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(54) AUSTENITIC STAINLESS STEEL

(57) An austenitic stainless steel includes base metal and a coating film formed on at least part of a surface of the base metal, a chemical composition of the base metal containing, in mass percent: C: 0.05% or less; Si: 1.0% or less; Mn: 2.0% or less; P: 0.040% or less; S: 0.010% or less; O: 0.020% or less; N: less than 0.050%; Ni: 12.0 to 27.0%; Cr: 15.0% or more to less than 20.0%; Cu: more than 3.5% to 8.0% or less; Mo: more than 2.0% to 5.0% or less; Co: 0.05% or less; Sn: 0.05% or less, V: 0 to 0.5%, Nb: 0 to 1.0%, Ti: 0 to 0.5%, W: 0 to 5.0%, Zr: 0 to 1.0%, Al: 0 to 0.5%, Ca: 0 to 0.01%, B: 0 to 0.01%, REM: 0 to 0.01%, and the balance: Fe and impurities, wherein a chemical composition at a maximum-Cr depth where a concentration of Cr in the coating film reaches a maximum satisfies, in at%, $[(Cr + Ni + Cu + Mo) / Fe \geq 1.0]$.

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Description

TECHNICAL FIELD

[0001] The present invention relates to an austenitic stainless steel, in particular to an austenitic stainless steel excellent in acid resistance.

[0002] Oil and coal, so-called "fossil fuels", used as boiler fuels for thermal power generation and industries contain sulfur (S). The fossil fuels therefore produce sulfur oxides (SO_x) in exhaust gas while burning. As the temperature of exhaust gas drops, SO_x reacts with moisture in the gas to form sulfuric acid, forming dew on a component surface at a temperature lower than a dew-point temperature. This may be a cause of sulfuric acid dew point corrosion.

[0003] Similarly, also in flue gas desulfurization facilities used in various industrial fields, when gas containing SO_x flows, the sulfuric acid dew point corrosion occurs as the temperature of the gas drops. Hereinafter, explanation will proceed with such gas containing SO_x as exhaust gas for simplicity.

[0004] In view of the phenomenon described above, in a heat exchanger or other device used in an exhaust gas system, the exhaust gas temperature is kept at as high as 150°C or a higher temperature so that sulfuric acid does not form dew on a component surface.

[0005] Due to a recent increase in demand for energy and from the viewpoint of effective use of energy, however, there is a trend toward lowering the temperature of exhaust gas from a heat exchanger, for example, below the dew point of the sulfuric acid to collect thermal energy as effective as possible, which has led to a demand for materials having a resistance against sulfuric acid.

[0006] If the exhaust gas temperature is not kept at 150°C or higher, about 80% high-concentration sulfuric acid forms dew on a component surface in a temperature range of about 140°C from exhaust gas of a typical composition. In such an environment, a so-called "low alloy steel" has been used as a steel for various components. This is because the low alloy steel has a higher corrosion resistance than a conventional stainless steel against such a high-temperature, high-concentration sulfuric acid.

[0007] In contrast, as described in Non-Patent Document 1, an amount of sulfuric acid that forms dew reaches the maximum at a temperature within a range lower than a dew point of the sulfuric acid by 20 to 60°C, and thus corrosion caused by the sulfuric acid becomes predominant. For this reason, if the exhaust gas temperature is not kept at 150°C or higher, a temperature range near 100°C is in general a range in which a corrosion resistance is required most, where a concentration of the sulfuric acid reaches about 70%. In this range, however, not only a conventional stainless steel but also even the low alloy steel cannot be used because of a large corrosion amount.

[0008] There has been a proposition that a specific corrosion resistant material can be used for a component in a sulfuric acid environment, and for example, Patent Document 1 discloses a sulfuric acid dew point corrosion resistant stainless steel that is excellent in hot workability.

[0009] In addition, Patent Document 2 discloses an austenitic stainless steel that has an excellent resistance to sulfuric acid corrosion as well as an excellent workability.

LIST OF PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0010]

Patent Document 1: JP4-346638A
Patent Document 2: JP3294282B

NON PATENT DOCUMENT

[0011] Non-Patent Document 1: Hiroo Nagano, "Sulfur Dewpoint Corrosion", Corrosion engineering, 1977, vol. 26, issue 12, p.731-740

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0012] A stainless steel described in Patent Document 1 is intended to stabilize an austenitic micro structure and to ensure a corrosion resistance by containing 0.05 wt% or more of N (nitrogen). However, when 0.05 wt% or more of N is contained, the austenitic stainless steel with Cu, Cr, and Mo added in combination rather decreases in corrosion resistance against sulfuric acid. In addition, in a case where a content of N is 0.05 wt% or more, increasing a content of Cu to enhance corrosion resistance against sulfuric acid raises a problem in that hot workability in a temperature range below 1000°C significantly decreases.

