

(19)



(11)

EP 4 446 442 A1

(12)

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

(43) Date of publication:

16.10.2024 Bulletin 2024/42

(51) International Patent Classification (IPC):

C21D 9/46 ^(2006.01) **C22C 38/00** ^(2006.01)
C22C 38/54 ^(2006.01)

(21) Application number: **22904135.5**

(52) Cooperative Patent Classification (CPC):

C21D 9/46; C22C 38/00; C22C 38/54

(22) Date of filing: **01.12.2022**

(86) International application number:

PCT/JP2022/044388

(87) International publication number:

WO 2023/106204 (15.06.2023 Gazette 2023/24)

(84) Designated Contracting States:

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

Designated Extension States:

BA

Designated Validation States:

KH MA MD TN

(72) Inventors:

- **FUJIMURA, Yoshitomo**
Tokyo 100-0005 (JP)
- **HAMADA, Takahito**
Tokyo 100-0005 (JP)
- **HAMADA, Jun-ichi**
Tokyo 100-0005 (JP)

(30) Priority: **09.12.2021 JP 2021200093**

(74) Representative: **Plasseraud IP**

**104 Rue de Richelieu
CS92104
75080 Paris Cedex 02 (FR)**

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

(54) **FERRITIC STAINLESS STEEL AND METHOD FOR MANUFACTURING SAME**

(57) A ferritic stainless steel in accordance with an aspect of the present invention contains not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than

0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass, and the other part composed of Fe and an inevitable impurity, the ferritic stainless steel having a dislocation density ρ of not less than 0.91×10^{14} [m⁻²] as derived by the Williamson and Hall method.

EP 4 446 442 A1

Description

Technical Field

5 **[0001]** The present invention relates to ferritic stainless steel and method for manufacturing the ferritic stainless steel.

Background Art

10 **[0002]** Ferritic stainless steels, which are used in: a catalytic carrier (including an electric type and a heating type) for exhaust gas purification provided in an automobile, a two-wheeled vehicle, or the like; a stove burning tube; a combustion gas exhaust device in a plant; or the like, are required to have high oxidation resistance at high temperatures (high-temperature oxidation resistance).

15 **[0003]** Patent Literature 1 discloses a high Al-containing ferritic stainless steel further improved in high-temperature oxidation resistance. The high Al-containing ferritic stainless steel disclosed in Patent Literature 1 contains 15% to 25% of Cr and 4.5% to 6.0% of Al. Further, the amounts of Mn and Si added are reduced to achieve a low Mn content and a low Si content, and Mo is contained as an essential element, so that the high Al-containing ferritic stainless steel has an improved high-temperature oxidation resistance.

Citation List

20

[Patent Literature]

[0004] [Patent Literature 1]
Japanese Patent No. 3351836

25

Summary of Invention

Technical Problem

30 **[0005]** However, the technology as described above may have reduce toughness due to excessive amounts of Al and Mo added, and this may adversely affect producibility.

[0006] An object of an aspect of the present invention is to provide a ferritic stainless steel which is excellent in high-temperature oxidation resistance and toughness.

35

Solution to Problem

40 **[0007]** In order to attain the object, a ferritic stainless steel in accordance with an aspect of the present invention is a ferritic stainless steel containing not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than 0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass, and the other part composed of Fe and an inevitable impurity, the ferritic stainless steel having a dislocation density ρ of not less than $0.91 \times 10^{14} [\text{m}^{-2}]$ as derived by the Williamson and Hall method, wherein in scanning electron microscope observation of random three $30 \mu\text{m} \times 30 \text{pm}$ portions in a cross section obtained by cutting the ferritic stainless steel along a plane perpendicular to a rolling direction, an average number of carbides each having (i) a Nb concentration of not less than 5 wt% as measured by energy dispersive X-ray spectroscopy and (ii) a particle diameter of not less than 0.1 μm is 2 to 15.

45

50 **[0008]** Further, a method for producing a ferritic stainless steel in accordance with an aspect of the present invention a method in which the ferritic stainless steel contains not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than 0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass, and the other part composed of Fe and an inevitable impurity, the method including: an annealing step of annealing a steel strip which has been hot-rolled, such that cooling time taken to cool the steel strip from an annealing temperature to 400 degrees after annealing is not less than 30 seconds; and a cold rolling step of carrying out, after a final annealing step, cold rolling until a dislocation density ρ derived by the Williamson and Hall method is not less than $0.91 \times 10^{14} [\text{m}^{-2}]$.

55

Advantageous Effects of Invention

[0009] According to an aspect of the present invention, it is possible to provide a ferritic stainless steel which is excellent in high-temperature oxidation resistance and toughness.

Brief Description of Drawings

[0010]

Fig. 1 is an enlarged view schematically illustrating a portion of a cross section of an alumina layer formed by heating an example ferritic stainless steel in accordance with an embodiment at 1050°C for 50 hours, the cross section being obtained by cutting the alumina layer in a thickness direction.

Fig. 2 is an enlarged view schematically illustrating a portion of an alumina layer in accordance with a comparative example.

Description of Embodiments

[Embodiments]

[0011] The following description will discuss in detail an embodiment of the present invention. In this specification, the term "stainless steel" means a stainless steel material the shape of which is not specifically limited. Examples of the stainless steel material include steel sheets, steel pipes, and steel bars. The unit "%" of the content of each constituent element is intended to mean "percent by mass" unless otherwise noted. Note also that, in the present application, the expression "A to B" indicates not less than A and not more than B.

(Composition of ferritic stainless steel)

[0012] Firstly, the following description will discuss essential elements contained in a ferritic stainless steel in accordance with the present embodiment.

[0013] The ferritic stainless steel in accordance with an embodiment of the present invention, in terms of a composition of components of the steel, contains not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than 0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass.

[0014] In the above composition, the Al content is reduced in comparison to conventional high Al-containing ferritic stainless steels. Since the ferritic stainless steel in accordance with an embodiment of the present invention has the above composition, it is possible to obtain a ferritic stainless steel which is excellent in toughness.

[0015] The following description will discuss the significance of the amount of each element contained in the ferritic stainless steel in accordance with an embodiment of the present invention. Note that the ferritic stainless steel contains, in addition to the components described below, iron (Fe) or a small amount of an impurity which is inevitably contained (inevitable impurity).

<C: carbon>

[0016] C is an essential element in a ferritic stainless steel in accordance with an embodiment of the present invention. As a C content increases, however, abnormal oxidation is more likely to occur. Further, in a case where C is excessively contained, a slab and a hot coil are deteriorated in toughness, and it becomes difficult to work the ferritic stainless steel into a plate material by hot working. Therefore, in an aspect of the present invention, the upper limit of the content of C is defined to be 0.030%. In a case where C is contained in an amount of not more than 0.020%, it is possible to further reduce the possibility of occurrence of abnormal oxidation and improve workability. In light of the above reason, a more preferable content of C is 0.002% to 0.015%.

<Si: silicon>

[0017] Si is an element effective for improving oxidation resistance and is an essential element in a ferritic stainless steel in accordance with an embodiment of the present invention. However, in a case where Si is excessively contained, toughness and workability may be reduced. Therefore, in an aspect of the present invention, Si is contained in an amount of 0.01% to 1.50%. In a case where Si is contained in an amount of 0.01% to 1.0%, more preferably 0.01% to 0.50%, an effect as a deoxidizing agent and workability are further improved.

<Mn: manganese>

5 [0018] Mn is an essential element in a ferritic stainless steel in accordance with an embodiment of the present invention. However, in a case where Mn is excessively contained, the ferrite phase may be destabilized, and high-temperature oxidation resistance may be reduced. Therefore, in an aspect of the present invention, Mn is contained in an amount of 0.01% to 1.00%. In a case where Mn is contained in an amount of 0.01% to 0.80%, more preferably 0.01% to 0.50%, the possibility of generation of a corrosion-initiated point is further reduced.

10 <P: phosphorus>

[0019] P is an essential element in a ferritic stainless steel in accordance with an embodiment of the present invention. However, in a case where P is excessively contained, oxidation resistance and toughness of a hot-rolled sheet may be deteriorated. Therefore, in an aspect of the present invention, the content of P is defined to be not more than 0.050%. In a case where P is contained in an amount of not more than 0.04%, it is possible to further reduce a deterioration in workability. In light of the above reason, a more preferable content of P is 0.005% to 0.03%.

