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(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 including, on a surface of the ferritic stainless steel, an Al-based oxide film having a thickness of not less than 8 nm and less than 20 nm.

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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]** High Al-containing ferritic stainless steels have high-temperature oxidation resistance and therefore are used in applications in which heat resistance is required, such as: a catalytic carrier (including an electric heating type) for exhaust gas purification provided in an automobile, a two-wheeled vehicle, or the like; a plant; a combustion tower; and the like.

15 **[0003]** Patent Literature 1 discloses that in a case where an oxide film of an Al₂O₃ columnar crystal has a thickness of not less than 0.1 μm and not more than 1.0 μm, it is possible to prepare an Fe-Cr-Al-based alloy foil that is sufficiently effective for oxidation resistance and high-temperature deformation resistance.

[0004] Patent Literature 2 discloses that in a case where an Al₂O₃ film has a thickness of not less than 20 nm and 200 nm, a stainless steel foil that is excellent in diffused junction properties and brazing properties can be prepared.

Citation List

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[Patent Literature]

[0005]

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[Patent Literature 1]
Japanese Patent Application Publication, Tokukai, No. 2003-105506
[Patent Literature 2]
Japanese Patent Application Publication, Tokukai, No. 2011-32524

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Summary of Invention

Technical Problem

35 **[0006]** However, although the technologies disclosed in Patent Literatures 1 and 2 are considered to be effective in terms of oxidation resistance, the technologies have the problem of poor brazing properties in a case where the technologies are applied to a product requiring brazing properties, such as a catalytic carrier.

[0007] An object of an aspect of the present invention is to provide a ferritic stainless steel which is oxidation resistant and is superior to conventional ferritic stainless steels in terms of brazing properties.

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Solution to Problem

45 **[0008]** In order to attain the object, 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 including, on a surface of the ferritic stainless steel, an Al-based oxide film having a thickness of not less than 8 nm and less than 20 nm.

50 **[0009]** A method for producing a ferritic stainless steel in accordance with an aspect of the present invention, 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 including:

55 a cold rolling step; and a final annealing step which is carried out after the cold rolling step, the final annealing step including a first step of carrying out heating to a temperature range of 900°C to 1200°C in an inert gas atmosphere and under a condition of a dew point of not higher than -40°C.

Advantageous Effects of Invention

[0010] According to an aspect of the present invention, it is possible to provide a ferritic stainless steel which is oxidation resistant and is superior to conventional ferritic stainless steels in terms of brazing properties.

Brief Description of Drawings

[0011] Fig. 1 is an SEM image of a cross section of an alumina layer which is mainly composed of alumina and is formed by heating a ferritic stainless steel in accordance with an embodiment of the present invention at 1050°C for 50 hours.

Description of Embodiments

[0012] 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)

[0013] Firstly, the following description will discuss essential elements contained in a ferritic stainless steel in accordance with the present embodiment.

[0014] 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.

[0015] 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.

[0016] 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>

[0017] 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>

[0018] 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>

[0019] 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

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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.

<P: phosphorus>

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[0020] 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%.
10 In a case where P is contained in an amount of not more than 0.040%, 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 0.030%.

<S: sulfur>

15 [0021] 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 Al₂O₃ 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%.

20 <Cr: chromium>

[0022] Cr is a fundamental alloy element which is necessary in order to improve the high-temperature oxidation resistance of a 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
25 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.

30 <Al: aluminum>

[0023] 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 Al₂O₃ is formed on the surface of the stainless steel, so that oxidation of the stainless steel is prevented. In a
35 case where REM or Y is added, the oxide film becomes 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.

40 <Ni: nickel>

[0024] Ni is an element which improves corrosion resistance of the 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
45 is excessively contained, the ferrite phase becomes unstable, and material costs increase. 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 an unstable ferrite phase and an increase in production costs, each of 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%.

50 <N: nitrogen>

[0025] 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
55 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)>

[0026] 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 prevents 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.

[0027] 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, compounds of B serve as inclusions (impurities).

[0028] 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 improving oxidation resistance. However, in a case where REM is excessively contained, a surface defect is generated during hot rolling, and producibility is reduced.

[0029] 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 not only further reduce the possibility of deterioration in workability but also improve oxidation resistance. 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)

[0030] 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>

[0031] 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>

[0032] 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>

[0033] 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 0.5%.

<Mo: molybdenum>

[0034] 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>

[0035] 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%.

