]

TABLE 1-2

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)											Tx
	Ca	N	Al	B	Sn	Ti	Nb	V	Zr	Hf	Ta	
35	1	0.0018	0.006	0.12	0.0005	0.001	0.44					0.440
	2	0.0036	0.007	0.08	0.0010	0.002	0.67	0.098				0.768
	3	0.0022	0.008	0.11	0.0022	0.003	0.56		0.010			0.570
40	4	0.0015	0.011	0.10	0.0002	0.022	0.55			0.050		0.600
	5	0.0038	0.009	0.08	0.0005	0.002	0.84				0.060	0.900
	6	0.0012	0.013	0.06	0.0008	0.011	0.72					0.800
	7	0.0025	0.003	0.09	0.0003	0.031	0.68	0.075				0.755
45	8	0.0022	0.009	0.04	0.0015	0.001	0.56		0.070	0.030		0.660
	9	0.0018	0.008	0.10	0.0026	0.003	0.70	0.083	0.010	0.020	0.030	0.863
	10	0.0005	0.007	0.10	0.0015	0.010	0.67	0.008	0.002			0.680
50	11	0.0018	0.002	0.11	0.0002	0.023	0.50	0.024	0.010			0.534
	12	0.0038	0.004	0.12	0.0005	0.003	0.65	0.001	0.003			0.654
	13	0.0015	0.008	0.09	0.0010	0.003	0.69	0.118	0.006			0.814
	14	0.0030	0.006	0.10	0.0005	0.035	0.41	0.085	0.010			0.505
55	15	0.0025	0.010	0.08	0.0012	0.040	0.65	0.020		0.080		0.750
	16	0.0023	0.009	0.06	0.0002	0.023	0.70	0.008				0.708
	17	0.0032	0.010	0.11	0.0008	0.002	0.50	0.032			0.050	0.582

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(continued)

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)											Tx
	Ca	N	Al	B	Sn	Ti	Nb	V	Zr	Hf	Ta	
18	0.0017	0.006	0.12	0.0005	0.041	0.78	0.005					0.785
19	0.0028	0.009	0.10	0.0001	0.005	0.64	0.005					0.645
20	0.0018	0.007	0.07	0.0002	0.018	0.65	0.005				0.080	0.735
21	0.0021	0.013	0.07	0.0011	0.004	0.66	0.005	0.250				0.915
22	0.0034	0.010	0.06	0.0025	0.010	0.98	0.005					0.985
23	0.0030	0.007	0.12	0.0002	0.001	0.85	0.150	0.098				1.098
24	0.0011	0.008	0.11	0.0007	0.002	0.75	0.085	0.120	0.090	0.090	0.002	1.137
25	0.0019	0.014	0.09	0.0009	0.032	0.40	0.003	0.001	0.002	0.001	0.003	0.410
26	0.0044	0.012	0.19	0.0021	0.022	0.40	0.001	0.002	0.005	0.005	0.001	0.414
27	0.0009	0.017	0.05	0.0002	0.025	0.75	0.030				0.020	0.800
28	0.0018	0.012	0.11	0.0012	0.003	0.42	0.001	0.002				0.423
29	0.0022	0.008	0.09	0.0011	0.028	0.65	0.001	0.002	0.003	0.002	0.001	0.659
30	0.0015	0.008	0.09	0.0002	0.023	0.69	0.080	0.006				0.776
31	0.0025	0.010	0.08	0.0005	0.015	0.86	0.069	0.025	0.030	0.005	0.005	0.994

[0203] A blank space in Table 1-2 means that the content of the corresponding element was 0% in the significant figures (numerical value to the least significant digit) defined in the embodiment. In other words, a blank space means that the content of the corresponding element was 0% when a fraction in the significant figures (numerical value to the least significant digit) defined in the above embodiment was rounded off.

[0204] For example, the content of Zr that is defined in the present embodiment is defined as a numerical value to the thousandths place. Therefore, in Test No. 1 in Table 1-2, the blank space with respect to the content of Zr means that the measured content of Zr was 0% when the ten thousandths place was rounded off.

[0205] Note that, the term "rounding off" means that if a digit (fraction) below the defined least significant digit is less than 5, it is rounded down, and if the digit (fraction) is 5 or more, it is rounded up.

[0206] Each of the produced ingots was subjected to hot forging to produce a starting material (alloy plate) having a thickness of 30 mm. The heating temperature of the ingot in the hot forging was 1000 to 1300°C. The produced starting material was subjected to hot rolling to produce an intermediate alloy material (alloy plate) having a thickness of 10 mm.