<S: sulfur>

20 [0020] S is an essential element in a ferritic stainless steel in accordance with an embodiment of the present invention. However, in a case where S is excessively contained, the ferritic stainless steel may be negatively affected in terms of formation of an Al_2O_3 film, and the oxidation resistance of the ferritic stainless steel may be deteriorated. Therefore, in an aspect of the present invention, the content of S is defined to be not more than 0.005%. In light of the above reason, a more preferable content of S is 0.0001% to 0.002%.

25 <Cr: chromium>

[0021] Cr is a fundamental alloy element which is necessary in order to improve the high-temperature oxidation resistance of the ferritic stainless steel. In a case where Cr is contained in not less than a predetermined amount, an oxide film is formed on the surface of the stainless steel, so that oxidation of the stainless steel is prevented. However, in a case where Cr is excessively contained, toughness is reduced and producibility is deteriorated. Therefore, in an aspect of the present invention, the content of Cr is defined to be 15.0% to 25.0%. In a case where Cr is contained in an amount of 16.0% to 22.0%, more preferably 17.0% to 20.0%, it is possible to further improve the oxidation prevention effect and producibility.

35 <Al: aluminum>

[0022] Al is a fundamental alloy element which is necessary in order to improve the high-temperature oxidation resistance of the ferritic stainless steel. In a case where Al is contained in not less than a predetermined amount, an oxide film of Al_2O_3 is formed on the surface of the stainless steel, so that the oxidation of the stainless steel is prevented. Further, in a case where REM or Y is added, the oxide film is dense and has an improved adhesion to the base steel, so that occurrence of abnormal oxidation is prevented. However, in a case where Al is excessively contained, toughness of the stainless steel is deteriorated, and producibility and workability are deteriorated. Therefore, in an aspect of the present invention, the content of Al is defined to be 2.0% to 4.0%. In a case where Al is contained in an amount of 2.5% to 3.7%, more preferably 2.8% to 3.5%, it is possible to further improve high-temperature oxidation resistance and producibility.

<Ni: nickel>

50 [0023] Ni is an element which improves corrosion resistance of a ferritic stainless steel and is an essential element in the ferritic stainless steel in accordance with an embodiment of the present invention. However, in a case where Ni is excessively contained, the ferrite phase is destabilized, and material costs are increased. Therefore, in an aspect of the present invention, the content of Ni is defined to be not more than 1.00%. In a case where Ni is contained in an amount of not more than 0.50%, it is possible to further prevent destabilization of the ferrite phase and an increase in production costs, which may otherwise be caused in a case where an excessive amount of Ni is contained. In light of the above reason, a more preferable content of Ni is 0.02% to 0.30%.

<N: nitrogen>

[0024] N is an essential element in a ferritic stainless steel in accordance with an embodiment of the present invention. However, in a case where N is excessively contained, N bonds to Al in the steel to form AlN, which may serve as a starting point of accelerated oxidation. Therefore, in an aspect of the present invention, the content of N is defined to be not more than 0.030%. In a case where N is contained in an amount of not more than 0.025%, it is possible to further reduce the possibility of hardening. In light of the above reason, a more preferable content of N is 0.003% to 0.020%.

<Nb (niobium), B (boron), and REM (rare earth element)>

[0025] Nb is an element which is added to ensure the high-temperature strength. Further, Nb has an effect of promoting formation of an Al₂O₃ film. Nb also reduces recrystallization of the stainless steel and causes the crystal grains to be finer, so that the grain boundaries have an increased area. However, in a case where Nb is excessively contained, toughness of a hot-rolled sheet may be deteriorated.

[0026] B is an element which improves secondary workability and oxidation resistance of a molded product manufactured with use of the ferritic stainless steel. However, in a case where B is excessively contained, the compound of B serves as inclusions (impurities).

[0027] REM (rare earth elements, rare earth metals) means lanthanoids (elements having an atomic number of 57 to 71, such as La, Ce, Pr, Nd, and Sm). REM is an element which improves the high-temperature oxidation resistance. In a case where REM is contained in not less than a predetermined amount, an Al oxide film is stabilized. Further, REM improves adhesion between a base material and an oxide, thereby improves oxidation resistance. However, in a case where REM is excessively contained, a surface defect is generated during hot rolling, and producibility is reduced.

[0028] For the above reason, in an aspect of the present invention, the content of Nb is defined to be 0.01% to 0.70%. In a case where Nb is contained in an amount of 0.05% to 0.50%, more preferably 0.08% to 0.30%, it is possible to further reduce the possibility of deterioration in workability. The upper limit of the content of Nb is yet even more preferably 0.20% or 0.15%. The content of B is defined to be 0.0003% to 0.01%. In a case where B is contained in an amount of 0.0003% to 0.005%, it is possible to further reduce the presence of inclusions and improve secondary workability. The content of REM is defined to be 0.01% to 0.20%. The content of REM is preferably 0.02% to 0.15%, and more preferably 0.04% to 0.10%.

(Other components)

[0029] The ferritic stainless steel in accordance with an aspect of the present invention can further contain, as an element other than the above elements, at least one element selected from the group consisting of Zr, V, Cu, Mo, W, Hf, Sn, Ta, Ti, Mg, and Ca.

<Zr: zirconium>

[0030] Zr is an element which improves the oxidation resistance. However, in a case where Zr is excessively added, the steel may be hardened to cause a decrease in toughness. As such, in an aspect of the present invention, Zr can be contained in an amount of not more than 0.50%. In consideration of reduction of hardening and the like, it is more preferable that Zr be contained in an amount of 0.01% to 0.40%.

<V: vanadium>

[0031] V is an element which improves workability and weld toughness. However, in a case where V is excessively added, toughness of a hot-rolled sheet may be deteriorated. In an aspect of the present invention, V can be contained in an amount of not more than 0.50%. In consideration of reduction of hardening and the like, it is more preferable that V be contained in an amount of 0.02% to 0.35%.

<Cu: copper>

[0032] Cu is an element which improves the corrosion resistance of the ferritic stainless steel. However, in a case where Cu is excessively contained, oxidation resistance and hot workability may be deteriorated. As such, in an aspect of the present invention, Cu can be contained in an amount of not more than 1.0%. In consideration of material costs and the like, it is more preferable that Cu be contained in an amount of 0.01% to 0.85%.

<Mo: molybdenum>

5 [0033] Mo is an element which improves the corrosion resistance. However, in a case where Mo is excessively contained, the ferritic stainless steel is hardened to cause a reduction in toughness and an increase in material costs. As such, in an aspect of the present invention, Mo can be contained in an amount of not more than 2.0%. In consideration of workability, material costs, and the like, it is more preferable that Mo be contained in an amount of 0.01% to 1.0%.

<W: tungsten>

10 [0034] W is an element which is added to ensure the high-temperature strength. However, in a case where W is excessively contained, toughness of a hot-rolled sheet is deteriorated, and material costs increase. As such, in an aspect of the present invention, W can be contained in an amount of not more than 2.0%. In consideration of material costs and the like, it is more preferable that W be contained in an amount of 0.01% to 1.0%.

15 <Hf: hafnium>

20 [0035] Hf is an element which improves the oxidation resistance. However, in a case where Hf is excessively contained, toughness of a hot-rolled sheet is reduced, and material costs increase. As such, in an aspect of the present invention, Hf can be contained in an amount of not more than 0.50%. In consideration of toughness and material costs, it is more preferable that Hf be contained in an amount of 0.001% to 0.20%.

<Sn: tin>

25 [0036] Sn (tin) is an element which improves the corrosion resistance of the ferritic stainless steel. However, in a case where Sn is excessively contained, workability is reduced, and material costs increase. As such, in an aspect of the present invention, Sn can be contained in an amount of not more than 0.50%. In consideration of workability, costs, and the like, it is more preferable that Sn be contained in an amount of 0.005% to 0.20%.

<Ta: tantalum>

30 [0037] Ta is an element which improves the cleanliness and the oxidation resistance of the steel. However, in a case where Ta is excessively contained, toughness is reduced, and material costs increase. As such, in an aspect of the present invention, Ta can be contained in an amount of not more than 0.5%. In consideration of toughness and material costs, it is more preferable that Ta be contained in an amount of not more than 0.40%. In light of the above reason, a more preferable content of Ta is 0.001% to 0.30%.

