

(19)



(11)

**EP 4 491 755 A1**

(12)

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

(43) Date of publication:

**15.01.2025 Bulletin 2025/03**

(51) International Patent Classification (IPC):

**C22C 38/00** <sup>(2006.01)</sup> **C22C 38/60** <sup>(2006.01)</sup>  
**C21C 7/06** <sup>(2006.01)</sup> **C21D 9/46** <sup>(2006.01)</sup>

(21) Application number: **22930973.7**

(52) Cooperative Patent Classification (CPC):

**C22C 38/00; C22C 38/60; C21C 7/06; C21D 9/46**

(22) Date of filing: **09.08.2022**

(86) International application number:

**PCT/JP2022/030359**

(87) International publication number:

**WO 2023/170996 (14.09.2023 Gazette 2023/37)**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

**BA ME**

Designated Validation States:

**KH MA MD TN**

(72) Inventors:

- **HAMADA, Jun-ichi**  
Tokyo 100-0005 (JP)
- **YOSHII, Chikako**  
Tokyo 100-0005 (JP)
- **HAYASHI, Atsutaka**  
Tokyo 100-0005 (JP)
- **FUJIMURA, Yoshitomo**  
Tokyo 100-0005 (JP)
- **HAMADA, Takahito**  
Tokyo 100-0005 (JP)

(30) Priority: **07.03.2022 JP 2022034594**

(71) Applicant: **NIPPON STEEL Stainless Steel  
Corporation**  
Tokyo 100-0005 (JP)

(74) Representative: **Zimmermann & Partner**  
**Patentanwälte mbB**  
**Postfach 330 920**  
**80069 München (DE)**

(54) **FERRITIC STAINLESS STEEL SHEET AND EXHAUST PARTS**

(57) There is provided a ferritic stainless steel sheet including a chemical composition that consists of, in mass%, C: 0.02% or less, Si: 1.0% or less, Mn: 1.0% or less, P: 0.01 to 0.10%, S: 0.0001 to 0.005%, N: 0.02% or less, Cr: 17.0 to 20.0%, Cu: 1.0 to 1.5%, Ti: 0.05 to 0.3%, Nb: 0.005 to 0.2%, Mo: 0.02 to 0.5%, B: 0.0001 to

0.0030%, Al: 0.005 to 0.5%, Ni: 0.01 to 0.2%, V: 0.01 to 0.2%, optional elements, with the balance: Fe and impurities and satisfies  $[86\text{ P} + 33\text{Nb} + \text{Mo} + 4\text{Al} \geq 5.0]$ , in which an area fraction of Cu particles having a diameter of 20 nm or less is 2.0% or less.

**EP 4 491 755 A1**

## Description

### TECHNICAL FIELD

5 **[0001]** The present disclosure relates to a ferritic stainless steel sheet and an exhaust member.

### BACKGROUND ART

10 **[0002]** In recent years, ferritic stainless steels, which are relatively satisfactory in properties including oxidation resistance and workability and have low coefficients of thermal expansion, have attracted considerable attention as starting materials of exhaust members for automobiles. Exhaust members are used in an environment in which the exhaust members are repeatedly exposed to heating and cooling to and from a high temperature. For this reason, the larger a coefficient of thermal expansion, the more a fracture resulting from thermal fatigue tends to occur.

15 **[0003]** As described above, for exhaust members, low coefficients of thermal expansion are important properties. Ferritic stainless steels, which have low coefficients of thermal expansion, are suitable for exhaust members. On the other hand, ferritic stainless steels have in some cases low high temperature strength compared with other starting materials and are thus required to be enhanced in high temperature strength. Accordingly, as disclosed in Patent Documents 1 to 5, ferritic stainless steels assumed to be applied to exhaust members have been developed.

### 20 LIST OF PRIOR ART DOCUMENTS

#### PATENT DOCUMENT

##### **[0004]**

25 Patent Document 1: WO 03/4714  
 Patent Document 2: JP2000-297355A  
 Patent Document 3: JP2000-303149A  
 Patent Document 4: JP2008-189974A  
 30 Patent Document 5: JP2010-248620A

### SUMMARY OF INVENTION

#### TECHNICAL PROBLEM

35 **[0005]** The ferritic stainless steels disclosed in Patent Documents 1 to 5 are enhanced in high temperature strength by containing Cu. However, in recent years, downsizing of engines or the like causes a rise in the temperature of exhaust gas. For this reason, there is a demand for high temperature strength at a higher level.

40 **[0006]** On the other hand, the ferritic stainless steels disclosed in Patent Documents 1 to 5 are still susceptible to improvement from a viewpoint of high temperature strength. In particular, the ferritic stainless steels are enhanced in high temperature strength by containing a high content of Nb, which is expensive, and thus have a room for making the ferritic stainless steels lean. In addition, to enhance high temperature strength raises a problem of, for example, decreasing workability. Thus, there is a problem of difficulty in enhancing all properties of workability, oxidation resistance, and high temperature strength in a well-balanced manner.

45 **[0007]** In light of the above, an objective of the present disclosure is to solve the problems described above and provide a ferritic stainless steel sheet having excellent workability, oxidation resistance, and high temperature strength.

#### SOLUTION TO PROBLEM

50 **[0008]** The gist of the present disclosure, which has been made to solve the problem described above, is the following ferritic stainless steel sheet.

##### **[0009]**

55 (1) A ferritic stainless steel sheet including a chemical composition that consists of, in mass%:

C: 0.02% or less,  
 Si: 1.0% or less,  
 Mn: 1.0% or less,

P: 0.01 to 0.10%,  
 S: 0.0001 to 0.005%,  
 N: 0.02% or less,  
 Cr: 17.0 to 20.0%,  
 Cu: 1.0 to 1.5%,  
 Ti: 0.05 to 0.3%,  
 Nb: 0.005 to 0.2%,  
 Mo: 0.02 to 0.5%,  
 B: 0.0001 to 0.0030%,  
 Al: 0.005 to 0.5%,  
 Ni: 0.01 to 0.2%,  
 V: 0.01 to 0.2%,  
 W: 0 to 2.0%,  
 Sn: 0 to 0.5%,  
 Mg: 0 to 0.01%,  
 Sb: 0 to 0.5%,  
 Zr: 0 to 0.3%,  
 Ta: 0 to 0.3%,  
 Hf: 0 to 0.3%,  
 Co: 0 to 0.3%,  
 Ca: 0 to 0.01%,  
 REM: 0 to 0.2%, and  
 Ga: 0 to 0.3%,  
 with the balance: Fe and impurities, and  
 satisfies Formula (i) shown below, wherein  
 an area fraction of Cu particles having a diameter of 20 nm or less is 2.0% or less:

$$86P + 33Nb + Mo + 4Al \geq 5.0 \quad (i)$$

where symbols of elements in Formula (i) shown above indicate contents (mass%) of elements contained in the steel sheet, and zero is set to a symbol of an element when the element is not contained.

(2) The ferritic stainless steel sheet according to (1) above, wherein the chemical composition contains, in mass%, one or more elements selected from:

W: 0.05 to 2.0%,  
 Sn: 0.01 to 0.5%,  
 Mg: 0.0002 to 0.01%,  
 Sb: 0.01 to 0.5%,  
 Zr: 0.01 to 0.3%,  
 Ta: 0.01 to 0.3%,  
 Hf: 0.01 to 0.3%,  
 Co: 0.01 to 0.3%,  
 Ca: 0.0001 to 0.01%,  
 REM: 0.001 to 0.2%, and  
 Ga: 0.0002 to 0.3%.

(3) The ferritic stainless steel sheet according to (1) above, wherein a maximum length of TiN is 15 μm or less.

(4) The ferritic stainless steel sheet according to (2) above, wherein a maximum length of TiN is 15 μm or less.

(5) The ferritic stainless steel sheet according to any one of (1) to (4) above, wherein an amount of precipitating Nb is 0.1% or less in mass%.

(6) An exhaust member including the ferritic stainless steel sheet according to any one of (1) to (4) above.

(7) An exhaust member including the ferritic stainless steel sheet according to (5) above.

## ADVANTAGEOUS EFFECTS OF INVENTION

**[0010]** According to the present disclosure, it is possible to provide a ferritic stainless steel sheet that has excellent

workability, oxidation resistance, and high temperature strength.

#### BRIEF DESCRIPTION OF DRAWINGS

- 5 **[0011]** [Figure 1] Figure 1 is a graph illustrating a correlation between left side values of Formula (i) and 0.2% proof stresses at 850°C.

#### DESCRIPTION OF EMBODIMENTS

- 10 **[0012]** In order to increase the high temperature strength of a ferritic stainless steel sheet, the present inventors studied precipitation behavior of compounds of the steel sheet at 850°C. As a result, the present inventors obtained the following findings (a) to (d).

15 (a) A ferritic stainless steel containing a certain amount of Cu is enhanced in high temperature strength. This is because Cu particles such as bcc-Cu, 9R, and  $\epsilon$ -Cu precipitate. The present inventors found that there is a correlation between precipitation of the Cu particles and a content of Cr. For example, a ferritic stainless steel containing 14% of Cr did not cause precipitation of Cu particles at 850°C. In contrast, a ferritic stainless steel containing 17% or more of Cr caused precipitation of Cu particles at 850°C, thus being enhanced in high temperature strength. This is considered to be due to an increase in an activity of Cu with an increase in the content of Cr.

20 (b) P (phosphorus), Nb (niobium), Mo (molybdenum), and Al (aluminum) are elements that increase strength, and the present inventors revealed that they influence high temperature strength through interaction with Cu. High temperature strength is influenced by precipitation strengthening by Cu particles, solid-solution strengthening by P, Nb, Mo, and Al, and formation of P compounds and Laves phases. For this reason, optimization of a balance among these strengthening mechanisms is effective.

25 (c) A composition of the Cu particles is almost 100% Cu. For this reason, Cu needs to diffuse sufficiently to cause Cu particles to nucleate and precipitate. The P compounds and the Laves phases precipitate competitively with the Cu particles. Therefore, if the precipitation of the Cu particles is delayed in a use environment, the precipitation strengthening becomes insufficient.

30 On the other hand, if the precipitation of the Cu particles is too rapid, Cu particles grow and coarsen, thus making the precipitation strengthening insufficient. In light of the above, allowing the precipitation strengthening by the Cu particles to exert to the maximum and controlling contents of P, Nb, Mo, and Al are effective. As a result, a ferritic stainless steel sheet that is applicable to an exhaust member even in such a high temperature region of an exhaust gas temperature that reaches 850°C is provided.