[Table 2]

[0207]

TABLE 2

Test Number	T(°C)	t (mins)	Z	75/(4Z)	ΣA	32260Z	Number Density (/ μ m)	Corrosion Rate (g/m ² ·hr)
1	1080	5	0.37	51	58	11875	2	0.06
2	1030	10	0.16	118	358	5134	1	0.05
3	1000	10	0.42	44	738	13695	4	0.08
4	1025	5	0.48	39	202	15641	3	0.06
5	980	30	0.27	70	3657	8626	10	0.14
6	970	15	0.20	96	2364	6315	12	0.16
7	1080	8	0.31	61	92	9881	1	0.04
8	950	25	0.37	51	6668	11855	12	0.14
9	1040	5	0.36	52	142	11605	5	0.08

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(continued)

Test Number	T(°C)	t (mins)	Z	75/(4Z)	ΣA	32260Z	Number Density (/μm)	Corrosion Rate (g/m ² ·hr)
5 10	1030	3	0.26	71	107	8546	2	0.06
11	1030	5	0.32	58	179	10369	1	0.06
12	940	30	0.75	25	10479	24111	12	0.11
10 13	1030	10	0.31	60	358	10089	5	0.09
14	980	15	0.36	53	1828	11515	9	0.12
15 15	1060	8	0.66	29	144	21199	15	14.12
16	1030	5	0.23	80	179	7517	22	16.94
17	950	30	0.34	55	8002	11089	30	9.88
18	1030	5	0.38	49	179	12401	4	3.00
19	1030	5	0.25	75	179	8111	26	19.76
20 20	1000	30	0.27	69	2215	8773	30	24.12
21	960	30	0.30	62	6138	9755	43	22.58
22	940	30	0.40	47	10479	12889	36	9.88
23	1060	10	0.13	146	179	4133	42	23.01
25 24	950	25	0.22	84	6668	7184	40	26.12
25	960	20	0.26	71	4092	8477	28	26.42
26	980	5	0.62	30	609	19933	23	7.99
27	1030	15	0.06	318	537	1904	30	8.85
30 28	1130	3	0.58	33	12	18562	25	10.00
29	1100	5	0.29	64	37	9442	28	16.36
30	910	30	0.34	55	24182	10921	50	22.82
35 31	920	15	0.22	85	9107	7114	36	24.55

[0208] The intermediate alloy material was subjected to a heat treatment process. In the heat treatment process, the heat treatment temperature T (°C), the holding time t (mins) at the heat treatment temperature T, ΣA defined by Formula (2), and Z defined by Formula (3) were as shown in Table 2. After the holding time t elapsed, the intermediate alloy material was water-cooled to normal temperature. An alloy material (alloy plate) of each test number was produced by the above process.

[Evaluation tests]

[0209] The following evaluation tests were performed using the produced alloy materials.

(Test 1) Test to measure number density of fine nitrogen-containing precipitates at grain boundaries

(Test 2) Intergranular corrosion resistance evaluation test

[0210] Hereunder, each evaluation test is described.

[(Test 1) Test to measure number density of fine nitrogen-containing precipitates at grain boundaries]

[0211] The number density (/μm) of fine nitrogen-containing precipitates at the grain boundaries of the alloy material of each test number was determined by the method described in the above [Method for determining number density of fine nitrogen-containing precipitates]. The determined number density (/μm) of fine nitrogen-containing precipitates is shown in the column "Number Density (/μm)" in Table 2.

[(Test 2) Intergranular corrosion resistance evaluation test]

[0212] The corrosion rate ($\text{g}/\text{m}^2\cdot\text{hr}$) of the alloy material of each test number was determined by the method described in the above [Method for evaluating intergranular corrosion resistance]. The determined corrosion rate is shown in the column "Corrosion Rate ($\text{g}/\text{m}^2\cdot\text{hr}$)" in Table 2. If the determined corrosion rate was $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$ or less, it was determined that excellent intergranular corrosion resistance was obtained.

[Evaluation results]

[0213] The test results are shown in Table 2.

[0214] The alloy materials of Test Nos. 1 to 14 satisfied Feature 1 to Feature 3. Therefore, the corrosion rate was $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$ or less, and excellent intergranular corrosion resistance was obtained in a strongly oxidizing corrosive environment.