<Ti: titanium>

40 [0038] Ti is an element which, by reacting with C and/or N, can form the ferritic stainless steel into a ferritic single layer at 900°C to 1000°C. However, in a case where Ti is excessively contained, TiO₂ may be produced in an oxide of Al, and oxidation lifetime may be deteriorated. As such, in an aspect of the present invention, Ti can be contained in an amount of not more than 0.20%. In consideration of workability and the like, it is more preferable that Ti be contained in an amount of 0.005% to 0.10%.

45 <Mg: magnesium>

50 [0039] Mg forms a Mg oxide with Al in molten steel and acts as a deoxidizing agent. However, in a case where Mg is excessively contained, toughness of the steel is reduced, and producibility is reduced. As such, in an aspect of the present invention, Mg can be contained in an amount of not more than 0.015%. In light of the above reason, a more preferable content of Ma is 0.0002% to 0.0080%.

<Ca: calcium>

55 [0040] Ca is an element which improves hot workability. However, in a case where Ca is excessively contained, toughness of the steel is reduced, and producibility is reduced. As such, in an aspect of the present invention, Ca can be contained in an amount of not more than 0.015%. In light of the above reason, a more preferable content of Ca is 0.0001% to 0.012%.

[0041] The ferritic stainless steel in accordance with the present embodiment can satisfy $100 \times [C]/[Nb] \leq 35$ where

[C] is a percent by mass of C and [Nb] is a percent by mass of Nb. This allows a Nb-based carbide to be generated at the time of hot rolling or annealing, so that the amount of strain accumulated during cold rolling is increased, and an intended dislocation density is successfully achieved.

5 (Dislocation density)

[0042] The ferritic stainless steel in accordance with the present embodiment has a dislocation density ρ of not less than 0.91×10^{14} [m⁻²] as derived by the Williamson and Hall method with use of X-ray diffraction. In the present embodiment, X-ray diffraction is measured from the surface.

10 **[0043]** A dislocation density is a value indicating the amount of dislocation in a crystal, and is represented as the number [m⁻²] of coordination lines penetrating a unit area of a cross section of the crystal or as a total [m/m⁻³] of the lengths of dislocation lines present in a unit volume of the crystal. Since the ferritic stainless steel in accordance with the present embodiment has a dislocation density ρ of not less than 0.91×10^{14} [m⁻²], Al and Cr are quickly diffused in the ferritic stainless steel, so that an alumina layer can be formed quickly. This enables an improvement in oxidation resistance.

15 **[0044]** In the present embodiment, the dislocation density ρ [m⁻²] is derived by the Williamson and Hall method. More specifically, for example, the dislocation density ρ [m⁻²] is derived as follows. With use of an X-ray diffraction instrument using a Co tube as an X-ray source, a diffraction intensity curve of a sample which has been subjected to electrolytic polishing is measured with respect to the following diffraction peaks (2 θ): $\alpha(110)52.2^\circ$, $\alpha(211)99.3^\circ$, and $\alpha(229)123.3^\circ$.
20 The diffraction peaks (2 θ) on the obtained diffraction intensity curve are separated to a peak by a $K\alpha_1$ ray and a peak by a $K\alpha_2$ ray. With respect to the separated diffraction peak by the $K\alpha_1$ ray, a peak top method is used to identify a diffraction angle 2 θ and calculate, as a half-value width, an angle between intensities each of which is 1/2 of the peak intensity. Note that a true half-value width β can be calculated by formula (1) below with use of a half-value width β_m of the steel material after cold rolling and a half-value width β_0 of the steel material after final annealing.

25

$$\beta^2 = \beta_m^2 - \beta_0^2 \quad (1)$$

30 The true half-value width β calculated by formula (1) above can be represented as a sum of broadening β_1 of a half-value width due to a crystallite size D and broadening β_2 of a half-value width due to a strain ε , as in formula (2) below.

$$\beta = \beta_1 + \beta_2 \quad (2)$$

35 It is known that the broadening β_1 of a half-value width due a crystallite size (D) can be represented by formula (3) below and that the broadening β_2 of a half-value width due to a strain (ε) can be represented by formula (4) below.

$$\beta_1 = 0.9\lambda / (D \cos\theta) \quad (3)$$

40

$$\beta_2 = 2\varepsilon \tan\theta \quad (4)$$

[0045] Note that λ in formula (3) is the wavelength of an X-ray.

45 **[0046]** By applying formulae (3) and (4) above to formula (2) and simplifying the result, formula (5) below is obtained.

$$\beta \cos\theta / \lambda = (0.9 / D) + (2\varepsilon \sin\theta / \lambda) \quad (5)$$

50 As indicated by formula (5) above, the strain ε can be calculated from the gradient of a graph created by plotting $\beta \cos\theta / \lambda$ against $\sin\theta / \lambda$.

[0047] Then, by using the calculated strain (ε), the magnitude b (= 0.25 nm) of a Burgers vector of the dislocation, and formula (6) below, the dislocation density ρ is calculated.

55

$$\rho = (14.4 \times \varepsilon^2) / b^2 \quad (3)$$

(Nb carbide)

[0048] The ferritic stainless steel in accordance with the present embodiment is such that in scanning electron microscope (SEM) observation of random three $30\ \mu\text{m}\times 30\ \mu\text{m}$ portions in a cross section obtained by cutting the ferritic stainless steel along a plane perpendicular to a rolling direction, an average number of Nb carbides each having (i) a Nb concentration of not less than 5 wt% as measured by energy dispersive X-ray spectroscopy (EDS) and (ii) a particle diameter of not less than 0.1 μm is 2 to 15. Since the average number is not less than 2, strain is easily accumulated in tissues during cold rolling. Further, since the average number is not more than 15, the toughness of the stainless steel is less likely to decrease. The particle diameter of a carbide is calculated on the basis of the dimensions of the particle in an image captured by scanning electron microscopy. Specifically, an average width between the largest width of the carbide and the smallest width of the carbide is determined as a particle diameter of the carbide.

(Alumina layer)

[0049] The ferritic stainless steel in accordance with the present disclosure is suitably applicable to purposes in which oxidation resistance at high temperatures is required. As such, a use condition means a high temperature condition. The following description will discuss an alumina layer 10 formed in a case where the ferritic stainless steel in accordance with the present disclosure is heated at 1050°C for 50 hours.

[0050] The inventors of the present invention discovered through diligent research that, regarding components of a ferritic stainless steel, in a case where Nb, Cr, and REM are contained as essential elements at concentrations within appropriate ranges, columnar crystallization of an alumina layer formed under a use condition is improved. This is considered to be due to increased concentrations of Nb, Cr, and REM in grain boundaries in the alumina layer. In the alumina layer 10 in accordance with the present embodiment, a total concentration of a Nb oxide, a Cr oxide, and a REM-based oxide which are present in grain boundaries is not less than 3.5 wt%. This prevents inward diffusion of oxygen, so that the alumina layer 10 is excellent in oxidation resistance. That is, the ferritic stainless steel in accordance with the present embodiment is excellent in oxidation resistance under high temperature conditions.

[0051] Further, the inventors of the present invention discovered that the columnar crystallization is improved also in a case where B is contained as an essential element at a concentration within an appropriate range.

[0052] The ferritic stainless steel in accordance with the present embodiment contains not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than 0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass.

[0053] The alumina layer 10 formed by heating the ferritic stainless steel containing the above components at 1050°C for 50 hours has the following feature. That is, in a cross section of the alumina layer 10 obtained by cutting the alumina layer in a thickness direction, a total length of grain boundaries included in a given region having an area of $2.25\ \mu\text{m}^2$ is not more than 5.5 μm .

[0054] Fig. 1 is an enlarged view schematically illustrating a portion of a cross section of the alumina layer 10 formed by heating an example ferritic stainless steel in accordance with the present embodiment at 1050°C for 50 hours, the cross section being obtained by cutting the alumina layer 10 in a thickness direction. The given region having an area of $2.25\ \mu\text{m}^2$ as illustrated in Fig. 1 can be a region which, for example, is surrounded by a $1.5\ \mu\text{m}\times 1.5\ \mu\text{m}$ square centered around the center of the alumina layer 10 in the thickness direction. The length of grain boundaries included in a region having an area of $2.25\ \mu\text{m}^2$ means a sum of all of the lengths of grain boundaries GB that are present in a region having an area of $2.25\ \mu\text{m}^2$. In the example illustrated in Fig. 1, the length of grain boundaries included in a $2.25\text{-sq-}\mu\text{m}$ region is not more than 5.5 μm .