<Hf: hafnium>

[0036] 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>

[0037] 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>

[0038] 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>

[0039] 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 0.15%.

<Mg: magnesium>

[0040] 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 Mg is 0.0002% to 0.0080%.

<Ca: calcium>

[0041] 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%.

[0042] The ferritic stainless steel in accordance with the present embodiment can satisfy $[Al]/(10 \times [Nb]) < 8$ where [Al] is a percent by mass of Al and [Nb] is a percent by mass of Nb. The inventors of the present invention have discovered that the amount of Nb added needs to be appropriate in accordance with the amount of Al added, and that when the above formula is satisfied, the various characteristics indicated in Examples described later, such as oxidation resistance, are satisfied.

(Al-based oxide film)

[0043] The following description will discuss an Al-based oxide film on a surface of the ferritic stainless steel in accordance with the present embodiment.

5 **[0044]** The ferritic stainless steel in accordance with the present embodiment includes, on a surface thereof, an Al-based oxide film having a thickness of not less than 8 nm and less than 20 nm. The Al-based oxide film is a film mainly composed of alumina and is formed through a final annealing step (described later). More specifically, an Al-based oxide film in accordance with the present disclosure means a film having an Al concentration of not less than 10%. By including
10 the Al-based oxide film having a thickness of not less than 8 nm, the ferritic stainless steel in accordance with the present embodiment has oxidation resistance. Further, since the thickness of the Al-based oxide film is less than 20 nm, it is possible to provide the ferritic stainless steel which is excellent in brazing properties.

(Alumina layer)

15 **[0045]** The inventors of the present invention discovered through diligent research that, regarding components of a ferritic stainless steel, in a case where Nb 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 and REM in grain boundaries in the alumina layer. Further, the inventors of the present invention discovered that the columnar crystallization is improved also in a case where B is
20 contained as an essential element at a concentration within an appropriate range.

[0046] 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, the use condition means a high temperature condition. For example, in the present embodiment, an alumina layer 20 formed in a case where heating is carried out at 1050°C for 50 hours is mentioned.

25 **[0047]** 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.

30 **[0048]** The alumina layer 20 formed by heating the ferritic stainless steel containing the above components at 1050°C for 50 hours has the following feature. That is, the alumina layer 20 is 100% made up of a columnar crystal or satisfies the following formula (1):

$$35 \quad (C)/(E) \geq 1.2 \dots(1)$$

where (C) is a thickness of a columnar crystal in a cross section obtained by cutting the alumina layer 20 in a thickness direction and (E) is a thickness of an equiaxial crystal in the cross section obtained by cutting the alumina layer 20 in the thickness direction.

40 **[0049]** Fig. 1 is an SEM image showing a cross section of the alumina layer 20 which is mainly composed of alumina and is formed in a case where the ferritic stainless steel 1 in accordance with an embodiment of the present invention is heated at 1050°C for 50 hours.

[0050] As shown in Fig. 1, in a case where the ferritic stainless steel including an Al-based oxide film is heated at 1050°C for 50 hours, the alumina layer 20 mainly composed of alumina is formed in the ferritic stainless steel 1. The alumina layer 20 includes a columnar crystal 201 and an equiaxial crystal 202.

45 **[0051]** The columnar crystal 201 is tissue in which crystal grains that have grown long and thin in the thickness direction of the alumina layer 20 are arranged. The equiaxial crystal 202 is polycrystalline tissue in which the shape and orientation of the crystal grains constituting the equiaxial crystal 202 are isotropic. The reference sign C in Fig. 1 indicates a thickness of the columnar crystal in a cross section obtained by cutting the alumina layer 20 in a thickness direction. The reference
50 sign E in Fig. 1 indicates a thickness of the equiaxial crystal in the cross section obtained by cutting the alumina layer 20 in the thickness direction.

[0052] The equiaxial crystal 202 has a grain boundary density greater than that of the columnar crystal 201 and therefore has increased routes through which oxygen is diffused at the grain boundaries. As such, the equiaxial crystal 202 has a shorter oxidation lifetime than the columnar crystal 201. The ferritic stainless steel in accordance with the
55 present embodiment is extremely excellent in oxidation resistance under high temperature conditions, since the alumina layer 20 satisfies formula (1) above or is 100% made up of a columnar crystal.

(Production method)

[0053] 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 first pickling step, a cold rolling step, a process annealing step, a final annealing step, and a second pickling step in this order.