[0215] On the other hand, in Test No. 15, the content of C was too high. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0216] In Test No. 16, the content of Ni was too low. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0217] In Test No. 17, the content of Ni was too high. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0218] In Test No. 18, the content of Cr was too low. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0219] In Test No. 19, the content of Cr was too high. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0220] In Test No. 20, the content of Mo was too high. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0221] In Test No. 21, the content of V was too high. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0222] In Test No. 22, the content of Ti was too high. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0223] In Test Nos. 23 and 24, although Feature 1 was satisfied, the total content Tx of Ti, Nb, V, Zr, Hf, and Ta was more than 1.000%. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0224] In Test Nos. 25 and 26, although Feature 1 was satisfied, the total content Tx of Ti, Nb, V, Zr, Hf, and Ta was less than 0.420%. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0225] In Test No. 27, the content of C was too low, the content of W was too high, and the content of N was too high. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0226] In Test Nos. 28 and 29, although Feature 1 and Feature 2 were satisfied, ΣA was less than $75/(4Z)$ in the heat treatment process. Consequently, Feature 3 was not satisfied. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0227] In Test Nos. 30 and 31, although Feature 1 and Feature 2 were satisfied, ΣA was more than 32260Z in the heat treatment process. Consequently, Feature 3 was not satisfied. Therefore, the corrosion rate was more than $0.20 \text{ g}/\text{m}^2\cdot\text{hr}$, and sufficient intergranular corrosion resistance was not obtained.

[0228] An embodiment of the present disclosure has been described above. However, the embodiment described above is merely an example for carrying out the present disclosure. Therefore, the present disclosure is not limited to the above-described embodiment, and can be implemented by appropriately modifying the above embodiment within a range that does not depart from the gist of the present disclosure.

Claims

1. An alloy material having a chemical composition consisting of, in mass%, C: 0.005 to 0.020%,

Si: 0.05 to 0.50%,
Mn: 0.05 to 1.00%,
P: 0.030% or less,
S: 0.0100% or less,

5 Cu: 1.5 to 3.0%,
Ni: 35.0 to 50.0%,
Cr: 20.0 to 30.0%,
Mo: 2.5 to 4.0%,
Co: 0.01 to 0.80%,
W: 0.01 to 0.30%,
Ca: 0.0050% or less,
N: 0.001 to 0.015%,
Al: 0.20% or less,
10 B: 0.0030% or less,
Sn: 0.050% or less,
Ti: 0.40 to 0.90%,
Nb: 0 to 0.150%,
V: 0 to 0.150%,
15 Zr: 0 to 0.150%,
Hf: 0 to 0.150%, and
Ta: 0 to 0.150%,
with the balance being Fe and impurities,
wherein:

20 a total content of Ti, Nb, V, Zr, Hf, and Ta is 0.420 to 1.000%, and
a number density of nitrogen-containing precipitates having a major axis of 10 to 100 nm at grain boundaries
of the alloy material is 20/ μm or less.

- 25 **2.** The alloy material according to claim 1, wherein the chemical composition contains one or more elements selected
from a group consisting of:

30 Nb: 0.001 to 0.150%,
V: 0.001 to 0.150%,
Zr: 0.001 to 0.150%,
Hf: 0.001 to 0.150%, and
Ta: 0.001 to 0.150%.

- 35 **3.** The alloy material according to claim 1 or claim 2, wherein:
the alloy material is an alloy pipe.