[0055] Fig. 2 is an enlarged view schematically illustrating a portion of an alumina layer 20 in accordance with a comparative example, the length of grain boundaries in $2.25\ \mu\text{m}^2$ of the alumina layer 20 being more than 5.5 μm . As illustrated in Fig. 2, the alumina layer 20, in which the length of grain boundaries in $2.25\ \mu\text{m}^2$ is more than 5.5 μm , has an equiaxial crystal ratio higher than that in the example illustrated in Fig. 1.

[0056] Note here that a columnar crystal means tissue in which crystal grains that have grown long and thin in the thickness direction of the alumina layer are arranged. An equiaxial crystal means polycrystalline tissue in which the shape and orientation of the crystal grains constituting an equiaxial crystal are isotropic.

[0057] As is clear from a comparison between Figs. 1 and 2, an alumina layer having a high columnar crystal ratio (Fig. 1) has a smaller length of grain boundaries GB per given unit area in comparison to an alumina layer having a high equiaxial crystal ratio (Fig. 2).

[0058] In a cross section obtained by cutting the alumina layer 10 in accordance with the present embodiment in a thickness direction, a length of grain boundaries included in a given $2.25\text{-sq-}\mu\text{m}$ region is not more than 5.5 μm . In other words, the alumina layer 10 has a high columnar crystal ratio. An equiaxial crystal has a grain boundary density greater than that of a columnar crystal, and therefore has increased routes through which oxygen is diffused at the grain bound-

aries. As such, equiaxial crystals have a shorter oxidation lifetime than columnar crystals. As such, the ferritic stainless steel in accordance with the present embodiment is excellent in oxidation resistance under high temperature conditions by having a high columnar crystal ratio.

5 (Production method)

[0059] Firstly, the following will provide a brief description of an example of a production process for a ferritic stainless steel in accordance with the present embodiment. The production process for a ferritic stainless steel in accordance with the present embodiment includes a pretreatment step, a hot rolling step, an annealing step, a pickling step, and a cold rolling step.

[0060] In the pretreatment step, first, steel which has been adjusted so as to have composition falling within the scope of the present invention is melted with use of a melting furnace having a vacuum atmosphere or an argon atmosphere, and this steel is cast to produce a slab. Subsequently, the slab is cut to obtain a slab piece for hot rolling. Then, the slab piece is heated to a temperature range of 1100°C to 1300°C in an air atmosphere. A time for which the slab piece is heated and held is not limited. Note that, in a case where the pretreatment step is industrially carried out, the above casting can be continuous casting.

[0061] The hot rolling step is a step of hot-rolling the slab (steel ingot), obtained in the pretreatment step, to produce a hot-rolled steel strip having a predetermined thickness.

[0062] The annealing step is a step of heating the hot-rolled steel strip obtained in the hot rolling step S2 to a temperature of, for example, 900°C to 1050°C, so as to soften the steel strip. In the annealing step, the steel strip after the annealing is cooled such that cooling time taken to cool the steel strip from the annealing temperature to 400°C is not less than 30 seconds. This allows a Nb carbide to be precipitated inside the tissue (i.e., in grain boundaries and inside the grains).

[0063] The pickling step is a step of washing off, with use of a pickle such as hydrochloric acid or a mixed solution of nitric acid and hydrofluoric acid, scales adhering to the surface of the annealed steel strip obtained in the annealing step.

[0064] The cold rolling step is a step of rolling the annealed steel strip from which the scales have been removed in the first pickling step, so as to make the annealed steel strip thinner. A rolling reduction ratio in the cold rolling step is not less than 65%, more preferably not less than 75%. In a case where the rolling reduction ratio in the cold rolling step is not less than 65%, it is possible to increase a strain in the steel. More specifically, in a case where the rolling reduction ratio in the cold rolling step is not less than 65%, a dislocation density ρ derived by the Williamson and Hall method with use of X-ray diffraction is not less than 0.91×10^{14} [m⁻²]. In other words, in order to prepare a cold-rolled sheet having a dislocation density ρ of not less than 0.91×10^{14} [m⁻²] as derived by the Williamson and Hall method with use of X-ray diffraction, the rolling reduction ratio in the cold rolling step should be not less than 65%, more preferably not less than 75%.

[0065] Note that the series of steps from the annealing step through the cold rolling step can be carried out a plurality of times. In a case where the series of steps is carried out only once, the annealing step is referred to as a final annealing step. In a case where the series of steps is carried out a plurality of times, one of the annealing steps which one is carried out last is referred to as a final annealing step, and the annealing step(s) is/are referred to as a process annealing step(s).

[0066] Further, in the production method in accordance with the present embodiment, a rolling reduction ratio in the cold rolling step after the final annealing step is not less than 65%. In other words, the cold rolling step after the final annealing step is a cold rolling step in which rolling is carried out until the dislocation density ρ derived by the Williamson and Hall method with use of X-ray diffraction becomes not less than 0.91×10^{14} [m⁻²].

[0067] The method for producing the ferritic stainless steel in accordance with the present embodiment is characterized by including no annealing step after the cold rolling step. That is, the ferritic stainless steel in accordance with the present embodiment is a cold-rolled steel strip after a cold rolling step. Since the ferritic stainless steel is a cold-rolled steel strip, strain remains accumulated in the steel. This accelerates diffusion of Al and Cr. This makes it possible to provide an alumina layer under high temperature conditions, thereby achieving high oxidation resistance at high temperatures. Further, since there is no need to carry out a final annealing after the cold rolling, it is possible to reduce production costs.

[0068] Aspects of the present invention can also be expressed as follows:

A ferritic stainless steel in accordance with Aspect 1 of the present disclosure contains not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than 0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass, and the other part composed of Fe and an inevitable impurity, the ferritic stainless steel having a dislocation density ρ of not less than 0.91×10^{14} [m⁻²] as derived by the Williamson and Hall method with use of X-ray diffraction.

[0069] According to the above configuration, the content of Al is not more than 4.0%. This allows the ferritic stainless steel to be excellent in toughness. Further, since the dislocation density ρ is not less than 0.91×10^{14} [m⁻²], it is possible to form an alumina layer sooner. This makes it possible to provide a ferritic stainless steel which is excellent in oxidation resistance at high temperatures.

[0070] In Aspect 2 of the present disclosure, the ferritic stainless steel in accordance with Aspect 1 can be configured

such that: in a case where the ferritic stainless steel is heated at 1050°C for 50 hours, the ferritic stainless steel forms an alumina layer mainly composed of alumina; and in a cross section of the alumina layer obtained by cutting the alumina layer in a thickness direction, a total length of grain boundaries included in a given region having an area of 2.25 μm^2 is not more than 5.5 μm .

[0071] In Aspect 3 of the present disclosure, the ferritic stainless steel in accordance with Aspect 2 can be configured such that a total concentration of a Nb oxide, a Cr oxide, and a REM-based oxide which are present in grain boundaries in the alumina layer is not less than 3.5 wt%.

[0072] In Aspect 4 of the present disclosure, the ferritic stainless steel in accordance with any one of Aspects 1 through 3 can be configured such that the ferritic stainless steel further contains at least one selected from the group consisting of not more than 0.50% of Zr, not more than 0.50% of V, not more than 1.0% of Cu, not more than 2.0% of Mo, not more than 2.0% of W, not more than 0.50% of Hf, not more than 0.50% of Sn, not more than 0.5% of Ta, not more than 0.20% of Ti, not more than 0.015% of Mg, and not more than 0.015% of Ca, in percent by mass.

[0073] In Aspect 5 of the present disclosure, the ferritic stainless steel in accordance with any one of Aspects 1 through 3 can be configured such that the ferric stain steel satisfies $100 \times [C]/[Nb] \leq 35$ where [C] is a percent by mass of C and [Nb] is a percent by mass of Nb.