[0054] 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.

[0055] 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.

[0056] The annealing step is a step of heating the hot-rolled steel strip obtained in the hot rolling step to a temperature of, for example, 900°C to 1050°C, so as to soften the steel strip. This annealing step is a step carried out as necessary, and may not be carried out.

[0057] The first 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.

[0058] 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, for example, 50% to 90%.

[0059] The process annealing step is a step of heating the steel strip obtained in the cold rolling step to a temperature of, for example, 900°C to 1050°C, so as to soften the steel strip. This annealing step is a step carried out as necessary, and may not be carried out.

[0060] The method for producing the ferritic stainless steel in accordance with the present embodiment includes the final annealing step after the process annealing (after the cold rolling step). In the final annealing step, a process is carried out, as a first step, in which heating is carried out in an inert gas atmosphere and under the condition of a dew point of not higher than -40°C until the temperature is in a temperature range of 900°C to 1200°C. After the first step, a process can be carried out as a second step in which the temperature is maintained in the temperature range of 900°C to 1200°C for not longer than 5 minutes in an inert gas atmosphere and under the condition of a dew point of not higher than -40°C. Carrying out the final annealing step makes it possible to produce a ferritic stainless steel which includes, on a surface thereof, an Al-based oxide film having a thickness of not less than 8 nm and less than 20 nm.

[0061] Note here that the inert gas can be, for example, Ar, H₂, or N₂. Alternatively, the inert gas can be a gas obtained by mixing two or three selected from the group consisting of Ar, H₂, or N₂ such that each of the two or three selected is mixed in a ratio ranging from 1% to 99% and the two or three selected constitute 100% together. More specifically, the inert gas can be, for example, a mixed gas of hydrogen, nitrogen, and/or argon. In this case, the mixed gas can contain 70% to 90% of hydrogen, 10% to 30% of nitrogen or argon, or the mixed gas can contain 70% to 90% of hydrogen and 5% to 25% of nitrogen and argon so that a content of nitrogen and argon is 30%.

[0062] The second pickling step is a step of, as necessary, washing off, with use of a pickle such as a mixed solution of nitric acid and hydrofluoric acid, scales adhering to the surface of the steel strip obtained in the final annealing step.

[0063] 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 including, on a surface of the ferritic stainless steel, an Al-based oxide film having a thickness of not less than 8 nm and less than 20 nm.

[0064] According to the above configuration, it is possible to provide a ferritic stainless steel which is excellent in oxidation resistance and brazing properties.

[0065] 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 forms an alumina layer 20 mainly composed of alumina; and the alumina layer is 100% made up of a columnar crystal or satisfies the following formula (1):

$$(C)/(E) \geq 1.2 \dots(1)$$

where (C) is a thickness of a columnar crystal 201 in a cross section obtained by cutting the alumina layer 20 in a thickness direction and (E) is a thickness of an equiaxial crystal 202 in the cross section obtained by cutting the alumina layer 20 in the thickness direction.

[0066] According to the above configuration, it is possible to provide a ferritic stainless steel which has an excellent effect in oxidation resistance under high temperature conditions. In particular, in a case where the alumina layer is 100% made up of a columnar crystal, it is possible to provide a ferritic stainless steel which has an even more excellent oxidation resistant effect.

[0067] In Aspect 3 of the present disclosure, the ferritic stainless steel in accordance with Aspect 1 or 2 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.

[0068] In Aspect 4 of the present disclosure, the ferritic stainless steel in accordance with Aspect 1 or 2 can be configured such that the ferritic stainless steel satisfies $[Al]/(10 \times [Nb]) < 8$

where [Al] is a percent by mass of Al and [Nb] is a percent by mass of Nb.

[0069] A method for producing a ferritic stainless steel in accordance with Aspect 5 of the present disclosure is a method for producing a ferritic stainless steel that 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, wherein a final annealing step after a cold rolling step includes a first step of carrying out heating in an inert gas atmosphere and under a condition of a dew point of not higher than -40°C until a temperature is in a temperature range of 900°C to 1200°C .

[0070] According to the above configuration, it is possible to produce a ferritic stainless steel which includes, on a surface thereof, an Al-based oxide film having a thickness of not less than 8 nm and less than 20 nm. This makes it possible to produce a ferritic stainless steel which is excellent in oxidation resistance and brazing properties.