35 (d) In addition, containing Ti is also effective. This is because Ti has an effect of enhancing high temperature strength by being contained in combination with Nb. On the other hand, Ti forms TiN. The TiN often has an angular shape. If coarse TiN in such an angular shape is formed, fatigue properties at a high temperature are decreased. For this reason, it is preferable to make formed TiN have a maximum length of 15  $\mu\text{m}$  or less.

- 40 **[0013]** An embodiment of the present disclosure has been made based on the above findings. Requirements of a ferritic stainless steel sheet of the present embodiment will be described below in detail.

#### 1. Chemical Composition

- 45 **[0014]** Reasons for limiting contents of elements are as follows. In the following description, the symbol "%" for the contents means "mass%."

C: 0.02% or less

- 50 **[0015]** C (carbon) decreases normal-temperature ductility and decreases workability. C also decreases corrosion resistance as well as high temperature strength and oxidation resistance. In addition, C may facilitate precipitation of fine Cu particles. For this reason, a content of C is set to 0.02% or less. The content of C is preferably set to 0.01% or less, more preferably set to 0.009% or less. Although C is desirably reduced as much as possible, excessive reduction of C increases refining costs. For this reason, the content of C is preferably set to 0.001% or more.

55 Si: 1.0% or less

- [0016]** Si (silicon) is an element used as a deoxidizer. Si is also an element that enhances high temperature strength and oxidation resistance. However, if Si is contained excessively, fine Cu particles may tend to precipitate in a large amount,

thus decreasing normal-temperature ductility. For this reason, a content of Si is set to 1.0% or less. The content of Si is preferably set to 0.8% or less, more preferably set to 0.5% or less, and still more preferably set to 0.4% or less. On the other hand, to provide the effects, the content of Si is preferably set to more than 0.1%, more preferably set to 0.2% or more. Here, with consideration given to pickling properties and toughness, the content of Si is preferably set to be within the range of 0.2 to 0.4%.

Mn: 1.0% or less

**[0017]** Mn (manganese) is an element used as a deoxidizer. In addition, Mn has an effect of enhancing high temperature strength in an intermediate temperature region. However, if Mn is contained excessively, Mn-based oxides form at an outer layer at high temperature, making scale adhesiveness and breakaway oxidation more likely to occur. As a result, oxidation resistance is decreased. In addition, fine Cu particles may tend to precipitate in a large amount, thus decreasing normal-temperature ductility as well. For this reason, a content of Mn is set to 1.0% or less. The content of Mn is preferably set to 0.8% or less, more preferably set to 0.5% or less, and further preferably set to 0.4% or less. On the other hand, to provide the effects, the content of Mn is preferably set to 0.05% or more. With consideration given to pickling properties and normal-temperature ductility in production of the steel sheet, the content of Mn is preferably set to be within the range of 0.05 to 0.4%.

P: 0.01 to 0.10%

**[0018]** P (phosphorus) has an effect of enhancing strength through solid-solution strengthening. P also has an effect of enhancing strength through causing precipitation strengthening of the steel sheet by forming P compounds such as FeP, FeTiP, and FeNbP. To reduce P requires use of a raw material with a low content of P. For this reason, a content of P is set to 0.01% or more. The content of P is preferably set to 0.02% or more, still more preferably 0.03% or more.

**[0019]** However, if P is contained excessively, significant hardening may occur, and fine Cu particles may tend to precipitate in a large amount, thus decreasing normal-temperature ductility and decreasing oxidation resistance. In addition, corrosion resistance, toughness, and pickling properties may be decreased. For this reason, the content of P is set to 0.10% or less. The content of P is preferably set to 0.08% or less, more preferably set to 0.06% or less. With consideration given to weldability and production costs, the content of P is preferably set to be within the range of 0.02 to 0.06%.

S: 0.0001 to 0.005%

**[0020]** S (sulfur) decreases oxidation resistance and normal-temperature ductility. In addition, S may decrease corrosion resistance. For this reason, a content of S is set to 0.005% or less. The content of S is preferably set to 0.003% or less. Although the content of S is preferably reduced as much as possible, excessive reduction of S increases refining costs. For this reason, the content of S is set to 0.0001% or more. The content of S is preferably set to 0.0005% or more. With consideration given to weldability and production costs, the content of S is preferably set to be within the range of 0.0005 to 0.003%.

N: 0.02% or less

**[0021]** As with C, N (nitrogen) decreases normal-temperature ductility. In particular, fine Cu particles may tend to precipitate in a large amount, thus decreasing workability. In addition, N decreases high temperature strength and oxidation resistance and may decrease corrosion resistance. For this reason, a content of N is set to 0.02% or less. The content of N is preferably set to 0.015% or less, more preferably set to 0.01% or less. Although the content of N is preferably reduced as much as possible, excessive reduction of N increases refining costs. For this reason, the content of N is preferably set to 0.003% or more.

Cr: 17.0 to 20.0%

**[0022]** Cr (chromium) is an element that is necessary to ensure oxidation resistance and corrosion resistance in the steel sheet of the present embodiment. In the present disclosure, it is newly revealed that precipitation strengthening by Cu more tends to develop at high temperature with an increase in the content of Cr. The increase in the content of Cr causes an increase in driving force for precipitation of Cu particles. It is then considered that Cr concentration regions appear around Cu particles having precipitated, which delays growth of the Cu particles. As a result, the precipitation strengthening tends to develop at high temperature. The steel sheet of the present embodiment is mainly assumed to be used at a temperature of 850°C or more, and with consideration given to precipitation of Cu particles in this temperature region, a content of Cr is

set to 17.0% or more. The content of Cr is preferably set to 17.2% or more.

**[0023]** However, if Cr is contained excessively, oxidation resistance is decreased. In addition, fine Cu particles may tend to precipitate in a large amount, thus decreasing normal-temperature ductility, and as a result, workability is decreased. Furthermore, toughness may be decreased. For this reason, the content of Cr is set to 20.0% or less. The content of Cr is preferably set to 19.0% or less. With consideration given to producibility and scale peeling properties, the content of Cr is preferably set to be within the range of 17.0 to 18.0%.

Cu: 1.0 to 1.5%

**[0024]** Cu (copper) has an effect of enhancing high temperature strength through precipitation strengthening by Cu particles. As described above, in the present disclosure, the present inventors obtained the finding that precipitation of Cu is promoted at high temperature when a content of Cr is 17.0% or more. In order to cause the precipitation strengthening by Cu particles to act stably at a high temperature of 850°C or more in combination with the content of Cr described above, a content of Cu is set to 1.0% or more. The content of Cu is preferably set to 1.1% or more. However, if Cu is contained excessively, workability is significantly decreased. For this reason, the content of Cu is set to 1.5% or less. The content of Cu is preferably set to 1.4% or less, more preferably set to 1.3% or less. With consideration given to high temperature fatigue properties, producibility, and weldability, the content of Cu is preferably set to be within the range of 1.1 to 1.4%. Furthermore, with consideration given to pickling properties, the content of Cu is preferably set to be within the range of 1.1 to 1.3%.

Ti: 0.05 to 0.3%

**[0025]** Ti (titanium) has an effect of enhancing corrosion resistance and intergranular corrosion resistance by combining with C, N, and S. Ti also has an effect of enhancing normal-temperature ductility and deep drawability. In particular, by causing precipitation of FeTiP, a Ti-based compound, an effect of enhancing normal-temperature workability is provided. For this reason, a content of Ti is set to 0.05% or more. The content of Ti is preferably set to 0.1% or more.

**[0026]** However, if Ti is contained excessively, an amount of dissolved Ti increases excessively, which rather decreases the normal-temperature ductility and forms coarse Ti-based precipitates serving as an origin of a crack during hole expanding. As a result, press workability is decreased. In addition, oxidation resistance may be decreased. For this reason, the content of Ti is set to 0.3% or less. The content of Ti is preferably set to 0.25% or less, more preferably set to 0.2% or less. Here, with consideration given to occurrence of surface defects and toughness, the content of Ti is preferably set to be within the range of 0.05 to 0.2%.

Nb: 0.005 to 0.2%

**[0027]** Nb (niobium) has an effect of causing solid-solution strengthening. In addition, Nb causes strengthening through refining precipitates. These strengthening mechanisms enhance high temperature strength. In addition, Nb immobilizes C and N in a form of carbo-nitrides, thus enhancing a corrosion resistance of a product sheet and contributing to development of recrystallization texture, which influences an r value. For this reason, a content of Nb in a chemical composition is set to 0.005% or more. The content of Nb is preferably set to 0.01% or more, more preferably set to 0.1% or more. As described above, in the steel sheet of the present embodiment, Nb is utilized together with high temperature strengthening elements such as P, Mo, and Al. However, Nb is an expensive element. For this reason, if Nb is contained excessively, alloy costs are increased. In addition, a recrystallization temperature is raised. Thus, production costs are also increased. Therefore, the content of Nb is set to 0.2% or less. The content of Nb is preferably set to 0.18% or less. With consideration given to toughness and an intergranular corrosiveness of a weld zone, the content of Nb is preferably set to be within the range of 0.1 to 0.2%.

Mo: 0.02 to 0.5%

**[0028]** As with Nb, Mo (molybdenum) is utilized together with high temperature strengthening elements such as P, Nb, and Al and has an effect of enhancing high temperature strength. For this reason, a content of Mo in a chemical composition is set to 0.02% or more. The content of Mo is preferably set to 0.05% or more, more preferably set to 0.1% or more, and further preferably set to 0.15% or more. However, Mo is an expensive element. Thus, with consideration given to the effects brought by the other elements, the content of Mo is set to 0.5% or less. The content of Mo is preferably set to 0.4% or less, more preferably set to 0.3% or less. With consideration given to oxidation resistance, workability, and producibility, the content of Mo is preferably set to be within the range of 0.1 to 0.3%, and with consideration further given to corrosion resistance, the content of Mo is preferably set to be within the range of 0.15 to 0.3%.

B: 0.0001 to 0.0030%

**[0029]** B (boron) is an element that enhances secondary workability during press working. For the steel sheet of the present embodiment, P compounds are utilized to enhance its normal-temperature workability and high temperature strength. At this time, when B is contained, coarsening of the P compounds under a high temperature environment is restrained. As a result, stability in strength is enhanced when the steel sheet is used under a high temperature environment.

**[0030]** This is because B segregates at crystal grain boundaries during a recrystallization process in a cold rolled sheet annealing step, and when the cold rolled sheet is thereafter exposed to high temperature, it is difficult for the Cu precipitates described above to precipitate at the grain boundaries. As a result, B has an effect of causing Cu precipitates to finely precipitate in grains. In addition, B causes a long term stability of precipitation strengthening to develop, thus restraining a decrease in strength and enhancing a thermal fatigue life. For this reason, a content of B is set to 0.0001% or more. The content of B is preferably set to 0.0002% or more. However, if B is contained excessively, the steel sheet is hardened. In particular, fine Cu particles may tend to precipitate in a large amount, thus decreasing normal-temperature ductility. In addition, oxidation resistance is decreased. In addition, intergranular corrosiveness may be decreased, or weld cracks may occur. For this reason, the content of B is set to 0.0030% or less. The content of B is preferably set to 0.0015% or less, more preferably set to 0.0010% or less. With consideration given to corrosion resistance and production costs, the content of B is preferably set to be within the range of 0.0002 to 0.0010%.