[0074] A method for producing a ferritic stainless steel in accordance with Aspect 6 of the present disclosure is a method in which the ferritic stainless steel contains not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than 0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass, and the other part composed of Fe and an inevitable impurity, the method including: an annealing step of annealing a steel strip which has been hot-rolled, such that cooling time taken to cool the steel strip from an annealing temperature to 400 degrees after annealing is not less than 30 seconds; and a cold rolling step of carrying out, after a final annealing step, cold rolling until a dislocation density ρ derived by the Williamson and Hall method is not less than 0.91×10^{14} [m^{-2}].

[0075] According to the above configuration, it is possible to provide a ferritic stainless steel which is excellent toughness and in oxidation resistance at high temperatures.

[0076] In Aspect 7 of the present disclosure, the method in accordance with Aspect 6 can be configured such that in the cold rolling step, a rolling reduction ratio is not less than 65%.

[0077] In Aspect 8 of the present disclosure, the method in accordance with Aspect 6 or 7 can be configured such that in scanning electron microscope observation of random three 30 $\mu\text{m} \times 30 \mu\text{m}$ portions in a cross section obtained by cutting, along a plane perpendicular to a rolling direction, of the ferritic stainless steel obtained through the cold rolling step, an average number of carbides each having (i) a Nb concentration of not less than 5 wt% as measured by energy dispersive X-ray spectroscopy and (ii) a particle diameter of not less than 0.1 μm is 2 to 15.

[0078] In Aspect 9 of the present disclosure, the method in accordance with any one of Aspects 6 through 8, wherein: the ferritic stainless steel forms an alumina layer in a case where the ferritic stainless steel is heated at 1050°C for 50 hours; and in a cross section of the alumina layer obtained by cutting the alumina layer in a thickness direction, a total length of grain boundaries included in a given region having an area of 2.25 μm^2 is not more than 5.5 μm .

[0079] In Aspect 10 of the present disclosure, the method for producing a ferritic stainless steel in accordance with Aspect 9 can be configured such that a total concentration of a Nb oxide, a Cr oxide, and a REM-based oxide which are present in grain boundaries in the alumina layer is not less than 3.5 wt%.

[0080] In Aspect 11 of the present disclosure, the method in accordance with any one of Aspects 6 through 10 can be configured such that the ferritic stainless steel further contains at least one selected from the group consisting of not more than 0.50% of Zr, not more than 0.50% of V, not more than 1.0% of Cu, not more than 2.0% of Mo, not more than 2.0% of W, not more than 0.50% of Hf, not more than 0.50% of Sn, not more than 0.5% of Ta, not more than 0.20% of Ti, not more than 0.015% of Mg, and not more than 0.015% of Ca, in percent by mass.

[0081] In Aspect 12 of the present disclosure, the method in accordance with any one of Aspects 6 through 11 can be configured such that the ferritic stainless steel satisfies $100 \times [C]/[Nb] \leq 35$ where [C] is a percent by mass of C and [Nb] is a percent by mass of Nb.

[0082] In Aspect 13 of the present disclosure, the method in accordance with any one of Aspects 6 through 12 can be configured such that a heating temperature in the final annealing step is 900°C to 1050°C. According to the above configuration, it is possible to provide an annealed steel strip suitable for providing a ferritic stainless steel which is excellent toughness and in oxidation resistance at high temperatures.

[Examples]

[0083] In order to evaluate the physical properties of ferritic stainless steels in accordance with embodiments of the present invention, ferritic stainless steels containing components shown in Fig. 1 below as raw materials were produced as steel types of inventive examples and steel types of comparative examples. In Table 1, steel types No. 1 through 16

are ferritic stainless steels which are examples of the present invention and were prepared within the scope of the present invention. In Table 1, steel types No. 17 through 27 are ferritic stainless steels which are comparative examples and were prepared under conditions falling outside the scope of the present invention.

5 [0084] In order to produce a steel material of a steel type shown in Table 1, first, a steel containing the components shown in Table 1 was melted in vacuum to produce 30 kg of slab. The slab was heated at 1230°C for 2 hours and then subjected to hot rolling to prepare a hot-rolled sheet having a thickness of 3 mm. The obtained hot-rolled sheet was annealed at a temperature of 900°C to 1050°C to prepare a hot-rolled annealed sheet. The obtained hot-rolled annealed sheet was subjected to two times of cold rolling and two times of annealing, and further subjected to a final cold rolling to produce a cold-rolled sheet having a thickness of 50 μ m. Cooling time taken to reduce the temperature from the annealing temperature to 400 degrees in an annealing step is shown in Table 2.

10 [0085] Note that up to the second time of cold rolling, each cold rolling was carried out at a rolling reduction ratio of 60% to 85%, both in the examples of the present invention and in the comparative examples, and annealing after each cold rolling was carried out at a temperature condition in a range of 900°C to 1050°C. A rolling reduction ratio in the final cold rolling is indicated in the item "final rolling reduction ratio" in Table 2. As shown in Table 2, the rolling reduction ratio in the final cold rolling in each of the examples of the present invention is not less than 65%. In contrast, the rolling reduction ratio in the final cold rolling in each of the comparative examples is less than 65%. Note that the production method described in Examples is merely an example, and does not limit the production method.

20 [Table 1]

20

25

30

35

40

45

50

55

5
10
15
20
25
30
35
40
45
50
55

Steel type No.	Essential element											Optional element											Category		
	C	Si	Mn	P	S	Cr	Al	Ni	Nb	N	B	REM	Zr	W	Ti	V	Mg	Ca	Sn	Cu	Ta	Hf		Mo	100× [C]/[Nb]
1	0.010	0.33	0.11	0.026	0.0014	17.96	3.54	0.10	0.17	0.012	0.0025	0.054	0.12											5.9	Example of present invention
2	0.008	0.42	0.24	0.025	0.0005	15.51	2.61	0.12	0.57	0.011	0.0021	0.091			0.32			0.08						1.4	
3	0.010	0.19	0.29	0.022	0.0008	19.31	3.19	0.15	0.18	0.007	0.0019	0.079	0.29											5.6	
4	0.008	0.32	0.34	0.028	0.0005	18.09	3.25	0.12	0.15	0.009	0.0011	0.056												5.3	
5	0.010	0.41	0.25	0.029	0.0009	19.06	2.29	0.18	0.18	0.011	0.0014	0.141				0.0017								5.6	
6	0.008	0.22	0.33	0.043	0.0007	17.99	3.68	0.08	0.19	0.009	0.0017	0.038										0.89	4.2		
7	0.011	0.19	0.18	0.028	0.0006	18.04	3.25	0.12	0.15	0.012	0.0014	0.045		0.91		0.0031								7.3	
8	0.008	0.39	0.12	0.028	0.0009	20.02	3.44	0.22	0.33	0.023	0.0029	0.058						0.17						2.4	
9	0.010	0.05	0.08	0.029	0.0008	24.51	2.98	0.12	0.20	0.011	0.0012	0.019			0.12									5.0	
10	0.022	0.04	0.22	0.022	0.0007	17.59	3.98	0.07	0.18	0.009	0.0009	0.066												12.2	
11	0.010	0.51	0.87	0.018	0.0006	20.01	2.51	0.08	0.15	0.011	0.0005	0.078					0.0114							6.7	
12	0.010	0.34	0.34	0.028	0.0008	19.04	3.91	0.07	0.24	0.007	0.0010	0.018												4.2	
13	0.008	0.43	0.55	0.029	0.0007	19.03	3.06	0.43	0.22	0.008	0.0011	0.054							0.81					3.6	
14	0.008	0.31	0.39	0.022	0.0009	18.09	3.91	0.28	0.31	0.009	0.0013	0.049	0.38											2.6	
15	0.025	0.39	0.28	0.018	0.0006	17.95	2.98	0.12	0.04	0.011	0.0071	0.065						0.11						30.0	
16	0.007	0.38	0.27	0.022	0.0009	16.31	3.21	0.13	0.21	0.009	0.0031	0.041									0.21			3.3	
17	0.006	0.29	0.21	0.034	0.0009	18.23	3.51	0.19	0.19	0.009	0.0002	0.043												3.2	
18	0.009	0.31	0.29	0.041	0.0014	18.91	3.22	0.18	0.21	0.011	0.0015	0.008	0.05		0.11									4.3	
19	0.007	0.19	0.13	0.029	0.0010	17.88	3.41	0.12	0.005	0.008	0.0002	0.081												140.0	
20	0.006	0.23	0.21	0.027	0.0008	13.98	2.43	0.08	0.21	0.011	0.0015	0.079	0.55				0.0003							2.9	
21	0.007	0.28	0.32	0.021	0.0008	17.23	3.39	0.12	0.18	0.007	0.0018	0.074				0.25								3.9	
22	0.010	0.43	0.19	0.031	0.0009	19.19	1.59	0.07	0.20	0.010	0.0025	0.081										1.54	5.0		
23	0.013	0.23	0.28	0.029	0.0012	20.07	2.88	0.09	0.15	0.009	0.0076	0.041												8.7	
24	0.009	0.43	0.43	0.033	0.0008	18.04	3.31	0.13	0.25	0.017	0.0141	0.031	0.19											1.2	
25	0.008	0.32	0.29	0.039	0.0014	18.31	5.09	0.21	0.23	0.011	0.0025	0.033												3.5	
26	0.011	0.29	0.19	0.027	0.0008	26.09	3.18	0.41	0.35	0.011	0.0022	0.081		0.32										3.1	
27	0.009	0.51	0.34	0.026	0.0009	20.12	3.82	0.09	0.03	0.008	0.0010	0.211				0.0012								30.0	