[0013] The austenitic stainless steel described in Patent Document 2 has excellent corrosion resistance against sulfuric acid and workability. The austenitic stainless steel is however susceptible to improvement in corrosion resistance against sulfuric acid.

[0014] An objective of the present invention is to provide an austenitic stainless steel with which the problem described above is solved and that has an excellent acid resistance in the environment where high-concentration sulfuric acid condenses.

[0015] Note that, in the following description, the "environment where high-concentration sulfuric acid condenses" refers to an environment where sulfuric acid at a concentration of 40 to 70% forms dew at a temperature of 50 to 100°C.

SOLUTION TO PROBLEM

[0016] The present invention has been made to solve the problems described above, and the gist of the present invention is the following austenitic stainless steel.

[0017]

(1) An austenitic stainless steel comprising base metal and a coating film formed on at least part of a surface of the base metal,
a chemical composition of the base metal consisting of, in mass percent:

C: 0.05% or less;
Si: 1.0% or less;
Mn: 2.0% or less;
P: 0.040% or less;
S: 0.010% or less;
O: 0.020% or less;
N: less than 0.050%;
Ni: 12.0 to 27.0%;
Cr: 15.0% or more to less than 20.0%;
Cu: more than 3.5% to 8.0% or less;
Mo: more than 2.0% to 5.0% or less;
Co: 0.05% or less;
Sn: 0.05% or less;
V: 0 to 0.5%;
Nb: 0 to 1.0%;
Ti: 0 to 0.5%;
W: 0 to 5.0%;
Zr: 0 to 1.0%;
Al: 0 to 0.5%;
Ca: 0 to 0.01%;
B: 0 to 0.01%;
REM: 0 to 0.01%, and
the balance: Fe and impurities, wherein
a chemical composition at a maximum-Cr depth where a concentration of Cr in the coating film reaches a maximum satisfies a following formula (i):

$$(Cr + Ni + Cu + Mo) / Fe \geq 1.0 \quad \ldots \quad (i)$$

where each symbol of element in the formula denotes a content (at%) of a corresponding element.

(2) The austenitic stainless steel according to the above (1), wherein
the chemical composition of the base metal containing one or more elements selected from, in mass percent:

V: 0.01 to 0.5%;
Nb: 0.02 to 1.0%;
Ti: 0.01 to 0.5%;

W: 0.1 to 5.0%;
Zr: 0.02 to 1.0%;
Al: 0.01 to 0.5%;
Ca: 0.0005 to 0.01%;
B: 0.0005 to 0.01%; and
REM: 0.0005 to 0.01%.

(3) The austenitic stainless steel according to the above (1) or (2), wherein
a minimum-Cr depth where the concentration of Cr in the coating film falls to a minimum lies closer to the base metal than the maximum-Cr depth, and
a chemical composition at the maximum-Cr depth satisfies a following formula (ii), and a chemical composition at the minimum-Cr depth satisfies a following formula (iii):

$$Cr / (Ni + Cu + Mo) \geq 1.0 \ldots \qquad (ii)$$

$$Cr / (Ni + Cu + Mo) < 1.0 \ldots \qquad (iii)$$

where each symbol of element in the formulas denotes a content (at%) of a corresponding element.

ADVANTAGEOUS EFFECTS OF INVENTION

[0018] According to the present invention, an austenitic stainless steel having an excellent acid resistance in the environment where high-concentration sulfuric acid condenses can be obtained.

DESCRIPTION OF EMBODIMENTS

[0019] The present inventors conducted intensive studies on methods for enhancing corrosion resistance against sulfuric acid, based on the austenitic stainless steel according to Patent Document 2, and as a result obtained the following findings.

[0020] To enhance the corrosion resistance against sulfuric acid, a composition of a coating film formed on a surface of base metal, which is to be in contact with a high-concentration sulfuric acid, is important. In the coating film, by making a total content of Cr, Ni, Cu, and Mo relatively higher than that of Fe, acid resistance is greatly improved.

[0021] In addition, the present inventors found that Cr, Ni, Cu, and Mo can be concentrated in a coating film by subjecting a steel to heat treatment under predetermined conditions to form an oxide film mainly containing Fe on its surface and then to acid treatment to dissolve an Fe component preferentially.