[0071] In Aspect 6 of the present disclosure, the method in accordance with Aspect 5 can be configured such that the final annealing step includes a second step of maintaining the temperature in the temperature range of 900°C to 1200°C for not longer than 5 minutes after the first step.

[0072] According to the above configuration, it is possible to produce a ferritic stainless steel which includes, on a surface thereof, an Al-based oxide film having a thickness of not less than 8 nm and less than 20 nm.

[0073] In Aspect 7 of the present disclosure, the method in accordance with Aspect 5 or 6 can be configured such that: in a case where the ferritic stainless steel obtained through the final annealing step is heated at 1050°C for 50 hours, the ferritic stainless steel forms an alumina layer mainly composed of alumina; and the alumina layer is 100% made up of a columnar crystal or satisfies the following formula (1):

$$(C)/(E) \geq 1.2 \dots(1)$$

[0074] where (C) is a thickness of a columnar crystal 201 in a cross section obtained by cutting the alumina layer in a thickness direction and (E) is a thickness of an equiaxial crystal 202 in the cross section obtained by cutting the alumina layer 20 in the thickness direction.

[0075] According to the above configuration, it is possible to provide a ferritic stainless steel which has an excellent effect in oxidation resistance under high temperature conditions. In particular, in a case where the alumina layer is 100% made up of a columnar crystal, it is possible to provide a ferritic stainless steel which has brazing properties and an even more excellent oxidation resistant effect.

[0076] In Aspect 8 of the present disclosure, the method in accordance with any one of Aspects 5 through 7 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.

[Examples]

[0077] 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 Table 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.

[0078] 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 three times of cold rolling and three times of process annealing to produce a cold-rolled sheet having a thickness of 50 μm. The obtained cold-rolled sheet was subjected to final annealing in an inert gas atmosphere under the conditions of temperature, time, and dew point indicated in Table 2. For steel types No. 1 through 27, the final annealing was carried out with use of, as the inert gas, a gas containing 70% to 90% of H₂ and 10% to 30% of N₂ or Ar.

[0079] Note that the cold rolling was carried out at a rolling reduction ratio of 60% to 85%, and the process annealing after the cold rolling was carried out at a temperature condition in a range of 900°C to 1050°C. Note that the production method described in Examples is merely an example, and does not limit the production method.

[Table 1]

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Steel type No.	Essential element											Optional element											[Al]/(10*[Nb])	Category	
	C	Si	Mn	P	S	Cr	Al	Ni	Nb	N	B	REM	Zr	W	Ti	V	Mg	Ca	Sn	Cu	Ta	Hf			Mo
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											2.1	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						0.5	
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										0.51	1.8	
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												2.2	
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												1.3	
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	1.9	
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												2.2	
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					1.0	
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										1.5	
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		0.15										2.2	
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					0.38	1.7	
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												1.6	
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						0.0007						1.4	
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											1.3	
15	0.012	0.39	0.28	0.018	0.0006	17.95	2.98	0.12	0.04	0.011	0.0071	0.065							0.11					7.5	
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			1.5	
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		0.11						0.18				1.8	
18	0.009	0.31	0.29	0.041	0.0014	18.91	3.22	0.18	0.21	0.011	0.0015	0.006	0.05	0.34										1.5	
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		0.09										68.2	
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						1.2	
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									1.9	
22	0.010	0.43	0.19	0.031	0.0009	18.19	1.59	0.07	0.20	0.010	0.0025	0.081		0.13								1.54		0.8	
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		0.55										1.9	
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											0.4	
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									0.12			2.2	
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		0.38										0.9	
27	0.009	0.51	0.34	0.026	0.0009	20.12	3.82	0.09	0.03	0.008	0.0010	0.191		0.06										12.7	

[Table 2]

Steel type No.	Temperature [°C]	Time [sec]	Dew point [°C]	Category
1	1050	30	-60	Example of present invention
2	1150	30	-45	
3	1050	260	-60	
4	1050	60	-55	
5	1000	60	-50	
6	1050	60	-55	
7	1050	60	-60	
8	1075	180	-65	
9	1100	30	-65	
10	1100	60	-65	
11	1050	60	-60	
12	1050	60	-60	
13	1050	60	-65	
14	1100	30	-60	
15	950	120	-70	
16	1000	60	-60	
17	1000	60	-55	
18	<u>880</u>	30	-65	
19	975	30	-60	
20	1050	60	-60	
21	1050	60	-55	
22	1050	30	-60	
23	1100	180	<u>-35</u>	
24	1150	60	-60	
25	1150	60	-70	
26	1100	30	-60	
27	1075	<u>360</u>	-65	

[0080] 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 film thickness)

[0081] The following description will discuss a thickness of an Al-based oxide film in each of the examples of the present invention and the comparative examples prepared under the conditions indicated in Tables 1 and 2.