[0086] In Table 1, the composition of components contained in each steel type is indicated in percent by mass. Note that a remainder other than the components shown in Table 1 is Fe or a small amount of an impurity which is inevitably contained (inevitable impurity). Underlines shown in Table 1 each indicate that the range of a component contained in a stainless steel of a comparative example of the present invention is outside a range in accordance with the present invention.

(Measurement of dislocation density)

[0087] The following description will discuss measurement of a dislocation density ρ carried out with respect to the cold-rolled sheets of the steel types of the examples of the present invention and the cold-rolled sheets of the steel types of the comparative examples shown in Table 1. The measurement of a dislocation density ρ was carried out in accordance with the method described in the section "(Dislocation density)" in the embodiments. Table 2 shows results of measurement of a dislocation density ρ . All of the steel types No. 1 through 16, which are examples of the present invention, had a dislocation density ρ of not less than 0.91×10^{14} [m^{-2}]. In contrast, comparative example steel types No. 17 through 27 all had a dislocation density ρ of less than 0.91×10^{14} [m^{-2}]. The results verified that, in a case where the rolling reduction ratio in the final cold rolling step is not less than 65%, a dislocation density ρ is not less than 0.91×10^{14} [m^{-2}]. The results also verified that, in a case where the rolling reduction ratio in the final cold rolling step is less than 65%, a dislocation density ρ is less than 0.91×10^{14} [m^{-2}].

(Nb carbide)

[0088] The cold-rolled sheets of the steel types of the examples of the present invention and the cold-rolled sheets of the steel types of the comparative examples were investigated as to the number of Nb carbides present in tissues of each cold-rolled sheet. The investigation was carried out as follows. First, the cold-rolled sheet was cut along a plane which was perpendicular to a rolling direction. Subsequently, random three $30 \mu m \times 30 \mu m$ portions in a cross section were observed with use of a scanning electron microscope to calculate an average number of carbides each having (i) a Nb concentration of not less than 5 wt% as measured by energy dispersive X-ray spectroscopy and (ii) a particle diameter of not less than 0.1 μm . The calculated average value of the Nb carbides is shown in Table 2 as "average number of Nb carbides". As shown in Table 2, all of the steel types No. 1 through 16, which are examples of the present invention, had an average number of carbides within a range of 2 to 15.

(Measurement of length of grain boundary)

[0089] Firstly, the cold-rolled sheets of the steel types of the examples of the present invention and the cold-rolled sheets of the comparative example steel types indicated in Table 1 were each heated at $1050^\circ C$ for 50 hours. After the heating, each steel sheet was STEM observation of a cross section. The STEM observation was carried out using HD-2700 manufactured by Hitachi High-Tech Corporation, at a voltage of 200 V and an observation magnification of 30,000 times. Measurement of a length of alumina grain boundaries was carried out such that a $1.5 \mu m \times 1.5 \mu m$ portion was randomly selected from a center part of the alumina film, and a total length of boundaries in the portion was determined. Note that an average of values of randomly selected three portions was used as a measured length.

[0090] In determination on a length of grain boundaries in Table 2, "Good" indicates that the length of grain boundaries within a $2.25\text{-}\mu m^2$ portion is not more than 5.5 μm , and "Poor" indicates that the length of grain boundaries within a $2.25\text{-}\mu m^2$ portion is more than 5.5 μm .

(Concentrations of elements in grain boundaries in alumina layer)

[0091] The following description will discuss the concentrations of elements Nb, Cr, and REM in alumina grain boundaries of the examples of the present invention and the comparative examples indicated in Table 1.

[0092] Firstly, the cold-rolled sheets of the steel types of the examples of the present invention and the cold-rolled sheets of the comparative example steel types indicated in Table 1 were each heated at $1050^\circ C$ for 50 hours. After the heating, each steel sheet was observed from a cross section thereof, and the concentrations of elements in grain boundaries were measured by STEM-EDX. The observation of a STEM image was carried out by spot analysis of center parts of grain boundaries with use of HD-2700 manufactured by Hitachi High-Tech Corporation, at a voltage of 200 V and an observation magnification of 4,000,000 times. For energy dispersive X-ray spectroscopy (EDX), an energy dispersive X-ray analyzer EDAX Octane T Ultra W manufactured by AMETEK, Inc. was used. The analysis time was 300 seconds.

[0093] Table 2 shows values each obtained by adding up concentrations of the elements Nb, Cr, Ce, La, and Nd. That is, the values are each a total concentration of a Nb oxide, a Cr oxide, and a REM-based oxide in grain boundaries.

[0094] In determination on an increased element concentration in Table 2, a case in which a total concentration of an Nb oxide, a Cr oxide, and a REM-based oxide in grain boundaries is not less than 3.5 wt% is indicated as "Good". A case in which a total concentration of an Nb oxide, a Cr oxide, and a REM-based oxide in grain boundaries is less than 3.5 wt% is indicated as "Poor" in Table 2.

5

(High-temperature oxidation resistance evaluation test)

[0095] The following description will discuss an evaluation test on high-temperature oxidation resistance carried out with respect to the examples of the present invention and the comparative examples shown in Tables 1 and 2. First, for each steel type indicated in Table 1, three test pieces each having a width of 20 mm and a length of 25 mm were taken from a cold-rolled sheet having a thickness of 50 μ m as described above regarding production of a steel material. The test pieces were subjected to an air atmosphere at 1050°C for 50 hours, and an average amount of increase in oxidation among the three test pieces was measured. The present high-temperature oxidation resistance evaluation test was carried out in an atmospheric air with use of an EREMA electric kiln. The results are shown in Table 3 below. In determination on high-temperature oxidation resistance in Table 3, "Good" indicates that an average increase in oxidation was not more than 1 mg/cm², and "Poor" indicates that the average increase in oxidation was more than 1 mg/cm².

10

15

(Toughness evaluation test)

[0096] The following description will discuss a toughness evaluation test carried out with respect to the examples of the present invention and the comparative examples shown in Table 1. First, a test piece to be used in the present evaluation test was prepared on the basis a V-notched test piece according to the JIS standard (JIS Z 2242 (2018)). Adjustment of the thickness of a hot-rolled sheet was carried out by cutting the surface of a hot-rolled sheet, which had a thickness of 3 mm as described above regarding production of a steel material, until the thickness was 2.5 mm. A test piece was taken from the steel sheet such that a longitudinal direction of the test piece was parallel to a rolling direction. Further, the test piece was notched such that the notch was perpendicular to the rolling direction.

20

25

[0097] The present evaluation test was carried out according to the JIS standard (JIS Z 2242 (2018)). The present evaluation test was carried out at room temperature (23°C \pm 2°C) for 5 test pieces per steel type, and a Charpy impact value (absorption energy) was determined. Note that a IC-30B type Charpy impact tester manufactured by Tokyo Koki Seizosho was used in the present evaluation test. The results are shown in Table 2 below. In Table 2, "Good" indicates that a Charpy impact value is not less than 20 J/cm², and "Poor" indicates that a Charpy impact value is less than 20 J/cm².