Al: 0.005 to 0.5%

**[0031]** Al (aluminum) is an element that is added as a deoxidizing element and enhances oxidation resistance. In the steel sheet of the present embodiment, Al is utilized together with high temperature strengthening elements such as P, Nb, and Mo. For this reason, a content of Al in a chemical composition is set to 0.005% or more. The content of Al is preferably set to 0.01% or more. However, if Al is contained excessively, fine Cu particles may tend to precipitate in a large amount, thus decreasing normal-temperature ductility and decreasing weldability. For this reason, a content of Al is set to 0.5% or less. The content of Al is preferably set to 0.2% or less, more preferably set to 0.1% or less. With consideration given to oxidation resistance, workability, and surface defects, the content of Al is preferably set to be within the range of 0.01 to 0.1%.

Ni: 0.01 to 0.2%

**[0032]** Ni (nickel) is an element that enhances toughness. For this reason, a content of Ni is set to 0.01% or more. The content of Ni is preferably set to 0.05% or more. However, if Ni is contained excessively, oxidation resistance is decreased, and alloy costs are increased. In addition, fine Cu particles may tend to precipitate in a large amount, thus decreasing normal-temperature ductility. For this reason, the content of Ni is set to 0.2% or less. The content of Ni is preferably set to 0.15% or less, more preferably set to 0.1% or less. With consideration given to producibility and oxidation resistance, the content of Ni is preferably set to be within the range of 0.05 to 0.1%.

V: 0.01 to 0.2%

**[0033]** V (vanadium) has an effect of enhancing high temperature strength by producing VC. V also has an effect of enhancing corrosion resistance. For this reason, a content of V is set to 0.01% or more. The content of V is preferably set to 0.02% or more, more preferably set to 0.05% or more. However, if V is contained excessively, fine Cu particles may tend to precipitate in a large amount, thus decreasing normal-temperature ductility, and raw material costs are increased. For this reason, the content of V is set to 0.2% or less. The content of V is preferably set to 0.15% or less, more preferably set to 0.1% or less. With consideration given to production costs and producibility, the content of V is preferably set to be within the range of 0.05 to 0.1%.

**[0034]** In addition to the elements described above, one or more elements selected from W, Sn, Mg, Sb, Zr, Ta, Hf, Co, Ca, REM, and Ga may be contained within their respective ranges described below. Reasons for limiting contents of the elements will be described.

W: 0 to 2.0%

**[0035]** As with Mo, W (tungsten) has an effect of causing solid-solution strengthening. W also has an effect of causing precipitation strengthening by producing Laves phases ( $\text{Fe}_2\text{W}$ ). In particular, when Nb and Mo are contained in combination, Laves phases of  $\text{Fe}_2(\text{Nb}, \text{Mo}, \text{W})$  are produced. In addition, W contained restrains the Laves phases from coarsening, thus enhancing precipitation strengthening ability. Note that coexistence of W with FeP-based precipitates

described above tends to make the Laves phases fine. For this reason, W may be contained as necessary.

**[0036]** However, if W is contained excessively, normal-temperature ductility is decreased, and alloy costs are increased as well. For this reason, a content of W in a chemical composition is set to 2.0% or less. The content of W is preferably set to 1.8% or less, more preferably set to 1.5% or less, and further preferably set to 1.0% or less. On the other hand, to provide the effects described above, the content of W is preferably set to 0.05% or more, more preferably set to 0.1% or more, and further preferably set to 0.2% or more. With consideration given to producibility, low temperature toughness, and oxidation resistance, the content of W is preferably set to be within the range of 0.2 to 1.5%.

Sn: 0 to 0.5%

**[0037]** Sn (tin) has an effect of enhancing corrosion resistance. Sn also has an effect of enhancing high temperature strength in an intermediate temperature region. For this reason, Sn may be contained as necessary. However, if Sn is contained excessively, producibility is significantly decreased. Thus, a content of Sn is set to 0.5% or less. The content of Sn is preferably set to 0.3% or less, more preferably set to 0.2% or less. On the other hand, to provide the effects described above, the content of Sn is preferably set to 0.01% or more, more preferably set to 0.05% or more. With consideration given to oxidation resistance and producibility, the content of Sn is preferably set to be within the range of 0.05 to 0.2%.

Mg: 0 to 0.01%

**[0038]** Mg (magnesium) is a deoxidizing element and also has an effect of refining a micro-structure of a slab, thus enhancing workability and toughness. In particular, Mg oxides, containing Mg, have an effect of serving as precipitation sites for carbo-nitrides such as Ti(C, N) and Nb(C, N) and causing the carbo-nitrides to finely precipitate in a dispersive manner. For this reason, W may be contained as necessary. However, if Mg is contained excessively, weldability and corrosion resistance are decreased. For this reason, a content of Mg is set to 0.01% or less. The content of Mg is preferably set to 0.001% or less, more preferably set to 0.0008% or less. On the other hand, to provide the effects described above, the content of Mg is preferably set to 0.0002% or more, more preferably set to 0.0003% or more. With consideration given to refining costs, the content of Mg is preferably set to be within the range of 0.0003 to 0.001%.

Sb: 0 to 0.5%

**[0039]** Sb (antimony) has an effect of enhancing corrosion resistance and high temperature strength. For this reason, Sb may be contained as necessary. However, if Sb is contained excessively, slab cracking in production of the steel sheet and a decrease in ductility tend to occur. For this reason, a content of Sb is set to 0.5% or less. The content of Sb is preferably set to 0.2% or less, more preferably set to 0.15% or less. On the other hand, to provide the effect described above, the content of Sb is preferably set to 0.01% or more. With consideration given to refining costs and producibility, the content of Sb is preferably set to be within the range of 0.01 to 0.15%.

Zr: 0 to 0.3%

**[0040]** As with Ti and Nb, Zr (zirconium) is an element that forms its carbo-nitride and has an effect of enhancing corrosion resistance and deep drawability. For this reason, W may be contained as necessary. However, if Zr is contained excessively, producibility is decreased. For this reason, a content of Zr is set to 0.3% or less. The content of Zr is preferably set to 0.2% or less. On the other hand, to provide the effect described above, the content of Zr is preferably set to 0.01% or more, more preferably set to 0.05% or more. With consideration given to costs, surface quality, and oxidation resistance, the content of Zr is preferably set to be within the range of 0.1 to 0.3%.

Ta: 0 to 0.3%

Hf: 0 to 0.3%

**[0041]** Ta (tantalum) has an effect of enhancing toughness by combining with C and N. For this reason, Ta may be contained as necessary. However, if Ta is contained excessively, alloy costs are increased, and producibility is significantly decreased. For this reason, a content of Ta is set to 0.3% or less. The content of Ta is preferably set to 0.2% or less, more preferably set to 0.08% or less. On the other hand, to provide the effect described above, the content of Ta is preferably set to 0.01% or more. With consideration given to refining costs and producibility, the content of Ta is preferably set to be within the range of 0.01 to 0.08%.

**[0042]** As with Ta, Hf (hafnium) has an effect of enhancing toughness by combining with C and N. For this reason, Hf may be contained as necessary. However, if Hf is contained excessively, alloy costs are increased, and producibility is



significantly decreased. For this reason, a content of Hf is set to 0.3% or less. The content of Hf is preferably set to 0.2% or less, more preferably set to 0.08% or less. On the other hand, to provide the effect described above, the content of Hf is preferably set to 0.01% or more. With consideration given to refining costs and producibility, the content of Hf is preferably set to be within the range of 0.01 to 0.08%.

Co: 0 to 0.3%

**[0043]** Co (cobalt) has an effect of enhancing high temperature strength. For this reason, Co may be contained as necessary. However, if Co is contained excessively, alloy costs are increased. For this reason, a content of Co is set to 0.3% or less. The content of Co is preferably set to 0.2% or less, more preferably set to 0.1% or less. On the other hand, to provide the effect described above, the content of Co is preferably set to 0.01% or more. With consideration given to refining costs and producibility, the content of Co is preferably set to be within the range of 0.01 to 0.1%.

Ca: 0 to 0.01%

**[0044]** Ca (calcium) has a desulfurizing effect. For this reason, Ca may be contained as necessary. However, if Ca is contained excessively, coarse CaS is produced, thus decreasing toughness and corrosion resistance. For this reason, a content of Ca is set to 0.01% or less. The content of Ca is preferably set to 0.0050% or less, more preferably set to 0.0020% or less. On the other hand, to provide the effect described above, the content of Ca is preferably set to 0.0001% or more, more preferably set to 0.0003% or more. With consideration given to refining costs and producibility, the content of Ca is preferably set to be within the range of 0.0003 to 0.0020%.

REM: 0 to 0.2%

**[0045]** REM (rare earth metal) has an effect of enhancing toughness and oxidation resistance by refining various types of precipitates. For this reason, REM may be contained as necessary. However, if REM is contained excessively, castability is significantly decreased, and ductility is decreased. For this reason, a content of REM is set to 0.2% or less. The content of REM is preferably set to 0.1% or less, more preferably set to 0.05% or less. On the other hand, to provide the effect, the content of REM is preferably set to 0.001% or more. With consideration given to refining costs and producibility, the content of REM is preferably set to be within the range of 0.001 to 0.05%.

**[0046]** REM refers to Sc (scandium), Y (yttrium), and lanthanoids, 17 elements in total, and the content of REM means a total content of these elements. Industrially, REM is often added in a form of misch metal.

Ga: 0 to 0.3%

**[0047]** Ga (gallium) has an effect of enhancing corrosion resistance. Ga also has an effect of restraining hydrogen embrittlement. For this reason, W may be contained as necessary. However, if Ga is contained excessively, alloy costs are increased. For this reason, a content of Ga is set to 0.3% or less. The content of Ga is preferably set to 0.1% or less. From viewpoints of producibility and costs as well as viewpoints of ductility and toughness, the content of Ga is preferably set to 0.0020% or less. On the other hand, to provide the effects, the content of Ga is preferably set to 0.0002% or more.