[0082] The thickness of the Al-based oxide film was measured with use of a glow discharge optical emission spectrometer (glow discharge spectroscopy: GDS) (GD-Profilier 2, manufactured by Horiba, Ltd.). Specifically, a cold-rolled annealed sheet having a thickness of 50 μm in accordance with each of the examples of the present invention and the comparative examples was subjected to measurement of an Al concentration, from a surface of the cold-rolled annealed

sheet to a position 0.1 μm deep from the surface, at a pitch of 0.0025 μm . Measurement conditions in the GDS measurement were as follows. Gas replacement time: 200 seconds, preliminary sputtering time: 30 seconds, background: 5 seconds, depth: 1.01 μm , pressure: 600 Pa, output: 35 W, effective value: 8.75 W. Module: 8 V, phase: 4 V, frequency: 100 Hz, duty cycle: 0.25.

5 **[0083]** Note that the thickness of a film mainly composed of alumina was determined such that a half-value width of an oxygen peak concentration was regarded as a thickness of the film mainly composed of alumina. The results are shown in Table 2 below. In determination of a film mainly composed of alumina in Table 2, "Good" indicates that the film mainly composed of alumina has a thickness of less than 20 nm, and "Poor" indicates that the film mainly composed of alumina has a thickness of not less than 20 nm.

10 (Brazing properties evaluation test)

15 **[0084]** The following description will discuss an evaluation test on brazing properties carried out with respect to the examples of the present invention and the comparative examples shown in Tables 1 and 2. The evaluation test on brazing properties was carried out by preparing a JIS 13B test piece from a cold-rolled annealed sheet having a thickness of 50 μm and then cutting the JIS 13B test piece in half. Specifically, the samples thus cut in half are placed so as to overlap with each other by 10 mm, and a brazing filler material (BNI-5: ASTM) was applied to one of the contact surfaces (12.5 mm \times 10 mm) so as to have a thickness of 0.1 mm. Then, with use of an atmosphere heat treatment furnace, the samples overlapping with each other were subjected to brazing in a vacuum (dew point: -65°C) at 1200°C , so that the samples were joined together. After the joining, a tensile test was carried out. The numerical values shown in Table 3 each indicate a tensile strength (MPa) at a time point when a breakage occurred. In a case where the tensile strength was not less than 250 MPa, it was determined that the brazing properties were good. In a case where a breakage occurred from the base material in the tensile test, it was determined that the brazing properties were good. In a case where a breakage occurred from the brazed part, it was determined that the brazing properties were poor. The brazing properties determined to be good are indicated as "Good" in Table 3. The brazing properties determined to be poor are indicated as "Poor" in Table 3.

(Measurement of ratio of columnar crystal to equiaxial crystal in alumina layer mainly composed of alumina)

30 **[0085]** The following description will discuss measurement of a ratio of a columnar crystal to an equiaxial crystal in an alumina layer mainly composed of alumina, carried out with respect to the examples of the present invention and the comparative examples shown in Tables 1 and 2. First, a test piece was heated at 1050°C for 50 hours and then immersed in liquid nitrogen for 5 minutes. Then, the test piece was taken out and immediately given an impact to break. Subsequently, with use of a scanning electron microscope (SEM) SU5000 (manufactured by Hitachi High-Tech Corporation), a cross section of the alumina layer was magnified and observed at a magnification of 20,000 times, and a thickness (C) of a columnar crystal and a thickness (E) of an equiaxial crystal were measured to calculate a ratio of the columnar crystal to the equiaxial crystal ((C)/(E)).

35 **[0086]** Note that the measurement of the ratio of the columnar crystal to the equiaxial crystal was carried out by SEM observation of the alumina layer magnified at a magnification of 20,000 times and calculation of an average value of data respectively measured at three random portions of the alumina layer. In a case where the equiaxial crystal was not formed in layers, a grain size of an equiaxial crystal that is present on its own was determined as the thickness of the equiaxial crystal.