[0022] The present invention has been made based on the findings described above. Requirements of the present invention will be described below in detail.

1. Structure

[0023] An austenitic stainless steel according to the present invention includes base metal and a coating film formed on at least part of a surface of the base metal. The base metal and the coating film will be each described below in detail.

2. Base Metal

[0024] A chemical composition of base metal will be described in detail. The reasons for limiting contents of elements are as described below. In the following description, the symbol "%" for contents means "percent by mass".

C: 0.05% or less

[0025] C (carbon) is an element that has a function of enhancing strength. However, C combines with Cr to form Cr carbide in grain boundaries, resulting in deterioration in intergranular corrosion resistance. Accordingly, a content of C is set at 0.05% or less. When there is a need to enhance strength, C is preferably contained at more than 0.03%. In contrast, when a priority is given to ensuring corrosion resistance, the content of C should be made as low as possible and is preferably set at 0.03% or less. Although no particular lower limit needs to be provided to the content of C, the content of C is preferably set at 0.01% or more to obtain the effect described above.

Si: 1.0% or less

[0026] Si (silicon) is an element that has deoxidation action. However, a content of Si more than 1.0% contributes to deterioration in hot workability, and combined with an increase in a Cu content, Si at such a content makes it very difficult to work the base material into a product on an industrial scale. Accordingly, a content of Si is set at 1.0% or less. The content of Si is preferably 0.6% or less. Although there is no particular lower limit of the content of Si provided because Si is not necessarily contained, the content of Si is preferably set at 0.05% or more to obtain the effect described above. In a case where the content of Si is set to be extremely low for enhancement of hot workability, it is preferable to contain 0.1% or more of Si to have Si exert its deoxidation action sufficiently.

Mn: 2.0% or less

[0027] Mn (manganese) has an action of immobilizing S to enhance hot workability as well as of stabilizing an austenite phase. Containing Mn at a content more than 2.0%, however, saturates its effect, resulting only in higher costs. Accordingly, a content of Mn is set at 2.0% or less. The content of Mn is preferably 1.5% or less. Although there is no particular lower limit of the content of Mn provided because Mn is not necessarily contained, the content of Mn is preferably set at 0.1% or more to obtain the effect described above.

P: 0.040% or less

[0028] P (phosphorus) is contained in steel as an impurity and degrades hot workability and corrosion resistance, and therefore a content of P is preferably made as low as possible. In particular, when the content of P is more than 0.040%, P markedly degrades corrosion resistance in an environment where high-concentration sulfuric acid condenses. Accordingly, the content of P is set at 0.040% or less.

S: 0.010% or less

[0029] S (sulfur) is contained in steel as an impurity and degrades hot workability, and therefore a content of S is preferably made as low as possible. In particular, when the content of S is more than 0.010%, S markedly degrades hot workability. Accordingly, the content of S is set at 0.010% or less.

O: 0.020% or less

[0030] O (oxygen) is contained in steel as an impurity and decreases hot workability and ductility, and therefore a content of O is preferably made as low as possible. In particular, when the content of O is more than 0.020%, O markedly decreases hot workability and ductility, and therefore the content of O is set at 0.020% or less.

N: less than 0.050%

[0031] In conventional practices, N (nitrogen) has been positively added for a purpose of stabilizing an austenitic structure or enhancing a resistance to local corrosion such as pitting and crevice corrosion. However, in the environment where high-concentration sulfuric acid condenses, an N content of 0.050% or more rather results in deterioration in corrosion resistance of an austenitic stainless steel containing more than 3.5% of Cu, more than 2.0% of Mo, and 15.0% or more to less than 20.0% of Cr. Furthermore, even in a case where upper limits of Cu and Mo are set at 8.0% and 5.0%, respectively, an N content of 0.050% or more results in deterioration in hot workability. To give an austenitic stainless steel corrosion resistance and hot workability in the environment where high-concentration sulfuric acid condenses, an N content is set less than 0.050%. The lower the content of N is, the more preferable it is, and the content of N is preferably 0.045% or less.

Ni: 12.0 to 27.0%

[0032] Ni (nickel) has an action of stabilizing an austenite phase, as well as of enhancing corrosion resistance in the environment where high-concentration sulfuric acid condenses. To ensure such an effect sufficiently, it is necessary to contain Ni in an amount of 12.0% or more. Containing more than 27.0% of Ni however saturates its effect. In addition, being an expensive element, Ni leads to an extremely high cost and is thus uneconomical to use. Accordingly, a content of Ni is set at 12.0 to 27.0%. To ensure a sufficient corrosion resistance in the environment where high-concentration sulfuric acid condenses, Ni is preferably contained in an amount more than 15.0%, more preferably more than 20.0%.