**[0048]** In the chemical composition of the steel sheet of the present embodiment, the balance is Fe and impurities. The "impurities" herein mean components that are mixed in the ferritic stainless steel sheet from raw materials such as ores and scraps and by various factors in a producing process in an industrial production of the ferritic stainless steel sheet and that are allowed to be mixed in the steel sheet of the present embodiment within their respective ranges in which the impurities have no adverse effect on the steel sheet. Examples of possible impurities include Bi, As, and Pb.

**[0049]** The chemical composition of the steel sheet of the present embodiment needs to satisfy Formula (i) shown below.

$$86P + 33Nb + Mo + 4Al \geq 5.0 \quad (i)$$

where symbols of elements in Formula (i) shown above indicate contents (mass%) of elements contained in the steel sheet, and zero is set to a symbol of an element when the element is not contained.

**[0050]** Figure 1 is a graph illustrating a correlation between left side values of Formula (i) and 0.2% proof stresses at 850°C. In measurement for Figure 1, a cold rolled sheet having a chemical composition of 17.5%Cr-0.005%C-0.2%Si-0.3%Mn-1.2%Cu-0.15%Ti-0.01%N was used. In this cold rolled sheet, a value of the left side value of Formula (i) was controlled by adjusting contents of elements constituting the left side value of Formula (i), P, Nb, Mo, and Al. Note that the 0.2% proof stresses at 850°C were measured by a high temperature tensile test conforming to JIS G 0567:2020. A rolling direction of a specimen used in the test was set as a tensile direction.

**[0051]** Figure 1 shows that 0.2% proof stresses at 850°C were 20 MPa or more when left side values of Formula (i) were 5.0 or more. This indicates that the cold rolled sheet had a satisfactory high temperature strength as high as those of Type429 (14%Cr-1%Si-0.4%Nb) and Type441 (17%Cr-0.2%Ti-0.4%Nb) containing 0.4% or more of Nb.

**[0052]** A reason for enhancing the high temperature strength in this manner is as follows. High temperature strength is influenced by a balance among the precipitation strengthening by Cu particles precipitating in a high temperature environment, the solid-solution strengthening by the elements described above, and formation of the P compounds and the Laves phases. Accordingly, the present inventors revealed that high temperature strength can be increased by optimizing contents of P, Nb, Mo, and Al.

**[0053]** When the left side value of Formula (i) is 5.0 or more, it is possible to make the high temperature strength satisfactory while reducing the content of Nb. For this reason, the left side value of Formula (i) is set to 5.0 or more. Here, to achieve a 0.2% proof stress of 30 MPa or more at 850°C, the left side value of Formula (i) is preferably set to 8.0 or more. An upper limit of the left side value of Formula (i) is not particularly limited. However, if the left side value is more than 10.0, the effect of enhancing the 0.2% proof stress diminishes, and thus the upper limit is preferably set to 10.0.

## 2. Metal Micro-Structure

### 2-1. Cu particles

**[0054]** In the steel sheet of the present embodiment, sizes of the formed Cu particles are limited. The Cu particles are Cu-based precipitates such as bcc-Cu, 9R, and  $\epsilon$ -Cu. Cu particles precipitate at temperatures of 350 to 800°C and have an effect of enhancing high temperature strength. However, if Cu particles precipitate finely in a large amount at normal temperature, normal-temperature ductility is decreased, and as a result, workability is decreased. For this reason, at normal temperature, it is desirable to restrain Cu particles from precipitating finely in a large amount and to keep the Cu particles in a dissolved-Cu state where the Cu particles are dissolved in a parent phase. Then, it is preferable to perform control such that Cu particles precipitate at a high temperature in a use environment so as to enhance high temperature strength.

**[0055]** Accordingly, an area fraction of Cu particles having diameters of 20 nm or less (hereinafter, will be denoted as a "fine-Cu-particle area fraction") is set to 2.0% or less. The fine-Cu-particle area fraction is preferably set to 1.5% or less, more preferably set to 1.0% or less, and further preferably set to 0.7% or less. This is because Cu particles having diameters more than 20 nm are relatively coarse and thus have a less adverse effect on normal-temperature ductility and high temperature strength. The fine-Cu-particle area fraction is desirably reduced as much as possible and is most preferably 0%. Note that Cu particles being 1 nm or more are determined to be the Cu particle described above.

**[0056]** Here, a method of measuring the fine-Cu-particle area fraction will be described. A thin film sample is created by an electrolytic polishing method and then photographed with a magnification of  $\times 100000$  under a transmission electron microscope (hereinafter, will be also denoted as a "TEM"). Image analysis software (e.g., ImageJ) is used to search for Cu particles that measure 20 nm or less in terms of equivalent circle diameter, and the area fraction is calculated. This process is performed in ten visual fields, and a division of a total area of the Cu particles having diameters of 20 nm or less by a total observation area is taken as the area fraction. A method for identifying the Cu particles is such that a point analysis is performed using a TEM-EDS on an image assumed to be an image of precipitates, and when Cu of a content equal to or higher than the content of Cu in the steel is detected, the precipitates are identified as Cu particles. In addition, a sample for observation is taken from a 1/4 width position from a sheet width center of the steel sheet and from a spot that is a sheet thickness center to 1/8, such that an observation surface is a section parallel to a rolling direction and parallel to a sheet thickness direction (hereinafter, will be also simply referred to as an "L section").

### 2-2. Maximum Length of TiN

**[0057]** When a steel sheet contains Ti, its high temperature strength can be enhanced. On the other hand, coarse TiN may be formed, thus decreasing high temperature fatigue properties. Accordingly, in the steel sheet of the present embodiment, TiN is preferably made to have a maximum length of 15  $\mu\text{m}$  or less. This is because if the maximum length of TiN is more than 15  $\mu\text{m}$ , fatigue properties at high temperature are decreased. For this reason, TiN is made to have a maximum length of 15  $\mu\text{m}$  or less and is preferably made to have a maximum length of 10  $\mu\text{m}$  or less. A lower limit of the maximum length of TiN is not particularly limited. However, it is often a case that the lower limit is 1.0  $\mu\text{m}$  in, for example, usual refining.

**[0058]** Here, a method of measuring the maximum length of TiN will be described. A sample is taken such that its L section serves as an observation surface. Note that it is preferable that a center of the L section be a 1/8 sheet thickness position, and the L section be positioned at a 1/4 to 1/2 position in a sheet width direction. Subsequently, the resultant sample is embedded in thermoset resin, with the observation surface facing upward. The maximum length is measured by observing the observation surface subjected to mirror polish by mechanical polishing, under a scanning electron

microscope (hereinafter, will be simply denoted as a "SEM").

[0059] In an SEM/EDS analysis, Ti, N, Fe, Cr, and Nb are determined as elements to be analyzed. When a total of the elements is taken as 100 at%, an inclusion that contains 40 at% or more of Ti and has a substantial polygonal shape is defined as TiN. A length of a longest axis of the TiN is taken as the maximum length and measured on an image. The length of the longest axis of the TiN is defined as a length of a longest line that connects two points on an outer circumference of the TiN and is usually a length of a straight line that diagonally connects substantial corners of the TiN. As a measurement range, ten measurement fields of view centered about a 1/8 sheet thickness position are set. The measurement fields of view are each made to have a size that is an area of 0.25 mm in the rolling direction  $\times$  0.20 mm in the sheet thickness direction, and a center position of each measurement field of view in the sheet thickness direction is made to match the 1/8 sheet thickness position. The number of TiNs to be measured is 50 or more in total in the ten fields of view. A maximum value of lengths of longest axes of all measured TiNs is determined and taken as the maximum length of TiN.

### 3. Amount of precipitating Nb

[0060] As described later, it is desirable to enhance a toughness of the steel sheet of the present embodiment for its application. To enhance the toughness, it is preferable to confine formation of Laves phases being precipitates within a certain range. If Laves phases are formed in a large amount, the Laves phases tend to serve as an origin of occurrence of a brittle fracture, and as a result, toughness tends to be decreased.

[0061] An amount of precipitating Laves phases can be checked by measuring an amount of precipitating Nb by an electrolytic extraction residue method. Specifically, the amount of precipitating Nb is preferably set to 0.1% or less in mass%. Note that, from a viewpoint of toughness and a viewpoint of other properties such as high temperature strength, the amount of precipitating Nb is more preferably made 0.05% or less in mass%.

[0062] As described above, by making the amount of precipitating Nb 0.1% or less, it is possible, for example, to provide a steel sheet that has a thickness of 2 mm to be used as an exhaust component of an automobile and has such a satisfactory toughness that a ductile-brittle transition temperature is  $-40^{\circ}\text{C}$  or less in a V-notch Charpy impact test as described in JIS Z 2242:2018. Note that the ductile-brittle transition temperature is a temperature at which a brittle fracture surface accounts for 50% of a fracture surface after the Charpy impact test.

[0063] The amount of precipitating Nb is preferably measured by the following procedure using the electrolytic extraction residue method. Specifically, about 0.4 g of a sample is electrolyzed with 10%-acetylacetone-1%-tetramethylammonium chloride/methanol with a current value of 20 mA/cm<sup>2</sup>. A solution of the electrolyzed sample is then filtered through a 0.2  $\mu\text{m}$  filter, and then the residue is subjected to acid decomposition. Then, an amount (mass%) of Nb that is analyzed as residues of electroextraction with an ICP atomic emission spectroscopy apparatus is calculated as the amount of precipitating Nb.

### 4. Application

[0064] The steel sheet of the present embodiment is preferably used in an application of an exhaust member of an automobile or a motorcycle. For example, examples of the exhaust member include an exhaust manifold, a catalytic converter case, an EGR cooler case, an exhaust recovering device, a DPF, a GPF, a center pipe, a muffler, a flange, a muffler hanger, a housing forming an outer frame of a turbocharger, a precision part inside a nozzle vane-type turbocharger (e.g., a precision part called a back plate, an oil deflector, a compressor wheel, a nozzle mount, a nozzle plate, a nozzle vane, a drive ring, or a drive lever). These are not limited to exhaust members for an engine-equipped vehicle and may be exhaust members for an electric vehicle or a fuel cell vehicle.

[0065] To be used in the applications described above, a sheet thickness of the steel sheet is preferably set to be within the range of 0.5 to 3.0 mm.

### 5. Production Method

[0066] A preferable method for producing the steel sheet of the present embodiment will be described. The steel sheet of the present embodiment can be stably produced by a production method described below.

#### (Melting Step)

[0067] A steel having the chemical composition described above is melted in an electric furnace or a converter and subsequently subjected to secondary refining. During the melting, a ratio ( $\text{Al}_2\text{O}_3/\text{MgO}$ ) of  $\text{Al}_2\text{O}_3$ , which is Al-based inclusions, to MgO, which is MgO-based inclusions is preferably set to 15.0 or less. This is for making TiN have a maximum length of 15  $\mu\text{m}$  or less.  $\text{Al}_2\text{O}_3/\text{MgO}$  is more preferably set to 13.0 or less. To make  $\text{Al}_2\text{O}_3/\text{MgO}$  15.0 or less, it is only required to control a composition of a slag to adjust activities of MgO and  $\text{Al}_2\text{O}_3$  in the slag.