30

35

40

45

50

55

[Table 2]

Steel type No.	Cooling time [sec]	Final rolling reduction ratio [%]	Dislocation density $\times 10^{14} [\text{m}^{-2}]$	Average number of Nb carbides	Length of grain boundary (μm)	Increased element concentration in alumina grain boundary [wt%]	Amount of increase in oxidation [mg/cm ²]	Charpy impact value [J/cm ²]	Category
1	60	75	3.87	4.0	4.9	4.8	0.65	58.6	Example of present invention
2	30	75	4.55	10.7	5.2	9.5	0.75	101.8	
3	60	75	3.61	5.0	4.1	6.1	0.67	55.4	
4	60	70	3.14	3.3	4.3	4.9	0.64	61.3	
5	60	70	3.73	4.3	5.4	12.8	0.97	31.9	
6	60	70	2.98	3.7	4.5	4.5	0.63	65.4	
7	60	70	3.37	3.3	4.3	4.9	0.66	79.3	
8	30	70	3.15	6.3	4.2	5.4	0.67	49.7	
9	60	70	3.55	5.7	4.7	4.1	0.66	50.3	
10	60	75	4.08	4.7	5.3	5.1	0.91	48.6	
11	90	75	2.82	4.3	5.1	8.6	0.84	63.5	
12	60	75	3.32	5.3	3.9	5.8	0.64	39.9	
13	60	80	4.31	5.3	4	6.1	0.63	53.4	
14	60	75	4.19	7.0	4.1	6.4	0.66	42.1	
15	90	75	3.16	2.3	4.8	5.7	0.61	48.1	
16	60	75	3.53	5.0	4.7	5.0	0.62	69.2	

(continued)

Steel type No.	Cooling time [sec]	Final rolling reduction ratio [%]	Dislocation density $\times 10^{14} [m^{-2}]$	Average number of Nb carbides	Length of grain boundary (μm)	Increased element concentration in alumina grain boundary [wt%]	Amount of increase in oxidation [mg/cm ²]	Charpy impact value [J/cm ²]	Category
17	60	55	0.43	4.7	5.3	3.2	1.25	35.2	Comparative Example
18	30	55	0.72	4.0	6.8	1.5	1.71	31.6	
19	20	60	0.38	0.3	5.6	3.4	3.32	48.4	
20	60	60	0.88	50	7.5	5.6	4.01	72.3	
21	60	60	0.86	4.3	5.1	6.7	0.69	16.1	
22	60	60	0.57	5.0	6.1	5.8	4.33	88.9	
23	60	60	0.90	3.3	6.9	4.7	4.05	59.2	
24	120	55	0.73	18.3	8.1	6.1	2.77	18.5	
25	60	55	0.90	5.3	5.4	5.5	0.67	15.1	
26	60	55	0.64	5.3	7.3	7.2	1.68	16.2	
27	20	55	0.88	12	5.2	8.7	0.70	16.3	

[0098] As shown in Fig. 2, inventive example steel types No. 1 through 16 all satisfied the above criteria in terms of high-temperature oxidation resistance and toughness. Comparative example steel types No. 17 through 27 did not satisfy the above criteria in terms of one or both of high-temperature oxidation resistance and toughness.

[0099] That is, it was verified that a ferritic stainless steel within the scope of the present invention is excellent in high-temperature oxidation resistance and toughness.

[0100] The following will explain the reason why comparative example steel types Nos. 17 through 27 did not exhibit results as good as the results of the steel types of the examples of the present invention.

[0101] Comparative example steel type No. 17 satisfied the criterion in terms of length of grain boundaries, but did not satisfy the criterion in terms of concentration of Nb, Cr, and REM in grain boundaries, due to having a low B content. Because of this, comparative example steel type No. 17 did not exhibit an excellent result in terms of high-temperature oxidation resistance.

[0102] Comparative example steel type No. 18 did not satisfy the criterion in terms of concentration of Nb, Cr, and REM in grain boundaries, due to having a REM content of less than 0.01%. Further, comparative example steel type No. 18 tended to have an equiaxial crystal and did not exhibit an excellent result in high-temperature oxidation resistance, due to having a Ti content greater than 0.20%.

[0103] Comparative example steel type No. 19 had a Nb content of less than 0.01%, did not satisfy the criterion in terms of concentration of Nb, Cr, and REM in grain boundaries, and did not exhibit an excellent result in terms of high-temperature oxidation resistance.

[0104] Comparative example steel type No. 20 had a Zr content of more than 0.50% and thus tended to have segregation of Zr at alumina grain boundaries to encourage equiaxial crystallization, and did not exhibit an excellent result in terms of high-temperature oxidation resistance.

[0105] Comparative example steel type No. 21 had a Si content of more than 1.5%, and exhibited an excellent result in terms of high-temperature oxidation resistance due to an effect of a Si-based oxide such as SiO_2 . However, comparative example steel type No. 21 had a Si content of more than 1.5%, and did not exhibit a good result in terms of toughness.

[0106] Comparative example steel type No. 22 has an Al content of less than 2.0%, and does not tend to have formation of an oxide film of Al_2O_3 . This creates a state in which the partial pressure of oxygen is high, and equiaxial crystallization is likely to occur. As such, Comparative example steel type No. 22 did not exhibit a good result in terms of high-temperature oxidation resistance.

[0107] Comparative example steel type No. 23 tended to have equiaxial crystallization and did not exhibit a good result in terms of high-temperature oxidation resistance, due to having a Ti content greater than 0.20%.

[0108] Comparative example steel type No. 24 had a Nb content of more than 0.70%, was likely to have equiaxial crystal, and therefore did not exhibit a good result in terms of high-temperature oxidation resistance.

[0109] Comparative example steel type No. 25 had an Al content of more than 4.0%, and therefore did not exhibit a good result in terms of toughness.

[0110] Comparative example steel type No. 26 had a Cr content of more than 25.0%, tended to have an increased Cr concentration at alumina grain boundaries to form equiaxial crystallization, and did not exhibit a good result in terms of high-temperature oxidation resistance.

[0111] Comparative Example steel type No. 27 had a REM content of more than 0.20%, so that an oxide such as Y_2O_3 or CeO_2 was formed. As such, Comparative Example steel type No. 27 did not exhibit a good result on toughness.

Reference Signs List

[0112] 10: Alumina layer

Claims

1. A ferritic stainless steel, comprising not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than 0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass, and the other part composed of Fe and an inevitable impurity, the ferritic stainless steel having a dislocation density ρ of not less than 0.91×10^{14} [m^{-2}] as derived by the Williamson and Hall method, wherein in scanning electron microscope observation of random three $30 \mu\text{m} \times 30 \text{pm}$ portions in a cross section obtained by cutting the ferritic stainless steel along a plane perpendicular to a rolling direction, an average number of carbides each having (i) a Nb concentration of not less than 5 wt% as measured by energy dispersive X-ray spectroscopy and (ii) a particle diameter of not less than 0.1 μm is 2 to 15.

2. The ferritic stainless steel as set forth in claim 1, wherein: in a case where the ferritic stainless steel is heated at

EP 4 446 442 A1

1050°C for 50 hours, the ferritic stainless steel forms an alumina layer mainly composed of alumina; and in a cross section of the alumina layer obtained by cutting the alumina layer in a thickness direction, a total length of grain boundaries included in a given region having an area of 2.25 μm^2 is not more than 5.5 μm .