40 **[0087]** The results are shown in Table 3 below. In determination of a ratio of a columnar crystal to an equiaxial crystal in an alumina layer in Table 2, "Good" indicates that the ratio of the columnar crystal to the equiaxial crystal in the alumina layer is not less than 1.2, and "Poor" indicates that the ratio of the columnar crystal to the equiaxial crystal in the alumina layer is less than 1.2.

(High-temperature oxidation resistance evaluation test)

50 **[0088]** 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 μm 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/cm^2 , and "Poor" indicates that the average increase in oxidation was more than 1 mg/cm^2 .

[Table 3]

Steel type No.	Thickness of Al-based oxide film < 20 nm [nm]		Tensile strength at room temperature after brazing (≥ 250 MPa) [MPa]		Ratio of columnar crystal to equiaxial crystal ($1050^{\circ}\text{C} \times 50$ h) [-]		Oxidation resistance $1050^{\circ}\text{C} \times 50$ h [mg/cm ²]		Category
1	18	Good	339	Good	4.1	Good	0.61	Good	Example of present invention
2	17	Good	368	Good	2.8	Good	0.71	Good	
3	19	Good	353	Good	2.5	Good	0.65	Good	
4	16	Good	332	Good	4.3	Good	0.62	Good	
5	18	Good	348	Good	3.9	Good	0.96	Good	
6	15	Good	353	Good	3.7	Good	0.59	Good	
7	16	Good	346	Good	3.4	Good	0.63	Good	
8	17	Good	341	Good	3.7	Good	0.62	Good	
9	14	Good	358	Good	3.6	Good	0.60	Good	
10	19	Good	336	Good	2.1	Good	0.88	Good	
11	15	Good	339	Good	3.3	Good	0.83	Good	
12	14	Good	355	Good	3.4	Good	0.61	Good	
13	17	Good	344	Good	3.5	Good	0.62	Good	
14	13	Good	359	Good	2.9	Good	0.65	Good	
15	18	Good	344	Good	3.2	Good	0.61	Good	
16	13	Good	348	Good	3.2	Good	0.64	Good	
17	31	Poor	224	Poor	0.9	Poor	1.23	Poor	Comparative example
18	54	Poor	165	Poor	1.1	Poor	1.63	Poor	
19	16	Good	350	Good	1.0	Poor	3.21	Poor	
20	17	Good	324	Good	1.1	Poor	3.92	Poor	
21	37	Poor	138	Poor	1.6	Good	0.66	Good	
22	15	Good	341	Good	1.0	Poor	4.31	Poor	
23	71	Poor	86	Poor	1.1	Poor	3.98	Poor	
24	18	Good	355	Good	0.8	Poor	2.65	Poor	
25	31	Poor	107	Poor	1.7	Good	0.63	Good	
26	49	Poor	88	Poor	1.1	Poor	1.56	Poor	
27	51	Poor	129	Poor	1.8	Good	0.64	Good	

[0089] As indicated in a column "Thickness of Al-based oxide film" in Table 3, steel types No. 1 through 16 of the inventive examples, which had been produced by a production method within the scope of the present invention, all included an Al-based oxide film having a thickness of less than 20 nm and had good brazing properties.

[0090] In contrast, comparative example steel types No. 17, 18, 21, 23, and 25 through 27 each included an Al-based oxide film having a thickness of not less than 20 nm and were poor in brazing properties.

[0091] Further, from the results in the column "Thickness of Al-based oxide film" in Table 3, it was verified that a ferritic stainless steel including an Al-based oxide film having a thickness of less than 20 nm was excellent in brazing properties.

[0092] Further, as indicated by the results in a column "Oxidation resistance" in Table 3, it was verified that steel types No. 1 through 16 of the inventive examples, each of which had been heated at 1050°C for 50 hours in the final annealing step, all exhibited a result that the steel type had a good oxidation resistance.

[0093] Further, from a column of results of a ratio of a columnar crystal to an equiaxial crystal and a column of results

of oxidation resistance in Table 3, it was verified that a good high-temperature oxidation resistance is exhibited in a case where the ratio of the columnar crystal to the equiaxial crystal is not less than 1.2.

[0094] That is, it was verified that in a case where a ferritic stainless steel within the scope of the present invention is heated at 1050°C for 50 hours, the ferritic stainless steel is excellent in brazing properties and oxidation resistance.

[0095] 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.

[0096] Comparative example steel type No. 17 had a Mn content of more than 1.0% and exhibited a result that the steel type had a decrease in high-temperature oxidation resistance. Further, comparative example steel type No. 17 not only decreased the secondary workability by having a B content of less than 0.0003% but also failed to exhibit a good result in terms of brazing properties.