[0068] The melted steel is formed into a slab in conformity with a known casting method (continuous casting, etc.). In

order to avoid excessive mixture of inclusions during the continuous casting to reduce nucleation sites for crystallizing TiN, it is preferable to provide a setting time of one minute or more, preferably five minutes or more before the continuous casting. As a result, it becomes easy to make TiN have a maximum length of 15  $\mu\text{m}$  or less.

#### 5 (Hot Rolling Step)

**[0069]** Subsequently, hot rolling is performed on the resultant slab to produce a hot rolled sheet having a predetermined sheet thickness. A heating temperature for the slab is not particularly limited. However, it is usually preferable that the heating temperature be set to be within the range of 1180 to 1250°C. The hot rolling is preferably continuous rolling, and the slab is rolled with a hot rolling mill with a plurality of stands. The hot rolled sheet is then coiled into a coil shape. A coiling temperature is not particularly limited. However, the coiling temperature is preferably 300 to 750°C from a viewpoint of refining a micro-structure. After being subjected to the hot rolling and coiled into a coil, the hot rolled sheet may be subjected to hot-rolled sheet annealing as necessary. In addition, after the annealing, pickling may be performed as necessary.

#### 15 (Cold Rolling Step)

**[0070]** Cold rolling is performed on the hot rolled sheet to produce a cold rolled sheet. For the cold rolling, a tandem rolling mill or a Sendzimir rolling mill is usually used. A rolling reduction of the cold rolling is not particularly limited. It is only required the rolling reduction is only required to be adjusted as appropriate in accordance with a desired sheet thickness.

#### (Cold Rolled Sheet Annealing)

**[0071]** The produced cold rolled sheet is annealed. The annealing of the cold rolled sheet is performed to provide a recrystallized structure. For the chemical composition of the steel sheet of the present embodiment, a recrystallization temperature is within the range of about 870 to 1000°C. For this reason, the annealing temperature is set within the temperature range. That is, the cold rolled sheet is retained at the annealing temperature that is set within the range of 870 to 1000°C.

**[0072]** If the annealing temperature is less than 870°C, recovery and recrystallization do not progress sufficiently, failing to provide a recrystallized structure. For this reason, the annealing temperature is preferably set to more than 870°C or more, more preferably 900°C or more. On the other hand, if the annealing temperature is less than 1000°C, grains coarsen, and in addition, an energy necessary for the annealing is increased, thus increasing production costs. For this reason, the annealing temperature is preferably set to 1000°C or less, more preferably 950°C or less.

**[0073]** An annealing duration of the annealing of the cold rolled sheet is not particularly limited. However, the annealing duration is preferably set to be within the range of 1 to 120 seconds in view of promoting recrystallization sufficiently and in view of production costs. The cold rolled sheet is retained at the annealing temperature for the annealing duration and then cooled. Although it is necessary to retain the cold rolled sheet within the temperature range of 870 to 1000°C so as to obtain a recrystallized structure, fine Cu particles may precipitate in a large amount when the cold rolled sheet is cooled from the temperature region. It is not desirable from a viewpoint of normal-temperature ductility. For this reason, two-stage cooling as described below is performed.

**[0074]** Specifically, it is preferable to perform cooling from the annealing temperature to 850°C at an average cooling rate of 5.0°C/s or less. Note that a temperature region from the annealing temperature to 850°C in the cooling will be called a first cooling region. The average cooling rate in the first cooling region is set to 5.0°C/s or less, so as to promote recrystallization of a ferritic phase in a parent phase and promote development of texture, which is effective in enhancing workability. If the average cooling rate in the first cooling region is more than 5.0°C/s, elongation to failure at normal temperature may be less than 30%, for example. When the cooling is performed in the first cooling region, Cu particles may precipitate. However, the Cu particles are relatively coarse, thus having a little influence on workability and yield stress. Therefore, it is important in the first cooling region to promote mainly recrystallization. The average cooling rate in the first cooling region is more preferably set to 4.0°C/s or less.

**[0075]** Note that, from a viewpoint of toughness, the average cooling rate in the first cooling region is preferably set to 1.5°C/s or more. If the average cooling rate in the first cooling region is as low as less than 1.5°C/s, the amount of precipitating Nb is more than 0.1% (mass%), thus causing Laves phases, which are coarse intermetallic compounds, to precipitate in a large amount in a cooling process. As a result, the Laves phases tend to serve as an origin of occurrence of a brittle fracture, and toughness becomes difficult to enhance. That is, a ductile-brittle transition temperature in a V-notch Charpy impact test becomes more than -40°C.

**[0076]** Thereafter, it is preferable to perform cooling from 850 to 350°C at an average cooling rate of more than 5.0°C/s. Note that a temperature region from 850°C to 350°C in the cooling will be called a second cooling region. The cooling rate in the second cooling region is set to more than 5.0°C/s, so as to restrain fine Cu particles from precipitating in a large amount.

**[0077]** With consideration given to pickling properties in a subsequent step and a sheet shape, the average cooling rate in the second cooling region is preferably set to 8.0°C/s or more. From a viewpoint of decreasing yield stress, the average cooling rate is preferably set to 10°C/s or more. An upper limit of the average cooling rate in the second cooling region is not particularly limited. However, the upper limit is usually 50°C/s. In light of the steel sheet being in a sheet shape, the upper

limit of the average cooling rate is more preferably 25°C/s.

**[0078]** By controlling the average cooling rates in the first cooling region and the second cooling region in this manner, it is possible to restrain fine Cu particles from precipitating in a large amount. That is, an area fraction of Cu particles having diameters of 20 nm or less can be made 2.0% or less. To make the fine-Cu-particle area fraction 1.0% or less, the cooling rate in the second cooling rate is preferably set to 7.0°C/s or more.

**[0079]** It is only required to select an annealing atmosphere for the cold rolled sheet as appropriate in accordance with necessity. In addition, after the annealing, thermal refining rolling, a tension leveler, or the like may be performed. After the annealing, the cooling, and the like, pickling is performed. Conditions for the pickling are only required to conform to a conventional method. The resultant cold rolled steel sheet is to be formed into an exhaust member in conformance with a conventional method.

**[0080]** The steel sheet of the present embodiment will be described below more specifically with examples. However, the present embodiment is not limited to these examples.

#### EXAMPLE 1

**[0081]** Steels having chemical compositions shown in Table 1 and Table 2 were melted and cast into slabs. In the melting,  $\text{Al}_2\text{O}_3/\text{MgO}$  was set to 15.0 or less. In addition, a setting time of one minute or more was provided before the casting. The resultant slabs were each heated at 1250°C, subjected to hot rolling into a hot rolled sheet having a thickness of 5 mm, and coiled at 450°C. The coil was then pickled and then subjected to cold rolling to have a thickness of 2 mm, thus being formed into a cold rolled sheet. The cold rolled sheet was annealed such that the cold rolled sheet was retained at a temperature of 920°C for 120 seconds and then cooled. In the cooling after the retention at the annealing temperature, the cooling rate in the temperature region from 920 to 850°C was set to 5.0°C/s, and the cooling rate in the temperature region from 850 to 350°C was set to 8.0°C/s. After the annealing, the cold rolled sheet was pickled, and thus a product sheet was obtained.

[Table 1]

Table 1

No.	Chemical composition (mass%, balance: Fe and impurities)																							Left side value of Formula (i)			
	C	Si	Mn	P	S	N	Cr	Cu	Ti	Nb	Mo	B	Al	Ni	V	W	Sn	Mg	Sb	Zr	Ta	Hf	Co	Ca	REM	Ga	
A1	0.006	0.20	0.20	0.04	0.0009	0.010	17.5	1.24	0.14	0.146	0.20	0.0003	0.04	0.06	0.05	-	-	-	-	-	-	-	-	-	-	-	8.2
A2	0.005	0.20	0.21	0.03	0.0012	0.009	17.6	1.24	0.15	0.150	0.05	0.0003	0.05	0.15	0.05	-	-	-	-	-	-	-	-	-	-	-	7.8
A3	0.006	0.41	0.20	0.03	0.0018	0.008	18.0	1.22	0.18	0.018	0.05	0.0002	0.36	0.05	0.05	-	-	-	-	-	-	-	-	-	-	-	5.0
A4	0.006	0.20	0.21	0.03	0.0030	0.009	17.5	1.22	0.15	0.160	0.30	0.0003	0.06	0.08	0.05	-	-	-	-	-	-	-	-	-	-	-	8.3
A5	0.004	0.40	0.19	0.03	0.0022	0.008	18.0	1.21	0.18	0.094	0.06	0.0004	0.47	0.05	0.05	-	-	-	-	-	-	-	-	-	-	-	8.0
A6	0.004	0.40	0.19	0.04	0.0027	0.011	18.0	1.21	0.17	0.096	0.48	0.0005	0.10	0.05	0.05	-	-	-	-	-	-	-	-	-	-	-	7.0
A7	0.004	0.38	0.19	0.04	0.0005	0.008	17.9	1.21	0.18	0.096	0.48	0.0005	0.26	0.05	0.03	-	-	-	-	-	-	-	-	-	-	-	7.7
A8	0.004	0.21	0.20	0.03	0.0018	0.010	17.4	1.24	0.14	0.146	0.10	0.0004	0.05	0.06	0.05	-	-	-	-	-	-	-	-	-	-	-	8.0
A9	0.004	0.23	0.20	0.04	0.0015	0.010	17.4	1.24	0.12	0.145	0.15	0.0003	0.03	0.06	0.08	-	-	-	-	-	-	-	-	-	-	-	8.0
A10	0.006	0.20	0.20	0.04	0.0012	0.010	17.5	1.24	0.14	0.146	0.20	0.0003	0.04	0.06	0.05	-	-	-	-	-	-	-	-	0.0010	-	-	8.2
A11	0.005	0.21	0.20	0.04	0.0039	0.010	17.6	1.19	0.13	0.156	0.17	0.0005	0.04	0.06	0.05	-	-	0.0004	-	-	-	-	-	-	-	-	8.7
A12	0.005	0.23	0.20	0.06	0.0025	0.010	17.6	1.19	0.11	0.154	0.17	0.0005	0.03	0.06	0.09	0.56	-	-	-	-	-	-	-	-	-	-	10.1
A13	0.005	0.25	0.19	0.09	0.0012	0.010	17.6	1.17	0.12	0.147	0.17	0.0005	0.05	0.06	0.05	-	-	-	-	-	-	-	-	0.0015	-	-	13.0
A14	0.007	0.39	0.21	0.03	0.0014	0.010	18.0	1.42	0.15	0.103	0.03	0.0003	0.05	0.01	0.15	0.15	-	-	0.12	-	-	-	-	0.0026	-	-	6.3
A15	0.006	0.39	0.21	0.03	0.0011	0.009	18.5	1.20	0.15	0.098	0.05	0.0010	0.05	0.01	0.10	-	0.05	-	-	-	-	-	-	0.02	-	-	6.1
A16	0.007	0.38	0.20	0.03	0.0018	0.009	18.0	1.21	0.14	0.197	0.05	0.0013	0.04	0.01	0.08	-	-	0.0023	-	0.10	-	-	-	-	-	-	9.5
A17	0.005	0.20	0.21	0.03	0.0028	0.009	17.6	1.24	0.15	0.150	0.05	0.0003	0.05	0.15	0.05	-	-	-	-	-	0.26	-	-	-	-	0.09	7.8
A18	0.006	0.20	0.21	0.03	0.0043	0.009	17.6	1.20	0.15	0.150	0.14	0.0003	0.05	0.10	0.05	-	-	-	-	-	-	-	0.22	-	-	-	7.8
A19	0.002	0.08	0.39	0.02	0.0002	0.015	19.5	1.50	0.08	0.090	0.40	0.0002	0.01	0.01	0.02	-	-	-	-	-	-	-	-	-	-	-	5.1
A20	0.005	0.11	0.94	0.03	0.0038	0.003	17.0	1.10	0.23	0.190	0.02	0.0023	0.23	0.02	0.18	-	-	-	-	-	-	-	-	-	-	-	9.8
A21	0.017	0.92	0.10	0.02	0.0047	0.019	18.2	1.25	0.18	0.080	0.20	0.0018	0.17	0.09	0.11	-	-	-	-	-	-	-	-	-	-	-	5.2
A22	0.006	0.20	0.21	0.03	0.0005	0.009	17.5	1.22	0.15	0.160	0.30	0.0003	0.06	0.08	0.05	-	-	-	-	-	-	0.02	-	-	-	-	8.3