FIG.1

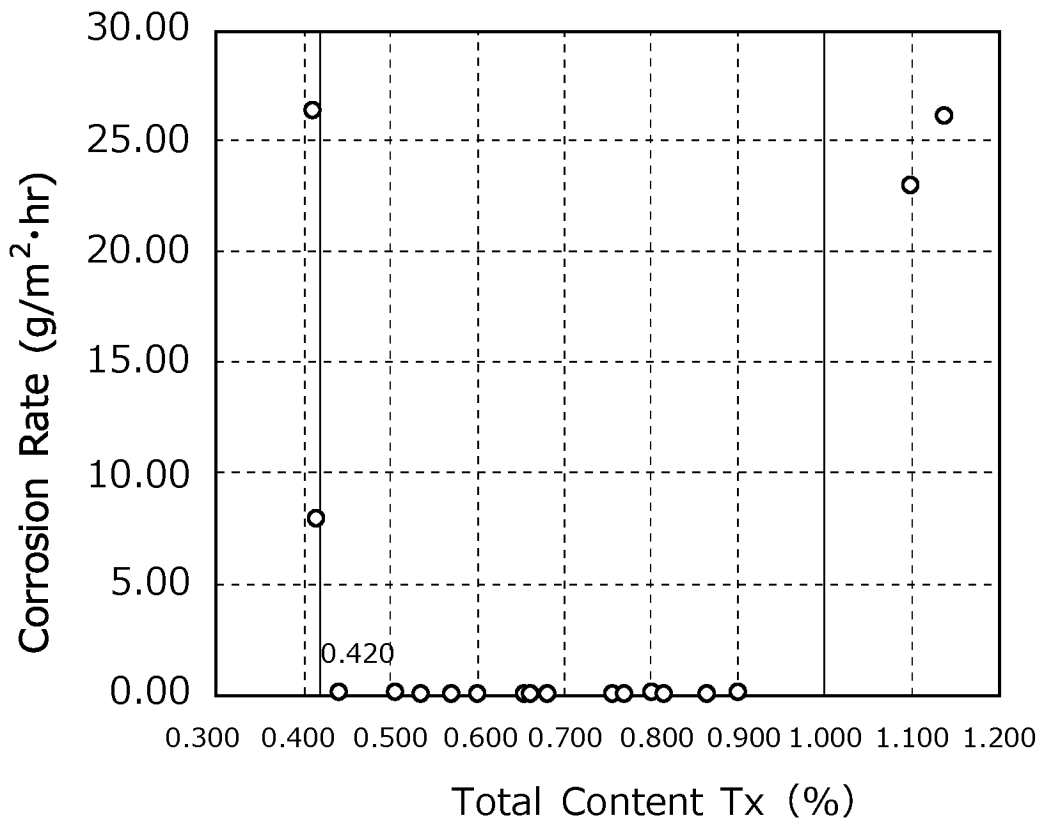
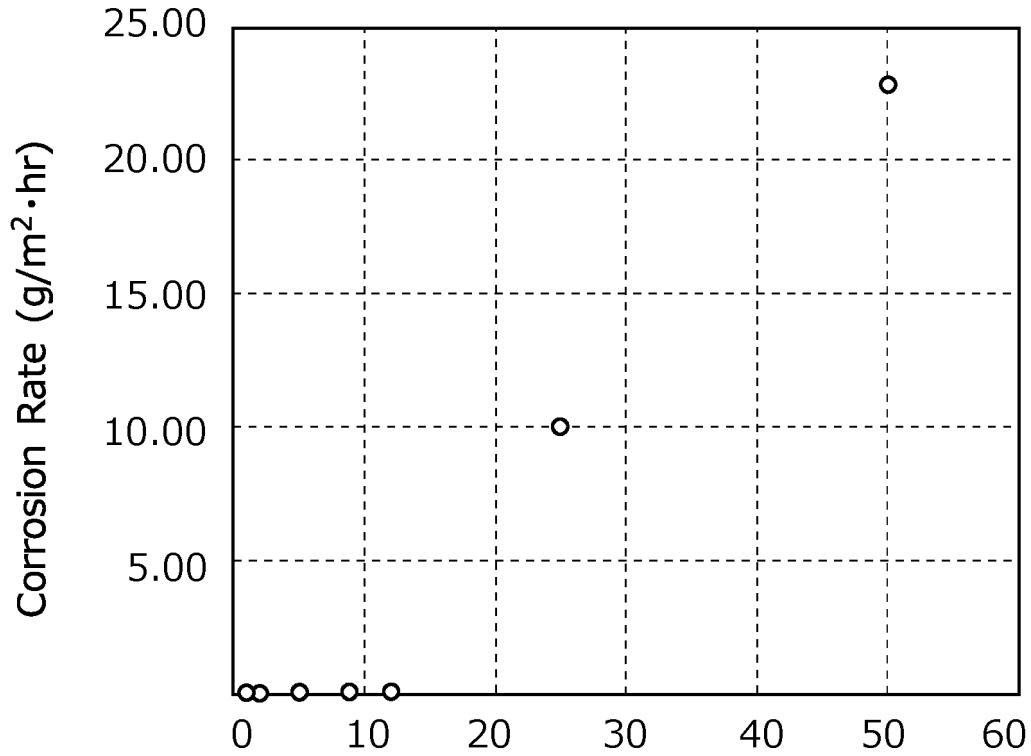
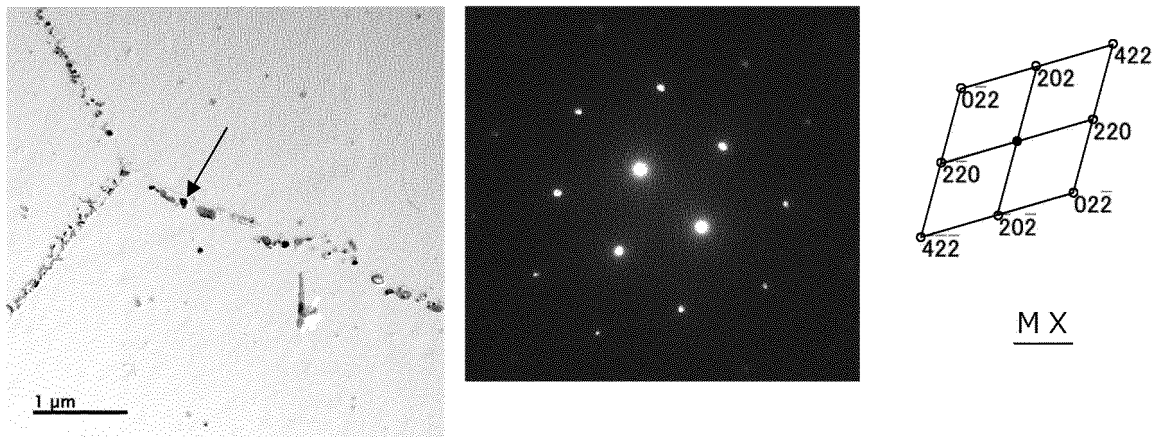