[0097] Comparative example steel type No. 18 tended to have equiaxial crystallization due to having a REM content of less than 0.01% and a Ti content of more than 0.20%. As such, comparative example steel type No. 18 did not exhibit an excellent result in terms of high-temperature oxidation resistance.

[0098] Comparative example steel type No. 19 had a Nb content of less than 0.01% and thus had a possibility of deterioration in high-temperature oxidation resistance and workability. As such, comparative example steel type No. 19 did not exhibit an excellent result in terms of high-temperature oxidation resistance. However, comparative example steel type No. 19 had a Ti content of less than 0.20% and therefore exhibited a good result in terms of brazing properties.

[0099] Comparative example steel type No. 20 contained no Ti and did not tend to form a Ti-based oxide. As such, comparative example steel type No. 20 exhibited a good result in terms of brazing properties. However, 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.

[0100] 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 SiO₂. However, comparative example steel type No. 21 did not exhibit a good result in terms of brazing properties due to the Si content of more than 1.5% and formation of the Si-based oxide.

[0101] Comparative example steel type No. 22 had an Al content of less than 2.0% and did not tend to have formation of an oxide film of Al₂O₃. As such, comparative example steel type No. 22 exhibited a good result in terms of brazing properties but did not exhibit a good result in terms of high-temperature oxidation resistance.

[0102] Comparative example steel type No. 23 tended to have formation of a Ti oxide such as TiO₂ due to having a Ti content of more than 0.20%. As such, comparative example steel type No. 23 did not exhibit a good result in terms of high-temperature oxidation resistance and brazing properties.

[0103] Comparative example steel type No. 24 had a Nb content of more than 0.70% and tended to have equiaxial crystallization. As such, comparative example steel type No. 24 did not exhibit a good result in terms of high-temperature oxidation resistance.

[0104] Comparative example steel type No. 25 had an Al content of more than 4.0% and tended to have formation of an oxide film of Al₂O₃. As such, comparative example steel type No. 25 exhibited a good result in terms of high-temperature oxidation resistance but did not exhibit a good result in terms of brazing properties.

[0105] Comparative example steel type No. 26 had a Cr content of more than 25.0%, and tended to have an increased Cr concentration at alumina grain boundaries to form an equiaxial crystal. Further, comparative example steel type No. 26 has formation of a Ti oxide such as TiO₂ due to having a Ti content of more than 0.20%. As such, comparative example steel type No. 26 did not exhibit a good result in terms of high-temperature oxidation resistance and brazing properties.

[0106] Comparative example steel type No. 27 had a REM content of more than 0.20% and therefore exhibited a good result in terms of high-temperature oxidation resistance. However, comparative example steel type No. 27 did not exhibit a good result in terms of brazing properties, due to the REM content of more than 0.20% and formation of an oxide such as Y₂O₃ or CeO₂.

(Supplementary note)

[0107] The present invention is not limited to the embodiments, but can be altered by a skilled person in the art within the scope of the claims. The present invention also encompasses, in its technical scope, any embodiment derived by combining technical means disclosed in differing embodiments.

Reference Signs List

[0108]

1: Ferritic stainless steel

20: Alumina layer
 201: Columnar crystal
 202: Equiaxial crystal
 C: Thickness of columnar crystal
 E: Thickness of equiaxial crystal

Claims

10 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 including, on a surface of the ferritic stainless steel, an Al-based oxide film having a thickness of not less than 8 nm and less than 20 nm.

15 2. The ferritic stainless steel as set forth in claim 1, wherein:

20 in a case where the ferritic stainless steel is heated at 1050°C for 50 hours, the ferritic stainless forms an alumina layer mainly composed of alumina; and the alumina layer is 100% made up of a columnar crystal or satisfies the following formula (1):

$$(C)/(E) \geq 1.2 \dots(1)$$

25 where (C) is a thickness of a columnar crystal in a cross section obtained by cutting the alumina layer in a thickness direction and (E) is a thickness of an equiaxial crystal in the cross section obtained by cutting the alumina layer in the thickness direction.

30 3. The ferritic stainless steel as set forth in claim 1 or 2, 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.

35 4. The ferritic stainless steel as set forth in claim 1 or 2, wherein the ferritic stainless steel satisfies $[Al]/(10 \times [Nb]) < 8$ where [Al] is a percent by mass of Al and [Nb] is a percent by mass of Nb.