- 5 **3.** The ferritic stainless steel as set forth in claim 2, wherein a total concentration of a Nb oxide, a Cr oxide, and a REM-based oxide which are present in grain boundaries in the alumina layer is not less than 3.5 wt%.
- 10 **4.** The ferritic stainless steel as set forth in any one of claims 1 through 3, wherein the ferritic stainless steel further comprises at least one selected from the group consisting of not more than 0.50% of Zr, not more than 0.50% of V, not more than 1.0% of Cu, not more than 2.0% of Mo, not more than 2.0% of W, not more than 0.50% of Hf, not more than 0.50% of Sn, not more than 0.5% of Ta, not more than 0.20% of Ti, not more than 0.015% of Mg, and not more than 0.015% of Ca, in percent by mass.
- 15 **5.** The ferritic stainless steel as set forth in any one of claims 1 through 3, wherein the ferric stain steel satisfies $100 \times [\text{C}]/[\text{Nb}] \leq 35$ where [C] is a percent by mass of C and [Nb] is a percent by mass of Nb.
- 20 **6.** A method for producing a ferritic stainless steel, the ferritic stainless steel containing not more than 0.030% of C, 0.01% to 1.5% of Si, 0.01% to 1.00% of Mn, not more than 0.050% of P, not more than 0.005% of S, 15.0% to 25.0% of Cr, 2.0% to 4.0% of Al, not more than 1.00% of Ni, 0.01% to 0.70% of Nb, not more than 0.030% of N, 0.0003% to 0.01% of B, and 0.01% to 0.20% of REM, in percent by mass, and the other part composed of Fe and an inevitable impurity, the method comprising:
- 25 an annealing step of annealing a steel strip which has been hot-rolled, such that cooling time taken to cool the steel strip from an annealing temperature to 400 degrees after annealing is not less than 30 seconds; and
 a cold rolling step of carrying out, after a final annealing step, cold rolling until a dislocation density ρ derived by the Williamson and Hall method is not less than $0.91 \times 10^{14} [\text{m}^{-2}]$.
- 30 **7.** The method as set forth in claim 6, wherein in the cold rolling step, a rolling reduction ratio is not less than 65%.
- 35 **8.** The method as set forth in claim 6 or 7, wherein in scanning electron microscope observation of random three $30 \mu\text{m} \times 30 \mu\text{m}$ portions in a cross section obtained by cutting, along a plane perpendicular to a rolling direction, of the ferritic stainless steel obtained through the cold rolling step, an average number of carbides each having (i) a Nb concentration of not less than 5 wt% as measured by energy dispersive X-ray spectroscopy and (ii) a particle diameter of not less than 0.1 μm is 2 to 15.
- 40 **9.** The method as set forth in claim 6 or 7, wherein: the ferritic stainless steel forms an alumina layer in a case where the ferritic stainless steel is heated at 1050°C for 50 hours;
 and
 in a cross section of the alumina layer obtained by cutting the alumina layer in a thickness direction, a total length of grain boundaries included in a given region having an area of 2.25 μm^2 is not more than 5.5 μm .
- 45 **10.** The method as set forth in claim 9, wherein a total concentration of a Nb oxide, a Cr oxide, and a REM-based oxide which are present in grain boundaries in the alumina layer is not less than 3.5 wt%.
- 50 **11.** The method as set forth in claim 6 or 7, wherein the ferritic stainless steel further contains at least one selected from the group consisting of not more than 0.50% of Zr, not more than 0.50% of V, not more than 1.0% of Cu, not more than 2.0% of Mo, not more than 2.0% of W, not more than 0.50% of Hf, not more than 0.50% of Sn, not more than 0.5% of Ta, not more than 0.20% of Ti, not more than 0.015% of Mg, and not more than 0.015% of Ca, in percent by mass.
- 55 **12.** The method as set forth in claim 6 or 7, wherein the ferritic stainless steel satisfies $100 \times [\text{C}]/[\text{Nb}] \leq 35$ where [C] is a percent by mass of C and [Nb] is a percent by mass of Nb.

FIG. 1
INVENTIVE EXAMPLE

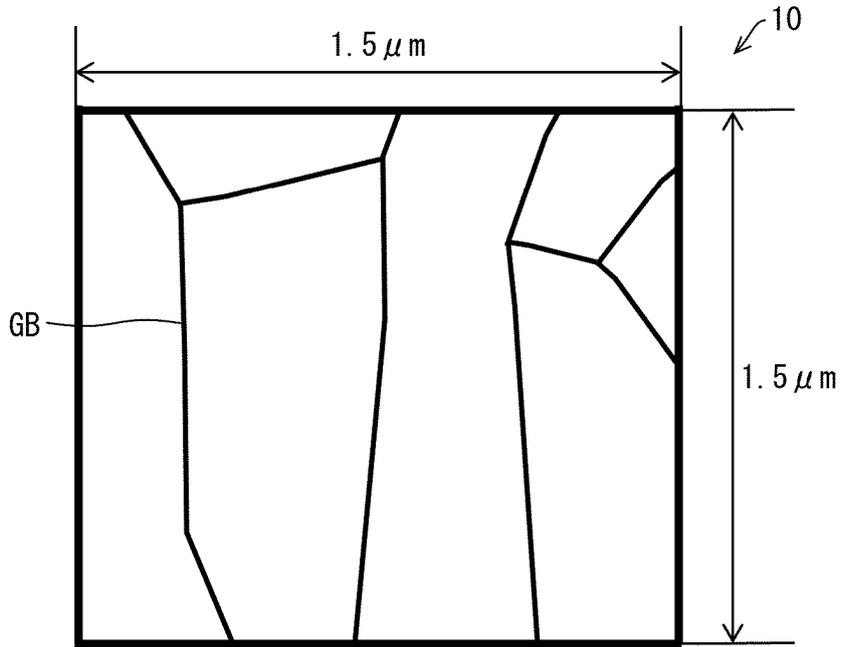
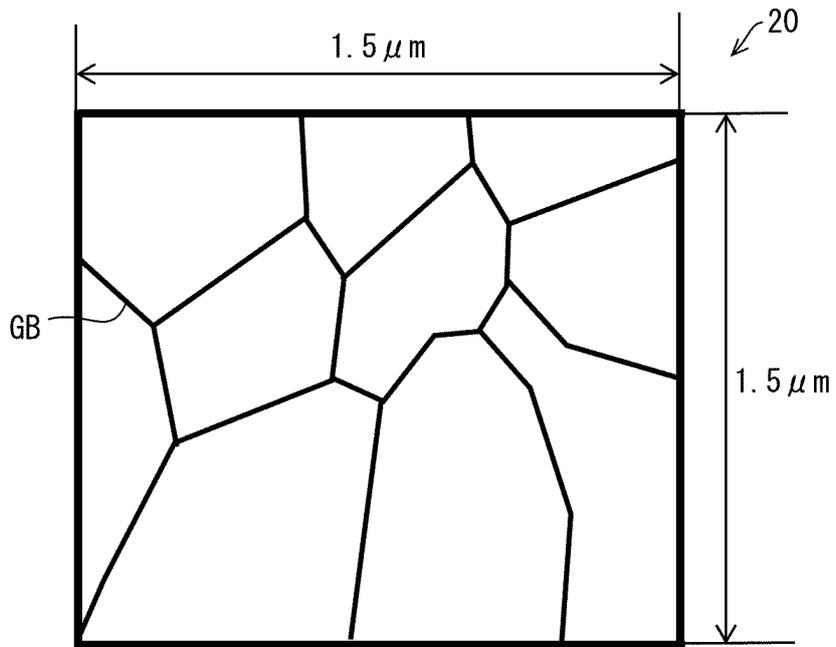


FIG. 2
COMPARATIVE EXAMPLE



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/044388

5	A. CLASSIFICATION OF SUBJECT MATTER		
	C21D 9/46(2006.01)i; C22C 38/00(2006.01)i; C22C 38/54(2006.01)i FI: C22C38/00 302Z; C22C38/54; C21D9/46 R		
	According to International Patent Classification (IPC) or to both national classification and IPC		
10	B. FIELDS SEARCHED		
	Minimum documentation searched (classification system followed by classification symbols) C21D9/46; C22C38/00; C22C38/54		
	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		
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
20	C. DOCUMENTS CONSIDERED TO BE RELEVANT		
	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	A	JP 2020-066794 A (NIPPON STEEL STAINLESS STEEL CORP) 30 April 2020 (2020-04-30)	1-12
25	A	JP 2002-146484 A (SANYO SPECIAL STEEL CO LTD) 22 May 2002 (2002-05-22)	1-12
	A	CN 111471938 A (WUHAN IRON AND STEEL CO LTD) 31 July 2020 (2020-07-31)	1-12
30			
35			
	<input type="checkbox"/> Further documents are listed in the continuation of Box C.		<input checked="" type="checkbox"/> See patent family annex.
40	* 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	
45	"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	Date of mailing of the international search report	
	25 January 2023	07 February 2023	
50	Name and mailing address of the ISA/IP	Authorized officer	
	Japan Patent Office (ISA/JP) 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915 Japan		
		Telephone No.	

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

55

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- JP 3351836 B [0004]