FIG.2



Number Density of Fine Nitrogen-containing Precipitates at Grain Boundaries (/μm)

FIG.3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/013313

5	A. CLASSIFICATION OF SUBJECT MATTER		
	<p><i>C22C 30/04</i>(2006.01)i; <i>C22C 19/05</i>(2006.01)i; <i>C22F 1/00</i>(2006.01)i; <i>C22F 1/10</i>(2006.01)i; <i>C22F 1/16</i>(2006.01)i FI: C22C30/04; C22C19/05 E; C22F1/00 612; C22F1/00 623; C22F1/00 624; C22F1/00 626; C22F1/00 630M; C22F1/00 640A; C22F1/00 640C; C22F1/00 640D; C22F1/00 640F; C22F1/00 641A; C22F1/00 641B; C22F1/00 651A; C22F1/00 682; C22F1/00 683; C22F1/00 684C; C22F1/00 685Z; C22F1/00 686A; C22F1/00 691B; C22F1/00 691C; C22F1/00 692A; C22F1/00 694A; C22F1/00 694B; C22F1/16 Z; C22F1/10 H</p>		
	According to International Patent Classification (IPC) or to both national classification and IPC		
	B. FIELDS SEARCHED		
15	Minimum documentation searched (classification system followed by classification symbols) C22C30/04; C22C19/05; C22F1/00; C22F1/10; C22F1/16		
	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 1971-2023 Registered utility model specifications of Japan 1996-2023 Published registered utility model applications of Japan 1994-2023		
20	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
	C. DOCUMENTS CONSIDERED TO BE RELEVANT		
25	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	A	JP 2021-183721 A (NIPPON STEEL CORP) 02 December 2021 (2021-12-02) entire text, all drawings	1-3
30	A	JP 2021-70838 A (NIPPON STEEL STAINLESS STEEL CORP) 06 May 2021 (2021-05-06) entire text, all drawings	1-3
35	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
40	<p>* Special categories of cited documents:</p> <p>“A” document defining the general state of the art which is not considered to be of particular relevance</p> <p>“E” earlier application or patent but published on or after the international filing date</p> <p>“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)</p> <p>“O” document referring to an oral disclosure, use, exhibition or other means</p> <p>“P” document published prior to the international filing date but later than the priority date claimed</p> <p>“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</p> <p>“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</p> <p>“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</p> <p>“&” document member of the same patent family</p>		
45	Date of the actual completion of the international search 08 June 2023		Date of mailing of the international search report 20 June 2023
50	Name and mailing address of the ISA/JP Japan Patent Office (ISA/JP) 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915 Japan		Authorized officer
55			Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. PCT/JP2023/013313

5

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2021-183721 A	02 December 2021	EP 3913103 A1 entire text, all drawings	
		CN 113718134 A	
JP 2021-70838 A	06 May 2021	(Family: none)	

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2017168904 A [0005] [0008]