\* indicates that the value fell out of the requirement in the present embodiment

[Table 2]

5

10

15

20

25

30

35

40

45

50

55

Table 2

No.	Chemical composition (mass%, balance : Fe and impurities)																							Left side value of Formula (i)			
	C	Si	Mn	P	S	N	Cr	Cu	Ti	Nb	Mo	B	Al	Ni	V	W	Sn	Mg	Sb	Zr	Ta	Hf	Co		Ca	REM	Ga
B1	0.006	0.37	0.20	0.03	0.0027	0.019	17.6	1.42	0.15	0.050	0.05	0.0005	0.03	0.05	0.05	-	-	-	-	-	-	-	-	-	-	-	47 *
B2	0.004	0.41	0.19	0.03	0.0022	0.009	17.7	1.19	0.16	0.010	0.05	0.0004	0.04	0.05	0.11	-	-	-	-	-	-	-	-	-	-	-	34 *
B3	0.004	0.40	0.19	0.03	0.0022	0.009	18.0	1.22	0.17	0.005	0.47	0.0004	0.07	0.05	0.05	-	-	-	-	-	-	-	-	-	-	-	38 *
B4	0.025 *	0.20	0.20	0.04	0.0012	0.010	17.5	1.24	0.14	0.146	0.20	0.0003	0.04	0.06	0.05	-	-	-	-	-	-	-	-	-	-	-	82
B5	0.004	1.20 *	0.25	0.04	0.0018	0.013	18.3	1.09	0.15	0.086	0.22	0.0005	0.03	0.09	0.13	-	-	-	-	-	-	-	-	-	-	-	70
B6	0.003	0.90	1.40 *	0.12 *	0.0033	0.019	19.5	1.11	0.09	0.146	0.06	0.0013	0.11	0.05	0.16	-	-	-	-	-	-	-	-	-	-	-	156
B7	0.013	0.83	0.92	0.16 *	0.0055 *	0.013	18.8	1.14	0.15	0.098	0.44	0.0005	0.09	0.08	0.04	-	-	-	-	-	-	-	-	-	-	-	178
B8	0.003	0.72	0.23	0.04	0.0018	0.015	19.2	1.21	0.12	0.103	0.12	0.0004	0.03	0.25 *	0.04	-	-	-	-	-	-	-	-	-	-	-	71
B9	0.018	0.20	0.83	0.03	0.0029	0.011	21.2 *	1.11	0.10	0.120	0.25	0.0009	0.11	0.15	0.05	-	-	-	-	-	-	-	-	-	-	-	72
B10	0.005	0.12	0.20	0.05	0.0027	0.010	17.2	0.90 *	0.11	0.098	0.33	0.0013	0.19	0.11	0.03	-	-	-	-	-	-	-	-	-	-	-	86
B11	0.003	0.53	0.12	0.02	0.0014	0.012	17.5	1.04	0.21	0.001 *	0.10	0.0003	0.04	0.04	0.12	-	-	-	-	-	-	-	-	-	-	-	20 *
B12	0.008	0.98	0.56	0.05	0.0013	0.015	17.5	1.23	0.14	0.135	0.01 *	0.0014	0.09	0.05	0.06	-	-	-	-	-	-	-	-	-	-	-	91
B13	0.008	0.23	0.22	0.03	0.0018	0.018	17.6	1.20	0.20	0.096	0.14	0.0005	0.04	0.06	0.35 *	-	-	-	-	-	-	-	-	-	-	-	60
B14	0.009	0.15	0.25	0.02	0.0022	0.008	17.0	1.20	0.01 *	0.103	0.15	0.0004	0.08	0.18	0.09	-	-	-	-	-	-	-	-	-	-	-	56
B15	0.013	0.09	0.77	0.01	0.0012	0.008	17.0	1.30	0.13	0.146	0.23	0.0003	0.60 *	0.15	0.03	-	-	-	-	-	-	-	-	-	-	-	83
B16	0.004	0.83	0.25	0.01	0.0005	0.004	17.5	1.43	0.11	0.171	0.19	0.0035 *	0.11	0.19	0.02	-	-	-	-	-	-	-	-	-	-	-	71
B17	0.008	0.14	0.39	0.12 *	0.0009	0.025 *	18.3	1.42	0.19	0.197	0.21	0.0018	0.30	0.15	0.16	-	-	-	-	-	-	-	-	-	-	-	182

\* indicates that the value fell out of the requirement in the present embodiment

[0082] The product sheet (cold rolled sheet) was examined in fine Cu particle area fraction, high temperature strength,



oxidation resistance, and workability by the following procedure.

(Fine-Cu-Particle Area Fraction)

**[0083]** A thin film sample was created by an electrolytic polishing method and then photographed with a magnification of x100000 under a transmission electron microscope (hereinafter, will be also denoted as a "TEM"). Subsequently, a photographed image was subjected to image analysis software (e.g., ImageJ) to search for Cu particles that measure 20 nm or less in terms of equivalent circle diameter, and the area fraction was calculated. This observation was performed in ten visual fields, and a division of a total area of the Cu particles having diameters of 20 nm or less by a total observation area was taken as the area fraction. A method for identifying the Cu particles was such that a point analysis was performed using a TEM-EDS on an image assumed to be an image of precipitates, and when Cu of a content equal to or higher than the content of Cu in the steel was detected, the precipitates were identified as Cu particles. An L section was adopted as an observation surface, and a sample for observation was taken from a sheet width center to a 1/4 width position of the steel sheet and a 1/4 to 1/2 position in the sheet thickness of the steel sheet.

(High Temperature Strength)

**[0084]** The high temperature strength was evaluated in terms of 0.2% proof stress at 850°C. The 0.2% proof stress was measured by a high temperature tensile test at 850°C conforming to JIS G 0567:2020. A specimen used in the test was taken from a sheet width center of the steel sheet. In a shape of the specimen, a gauge length was set to 35 mm. In the test, a rolling direction of the specimen was set as a tensile direction. A case where a 0.2% proof stress at 850°C was 20 MPa or more was determined to be satisfactory in high temperature strength and written as good, and a case where the 0.2% proof stress at 850°C was 30 MPa or more was determined to be satisfactory in high temperature strength and written as excellent. In contrast, a case where the 0.2% proof stress at 850°C was less than 20 MPa was determined to be bad in high temperature strength and written as bad.

(Oxidation Resistance)

**[0085]** The oxidation resistance was evaluated by conducting a continuous oxidization test. Specifically, a continuous oxidization test in which a specimen was retained in the atmosphere at 950°C for 200 h was conducted. Note that the continuous oxidization test was conducted in conformity with JIS Z 2281:1993. When scale peeling or breakaway oxidation did not occur in the continuous oxidization test, the oxidation resistance was determined to be satisfactory and written as good. In contrast, when scale peeling or breakaway oxidation occurred in the continuous oxidization test, the oxidation resistance was determined to be bad and written as bad. Note that the specimen was taken from a vicinity of a sheet width center of the steel sheet.

(Workability)

**[0086]** The workability was evaluated in terms of normal-temperature ductility. The normal-temperature ductility was measured by conducting a tensile test at normal temperature. The tensile test was conducted in conformity with JIS Z 2241:2011. In the tensile test, a JIS No. 13B test coupon was fabricated from a vicinity of a sheet width center of the steel sheet such that a rolling direction of the steel sheet is parallel to a tensile direction, and the test coupon was used. As a result of the tensile test, an elongation to failure of 30% or more was determined to be satisfactory in normal-temperature ductility and written as good. In contrast, an elongation to failure of less than 30% was determined to be bad in normal-temperature ductility and written as bad. Results are collectively shown in Table 3 below.