40 5. 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:

45 a cold rolling step; and a final annealing step which is carried out after the cold rolling step, the final annealing step including a first step of carrying out heating in an inert gas atmosphere and under a condition of a dew point of not higher than -40°C until a temperature is in a temperature range of 900°C to 1200°C.

50 6. The method as set forth in claim 5, wherein the final annealing step includes a second step of maintaining the temperature in the temperature range of 900°C to 1200°C for not longer than 5 minutes after the first step.

7. The method as set forth in claim 5 or 6, wherein:

55 in a case where the ferritic stainless steel obtained through the final annealing step is heated at 1050°C for 50 hours, the ferritic stainless steel forms an alumina layer mainly composed of alumina; and the alumina layer is 100% made up of a columnar crystal or satisfies the following formula (1):

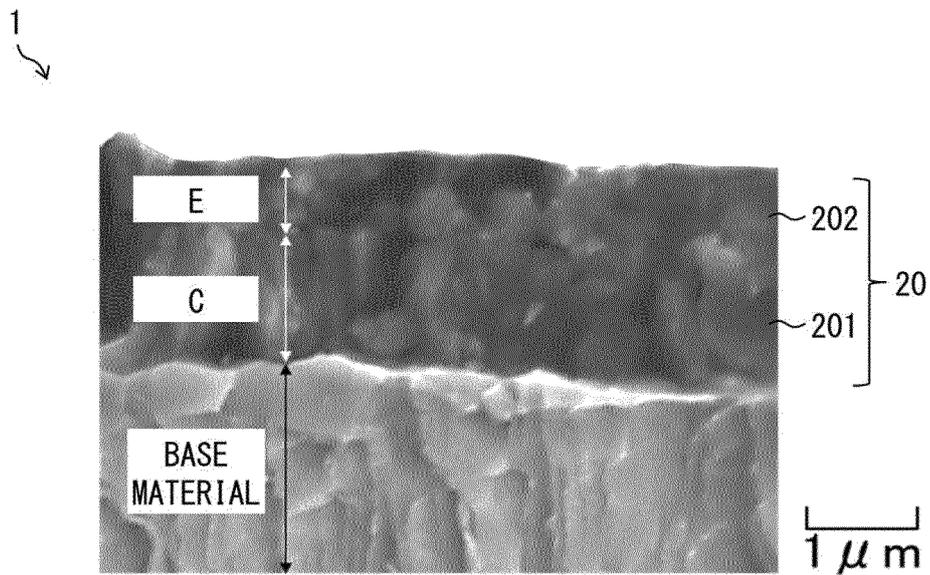
$$(C)/(E) \geq 1.2 \dots(1)$$

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where (C) is a thickness of a columnar crystal in a cross section obtained by cutting the alumina layer in a thickness direction and (E) is a thickness of an equiaxial crystal in the cross section obtained by cutting the alumina layer in the thickness direction.

8. The method as set forth in claim 5 or 6, 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.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/044386

A. CLASSIFICATION OF SUBJECT MATTER	
<p><i>C21D 9/46</i>(2006.01)i; <i>C22C 38/00</i>(2006.01)i; <i>C22C 38/54</i>(2006.01)i; <i>C23C 8/14</i>(2006.01)i FI: C22C38/00 302Z; C22C38/54; C21D9/46 R; C23C8/14</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>	
B. FIELDS SEARCHED	
Minimum documentation searched (classification system followed by classification symbols) C21D9/46; C22C38/00; C22C38/54; C23C8/14	
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	
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
A	JP 2021-004384 A (NIPPON STEEL STAINLESS STEEL CORP.) 14 January 2021 (2021-01-14)
A	JP 2021-055141 A (NIPPON STEEL STAINLESS STEEL CORP.) 08 April 2021 (2021-04-08)
A	JP 2021-161470 A (NIPPON STEEL STAINLESS STEEL CORP.) 11 October 2021 (2021-10-11)
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.	
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Date of the actual completion of the international search	Date of mailing of the international search report
25 January 2023	07 February 2023
Name and mailing address of the ISA/JP	Authorized officer
Japan Patent Office (ISA/JP) 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915 Japan	
	Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. PCT/JP2022/044386

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JP 2021-161470 A	11 October 2021	(Family: none)	

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REFERENCES CITED IN THE DESCRIPTION

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