[Table 3]

**[0087]**

Table 3

No.	Fine-Cu-particle area fraction (%)	Properties			
		High temperature strength 0.2% proof stresses at 850°C	Oxidation resistance Contamious oxidization at 950°C	Workability Normal-temperature ductility	
A1	0.5	Excellent	Good	Good	

# EP 4 491 755 A1

(continued)

	No.	Fine-Cu- particle area fraction (%)	Properties			
			High temperature strength 0.2% proof stresses at 850°C	Oxidation resistance Contamious oxidization at 950°C	Workability Normal- temperature ductility	
5	A2	0.2	Good	Good	Good	Inventive example
10	A3	0.1	Good	Good	Good	
	A4	0.5	Excellent	Good	Good	
	A5	03	Excellent	Good	Good	
15	A6	0.4	Good	Good	Good	
	A7	1.2	Good	Good	Good	
	A8	02	Excellent	Good	Good	
	A9	0.1	Excellent	Good	Good	
20	A10	03	Excellent	Good	Good	
	A11	0.5	Excellent	Good	Good	
	A12	02	Excellent	Good	Good	
25	A13	0.0	Excellent	Good	Good	
	A14	0.3	Good	Good	Good	
	A15	1.0	Good	Good	Good	
	A16	1.2	Excellent	Good	Good	
30	A17	0.3	Good	Good	Good	
	A18	0.5	Good	Good	Good	
	A19	2.0	Good	Good	Good	
	A20	0.9	Excellent	Good	Good	
35	A21	1.5	Good	Good	Good	
	A22	1.3	Excellent	Good	Good	
40	B1 *	1.8	<u>Bad</u>	Good	Good	Comparative example
	B2 *	0.6	<u>Bad</u>	Good	Good	
	B3 *	1.1	<u>Bad</u>	Good	Good	
	B4 *	2.1 *	<u>Bad</u>	<u>Bad</u>	<b>Bad</b>	
	B5 *	23 *	Good	Good	<u>Bad</u>	
45	B6 *	2.1 *	Excellent	<u>Bad</u>	<b>Bad</b>	
	B7 *	2.2 *	Excellent	<u>Bad</u>	<u>Bad</u>	
	B8 *	2.5 *	Good	<u>Bad</u>	<u>Bad</u>	
50	B9 *	2.1 *	Good	<u>Bad</u>	<u>Bad</u>	
	B10 *	0.1	<u>Bad</u>	Good	Good	
	B11 *	0.5	<u>Bad</u>	<u>Bad</u>	Good	
	B12 *	03	<u>Bad</u>	Good	Good	
55	B13 *	2.1 *	Good	Good	<u>Bad</u>	
	B14 *	1.6	<u>Bad</u>	<u>Bad</u>	Good	
	B15 *	2.2 *	Excellent	Good	<u>Bad</u>	

# EP 4 491 755 A1

(continued)

No.	Fine-Cu- particle area fraction (%)	Properties			
		High temperature strength 0.2% proof stresses at 850°C	Oxidation resistance Contamious oxidization at 950°C	Workability Normal- temperature ductility	
B16 *	2.5 *	Good	<u>Bad</u>	<u>Bad</u>	
B17 *	3.3 *	<u>Bad</u>	<u>Bad</u>	<u>Bad</u>	
* indicates that the value fell out of the requirement in the present embodiment					

**[0088]** A1 to A22, which satisfied the requirements of the present embodiment, each showed satisfactory high temperature strength, oxidation resistance, and workability. In contrast, B1 to B19, which did not satisfy the requirements of the present embodiment, each showed a result that at least one of high temperature strength, oxidation resistance, and workability was poor.

## EXAMPLE 2

**[0089]** The same procedure as in EXAMPLE 1, up to the cold rolling was performed on a steel having a composition as No. A1 in Table 1, and as shown in Table 4, cold rolled sheets were subjected to the annealing with various annealing temperatures and the cooling rates and were pickled. Thus, cold rolled sheets as product sheets were produced. Note that a retention duration in the annealing was the same as in EXAMPLE 1. For each product sheet (cold rolled sheet), the amount of precipitating Nb and the ductile-brittle transition temperature were calculated by a procedure described below, and the fine-Cu-particle area fraction, the high temperature strength, the oxidation resistance, and the workability were examined by the same procedure as in EXAMPLE 1. In addition, lengths of TiN of inventive examples of the present invention were measured by the same procedure as in EXAMPLE 3, and it was confirmed that maximum lengths of the lengths were all 15 μm or less.

(Amount of Precipitating Nb)

**[0090]** The amount of precipitating Nb was measured by the following procedure. Specifically, about 0.4 g of a sample that was cut from each steel sheet was electrolyzed with 10%-acetylacetone-1%-tetramethylammonium chloride/methanol at a current value of 20 mA/cm<sup>2</sup>. A solution of the electrolyzed sample was then filtered through a 0.2 μm filter, and then the residue was subjected to acid decomposition. Then, an amount (mass%) of Nb that was analyzed as residues of electroextraction with an ICP atomic emission spectroscopy apparatus was calculated as the amount of precipitating Nb.

(Ductile-Brittle Transition Temperature)

**[0091]** In addition, a Charpy specimen was taken from the resultant steel sheet, and a V-notch Charpy impact test as described in JIS Z 2242:2018 was conducted on the Charpy specimen to measure the ductile-brittle transition temperature. The Charpy specimen was taken such that a rolling direction of the steel sheet was a longitudinal direction of the specimen, and a direction perpendicular to the rolling direction was a width direction of the specimen. The Charpy specimen that was made to have a size of 55 mm × 10 mm × 2 mm and into which a V notch was introduced in the direction perpendicular to the rolling direction was used.

[Table 4]

[0092]

Table 4

No.	Production condition			Fine-Cu- particle area fraction (%)	The amount of precipitating Nb (%)	Properties				
	Annealing temperature (°C)	Average cooling rate (°C/s)				High temperature strength 0.2% proof stresses at 850°C	Oxidation resistance Continuous oxidization at 950°C	Workability Normal- temperature ductility	Ductile-brittle transition temperature (°C)	
		From annealing temperature to 850°C	From 850°C to 350°C							
C1	920	5.0	11.0	0.5		Excellent			-60	Inventive ex- ample
C2	900	4.0	10.0	0.7	0.05	Excellent	Good	Good	-50	
C3	880	5.0	16.0	0.2	0.05	Excellent	Good	Good	-60	
C4	920	5.0	6.0	1.2	0.06	Good	Good	Good		
C5	900	4.0	7.0	1.0	0.08	Good	Good	Good	-40	Comparative example
C6	880	4.0	6.0	1.9		Good	Good	Good	-40	
C7		3.0	<u>4.0</u>	3.1 *	0.09	Good	Good	<u>Bad</u>	-40	
C8	880	3.0	<u>3.0</u>	4.2 *	0.10	Good	Good	<u>Bad</u>	-40	
	920	<u>1.2</u>	11.0	0.7	0.15 **	Good	Good	Good	<u>0</u>	Inventive ex.
* indicates that the value fell out of the requirement in the present embodiment										
** indicates that the value fell out of the preferable range described in the present invention underline indicates that the value fell out of the preferable producing condition described in the present invention double underline indicates that the value fell out of the more preferable production condition described in the present invention, or the value fell out of its targeted property value of toughness										

**[0093]** In cases where the fine-Cu-particle area fraction satisfied the preferable range according to the present embodiment, the high temperature strength was enhanced. C7 and C8 did not satisfy preferable production conditions according to the present embodiment and did not satisfy the specification of the fine-Cu-particle area fraction, and thus their workabilities were decreased. Although C9 was an inventive example of the present invention, the average cooling rate from the annealing temperature to 850°C was rather low. Thus, its ductile-brittle transition temperature was increased, and its toughness was decreased.

### EXAMPLE 3

**[0094]** A steel having the composition shown as No. A1 in Table 1 was melted. In the melting,  $\text{Al}_2\text{O}_3/\text{MgO}$  was adjusted, and then the steel was subjected to hot rolling, coiling, cold rolling, cold rolled sheet annealing, and pickling under the same conditions as in EXAMPLE 1. For this steel sheet, the maximum length of TiN was measured, and high temperature fatigue properties were examined by a procedure described below. In addition, the fine Cu particle area fraction, the high temperature strength, the oxidation resistance, and the workability were calculated by the same procedure as in EXAMPLE 1. Note that, in EXAMPLE 3, all fine-Cu-particle area fractions were 2.0% or less. In addition, amounts of precipitating Nb of inventive examples of the present invention were measured by the same procedure as in EXAMPLE 2, and it was confirmed that their values were all 0.1% or less in terms of mass%.

(Maximum Length of TiN)

**[0095]** A sample was taken such that its L section served as an observation surface. Note that a center of the L section was a 1/8 sheet thickness position, and the L section was positioned at a center to a 1/4 width position in a sheet width direction. Subsequently, the resultant sample was embedded in thermoset resin, with the observation surface facing upward. The maximum length was measured by observing the observation surface subjected to mirror polish by mechanical polishing, under a scanning electron microscope (hereinafter, will be simply denoted as a "SEM").

**[0096]** In an SEM/EDS analysis, Ti, N, Fe, Cr, and Nb were determined as elements to be analyzed. When a total of the elements was taken as 100 at%, an inclusion that contained 40 at% or more of Ti and had a substantial polygonal shape was defined as TiN. A length of a longest axis of the TiN was taken as the maximum length and measured on an image. The length of the longest axis of the TiN is defined as a length of a longest line that connects two points on an outer circumference of the TiN and is usually a length of a straight line that orthogonally connects substantial corners of the TiN. As a measurement range, ten measurement fields of view centered about a 1/8 sheet thickness position were set. The measurement fields of view were each made to have a size that was an area of 0.25 mm in the rolling direction  $\times$  0.20 mm in the sheet thickness direction, and a center position of each field of view in the sheet thickness direction was made to match the 1/8 sheet thickness position. The number of TiNs to be measured was 50 or more in total in the ten fields of view. A maximum value of lengths of longest axes of all measured TiNs was determined and taken as the maximum length of TiN.

(High Temperature Fatigue Properties)

**[0097]** The high temperature fatigue properties were evaluated by conducting an 800°C plane bending fatigue test. JIS No. 1 test coupons were taken from a vicinity of a sheet width center of a resultant product sheet such as a longitudinal direction of each test coupon was parallel to a rolling direction of the product sheet, seven of the test coupons were subjected to the test in conformity with JIS Z 2275:1978, an S-N curve was taken from the test, and a fatigue limit was determined. The fatigue limit was defined as an average value of a strength with which a test coupon did not rupture and a minimum strength of strengths with which a test coupon ruptured at  $1 \times 10^7$  cycles. A case where the fatigue limit was 45 MPa or more was determined to be good, and a case where the fatigue limit was less than 45 MPa was determined to be bad. A test temperature was set to 800°C. Note that the seven test coupons were taken at certain intervals so that taking the test coupons had no influence.

[Table 5]

**[0098]**

Table 5

No.	Production condition	Maximum length of TiN (μm)	Properties				
	Al <sub>2</sub> O <sub>3</sub> /MgO		High temperature strength 0.2% proof stresses at 850°C	Oxidation resistance Continuous oxidization at 950°C	Workability Normal-temperature ductility	High temperature fatigue properties	
D1	12	4	Excellent	Good	Good	Good	Inventive example
D2	13	8	Excellent	Good	Good	Good	
D3	12	5	Excellent	Good	Good	Good	
D4	8	2	Excellent	Good	Good	Good	
D5	14	14	Excellent	Good	Good	Good	
D6	19	18 **	Excellent	Good	Good	<u>Bad</u>	
** indicates that the value fell out of the preferable range described in the present invention							

**[0099]** In cases where the maximum length of TiN was 15  $\mu\text{m}$  or less, the high temperature fatigue properties were enhanced. In the example of D6, in which the maximum length of TiN was more than 15  $\mu\text{m}$ , its high temperature fatigue properties were decreased.

#### Appendix

#### **[0100]**

(1) A ferritic stainless steel sheet comprising a chemical composition that consists of, in mass%:

C: 0.02% or less,  
 Si: 1.0% or less,  
 Mn: 1.0% or less,  
 P: 0.01 to 0.10%,  
 S: 0.0001 to 0.005%,  
 N: 0.02% or less,  
 Cr: 17.0 to 20.0%,  
 Cu: 1.0 to 1.5%,  
 Ti: 0.05 to 0.3%,  
 Nb: 0.005 to 0.2%,  
 Mo: 0.02 to 0.5%,  
 B: 0.0001 to 0.0030%,  
 Al: 0.005 to 0.5%,  
 Ni: 0.01 to 0.2%,  
 V: 0.01 to 0.2%,  
 W: 0 to 2.0%,  
 Sn: 0 to 0.5%,  
 Mg: 0 to 0.01%,  
 Sb: 0 to 0.5%,  
 Zr: 0 to 0.3%,  
 Ta: 0 to 0.3%,  
 Hf: 0 to 0.3%,  
 Co: 0 to 0.3%,  
 Ca: 0 to 0.01%,  
 REM: 0 to 0.2%, and  
 Ga: 0 to 0.3%,

with the balance: Fe and impurities, and  
satisfies Formula (i) shown below, wherein  
an area fraction of Cu particles having a diameter of 20 nm or less is 2.0% or less:

$$86P + 33Nb + Mo + 4Al \geq 5.0 \quad (i)$$

where symbols of elements in Formula (i) shown above indicate contents (mass%) of elements contained in the steel sheet, and zero is set to a symbol of an element when the element is not contained.

(2) The ferritic stainless steel sheet according to (1) above, wherein the chemical composition contains, in mass%, one or more elements selected from:

W: 0.05 to 2.0%,  
Sn: 0.01 to 0.5%,  
Mg: 0.0002 to 0.01%,  
Sb: 0.01 to 0.5%,  
Zr: 0.01 to 0.3%,  
Ta: 0.01 to 0.3%,  
Hf: 0.01 to 0.3%,  
Co: 0.01 to 0.3%,  
Ca: 0.0001 to 0.01%,  
REM: 0.001 to 0.2%, and  
Ga: 0.0002 to 0.3%.

(3) The ferritic stainless steel sheet according to (1) or (2) above, wherein a maximum length of TiN is 15 μm or less.

(4) The ferritic stainless steel sheet according to any one of (1) to (3) above, wherein an amount of precipitating Nb is 0.1% or less in mass%.

(5) An exhaust member comprising the ferritic stainless steel sheet according to any one of (1) to (4) above.

## Claims

1. A ferritic stainless steel sheet comprising a chemical composition that consists of, in mass%:

C: 0.02% or less,  
Si: 1.0% or less,  
Mn: 1.0% or less,  
P: 0.01 to 0.10%,  
S: 0.0001 to 0.005%,  
N: 0.02% or less,  
Cr: 17.0 to 20.0%,  
Cu: 1.0 to 1.5%,  
Ti: 0.05 to 0.3%,  
Nb: 0.005 to 0.2%,  
Mo: 0.02 to 0.5%,  
B: 0.0001 to 0.0030%,  
Al: 0.005 to 0.5%,  
Ni: 0.01 to 0.2%,  
V: 0.01 to 0.2%,  
W: 0 to 2.0%,  
Sn: 0 to 0.5%,  
Mg: 0 to 0.01%,  
Sb: 0 to 0.5%,  
Zr: 0 to 0.3%,  
Ta: 0 to 0.3%,  
Hf: 0 to 0.3%,  
Co: 0 to 0.3%,

Ca: 0 to 0.01%,  
 REM: 0 to 0.2%, and  
 Ga: 0 to 0.3%,  
 with the balance: Fe and impurities, and  
 satisfies Formula (i) shown below, wherein  
 an area fraction of Cu particles having a diameter of 20 nm or less is 2.0% or less:

$$86P + 33Nb + Mo + 4Al \geq 5.0 \quad (i)$$

where symbols of elements in Formula (i) shown above indicate contents (mass%) of elements contained in the steel sheet, and zero is set to a symbol of an element when the element is not contained.

2. The ferritic stainless steel sheet according to claim 1, wherein the chemical composition contains, in mass%, one or more elements selected from:

W: 0.05 to 2.0%,  
 Sn: 0.01 to 0.5%,  
 Mg: 0.0002 to 0.01%,  
 Sb: 0.01 to 0.5%,  
 Zr: 0.01 to 0.3%,  
 Ta: 0.01 to 0.3%,  
 Hf: 0.01 to 0.3%,  
 Co: 0.01 to 0.3%,  
 Ca: 0.0001 to 0.01%,  
 REM: 0.001 to 0.2%, and  
 Ga: 0.0002 to 0.3%.

3. The ferritic stainless steel sheet according to claim 1, wherein a maximum length of TiN is 15 μm or less.

4. The ferritic stainless steel sheet according to claim 2, wherein a maximum length of TiN is 15 μm or less.

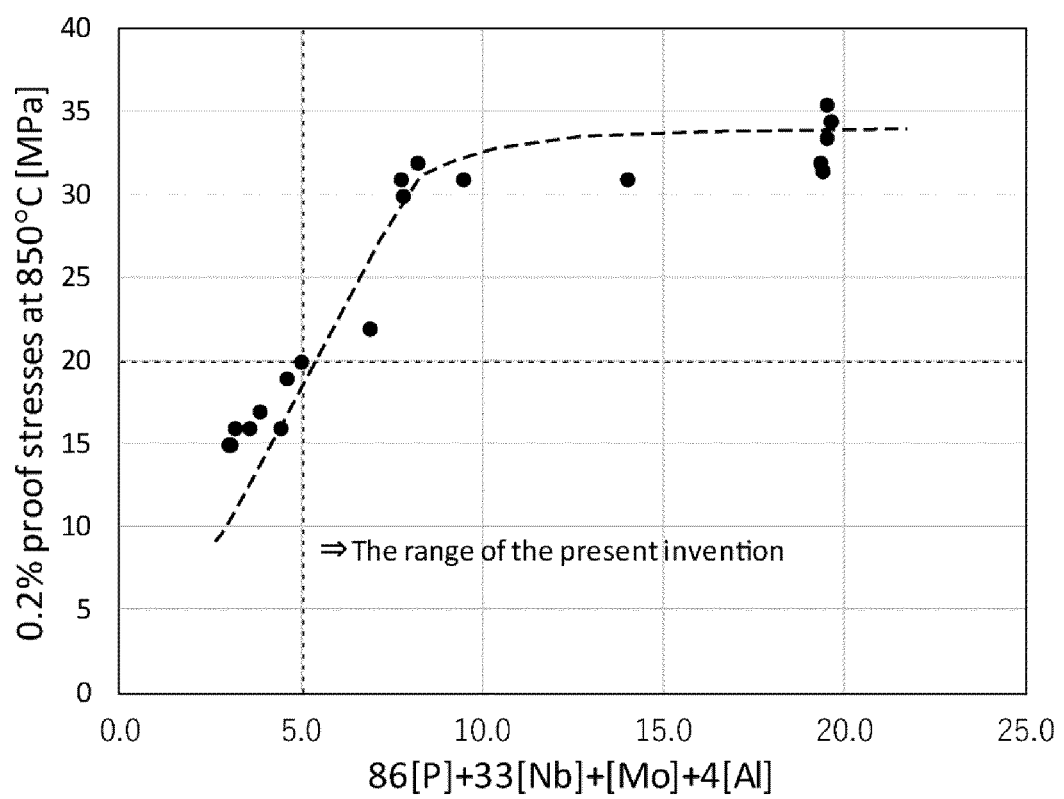
5. The ferritic stainless steel sheet according to any one of claims 1 to 4, wherein an amount of precipitating Nb is 0.1% or less in mass%.

6. An exhaust member comprising the ferritic stainless steel sheet according to any one of claims 1 to 4.

7. An exhaust member comprising the ferritic stainless steel sheet according to claim 5.



FIGURE 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/030359

## A. CLASSIFICATION OF SUBJECT MATTER

**C22C 38/00**(2006.01)i; **C22C 38/60**(2006.01)i; **C21C 7/06**(2006.01)n; **C21D 9/46**(2006.01)n  
 FI: C22C38/00 302Z; C22C38/60; C21C7/06; C21D9/46 R

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 C22C38/00-38/60; C21C7/06; C21D9/46

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996  
 Published unexamined utility model applications of Japan 1971-2022  
 Registered utility model specifications of Japan 1996-2022  
 Published registered utility model applications of Japan 1994-2022

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2017-206725 A (JFE STEEL CORP.) 24 November 2017 (2017-11-24) claims, paragraphs [0034], [0035], [0040], [0047]-[0057]	1-2, 5
A		3-4, 6-7
A	JP 2013-100595 A (JFE STEEL CORP.) 23 May 2013 (2013-05-23)	1-7
A	WO 03/004714 A1 (NISSHIN STEEL CO., LTD.) 16 January 2003 (2003-01-16)	1-7
A	JP 2014-141735 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP.) 07 August 2014 (2014-08-07)	1-7

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

16 September 2022

Date of mailing of the international search report

27 September 2022

Name and mailing address of the ISA/JP

Japan Patent Office (ISA/JP)  
 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915  
 Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.  
**PCT/JP2022/030359**

5  
  
10  
  
15  
  
20  
  
25  
  
30  
  
35  
  
40  
  
45  
  
50  
  
55

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
JP	2017-206725	A	24 November 2017	(Family: none)			
JP	2013-100595	A	23 May 2013	US	2014/0241931	A1	
				EP	2767605	A1	
				CN	103874778	A	
				KR	10-2014-0068199	A	
WO	03/004714	A1	16 January 2003	US	2004/0170518	A1	
				EP	1413640	A1	
				KR	10-2004-0007764	A	
				CN	1524130	A	
JP	2014-141735	A	07 August 2014	KR	10-2015-0083457	A	
				CN	104884657	A	

**REFERENCES CITED IN THE DESCRIPTION**

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

**Patent documents cited in the description**

- WO 034714 A [0004]
- JP 2000297355 A [0004]
- JP 2000303149 A [0004]
- JP 2008189974 A [0004]
- JP 2010248620 A [0004]