Cr: 15.0% or more to less than 20.0%

[0033] Cr (chromium) is an element effective to ensure the corrosion resistance of an austenitic stainless steel. In particular, in a case of an austenitic stainless steel with N restricted to the content described above, containing 15.0% or more of Cr, preferably 16.0% or more of Cr, with Cu and Mo in amounts to be described later enables a good corrosion resistance to be ensured in the environment where high-concentration sulfuric acid condenses. However, containing an excessive amount of Cr rather degrades the corrosion resistance in the environment even in a case of an austenitic stainless steel with a low N content and with Cu and Mo added in combination, and in addition, the content also causes deterioration in workability. In particular, a content of Cr of 20.0% or more results in a significant degradation in the corrosion resistance of an austenitic stainless steel in the above environment. In addition, by setting a content of Cr at less than 20.0%, it is possible to increase the hot workability of the austenitic stainless steel with Cu and Mo added in combination, making it easy to work the base metal into a product on an industrial scale. Accordingly, the content of Cr is set at 15.0% or more to less than 20.0%.

Cu: more than 3.5% to 8.0% or less

[0034] Cu (copper) is an element indispensable for ensuring corrosion resistance in a sulfuric acid environment. Containing more than 3.5% of Cu together with Cr in the amount described above and Mo in an amount to be described later, an austenitic stainless steel with an N content set at the content described above can be provided with a good corrosion resistance in the environment where high-concentration sulfuric acid condenses. A larger content of Cu with Cu and Mo added in combination produces a greater advantageous effect of improving corrosion resistance, and thus a content of Cu is preferably set at a content of more than 4.0%. Note that increasing the content of Cu enables the improvement of the corrosion resistance in the environment but causes deterioration of hot workability, and in particular, a content of Cu more than 8.0% causes a significant degradation in hot workability even when the N content is set at the content described above. Accordingly, the content of Cu is set at more than 3.5% to 8.0% or less.

Mo: more than 2.0% to 5.0% or less

[0035] Mo (molybdenum) is an element effective to ensure the corrosion resistance of an austenitic stainless steel. Containing Mo at a content of more than 2.0% together with Cr and Cu at the contents described above, an austenitic stainless steel with an N content set at a content described above can be provided with a good corrosion resistance in the environment where high-concentration sulfuric acid condenses. However, containing an excessive amount of Mo leads to deterioration in hot workability, and in particular, a content of Mo more than 5.0% causes a significant deterioration in hot workability even with the content of N described above. Accordingly, a content of Mo is set at more than 2.0% to 5.0% or less. To ensure a sufficient corrosion resistance in the environment where high-concentration sulfuric acid condenses, Mo is preferably contained at a content more than 3.0%.

Co: 0.05% or less

[0036] Co (cobalt) is an element contained in steel as an impurity. Co is an element effective in enhancing toughness of steel but need not be added positively because Co is an expensive element. Accordingly, a content of Co is set at 0.05% or less.

Sn: 0.05% or less

[0037] Sn (tin) is contained in steel as an impurity and degrades hot workability, and therefore a content of Sn is preferably made as low as possible. In particular, the content of Sn being more than 0.05% leads to a marked deterioration in hot workability. Accordingly, a content of Sn is set at 0.05% or less.

V: 0.5% or less

[0038] V (vanadium) has an action of immobilizing C to enhance corrosion resistance, especially intergranular corrosion resistance, and therefore V may be contained as needed. However, if its content is more than 0.5%, its nitride forms even with the content of N set at the content described above, which rather results in deterioration in corrosion resistance, and its content being more than 0.5% also leads to deterioration in hot workability. Accordingly, a content of V is set at 0.5% or less. To obtain the above effect, it is preferable to set the content of V at 0.01% or more.

Nb: 0 to 1.0%

[0039] Nb (niobium) has an action of immobilizing C to enhance corrosion resistance, especially intergranular corrosion resistance, and therefore Nb may be contained as needed. However, if its content is more than 1.0%, its nitride forms even with the content of N set at the content described above, which rather results in deterioration in corrosion resistance, and its content being more than 0.5% also leads to deterioration in hot workability. Accordingly, a content of Nb is set at 1.0% or less. To obtain the above effect, it is preferable to set the content of Nb at 0.02% or more.

Ti: 0 to 0.5%

[0040] As with Nb, Ti (titanium) has an action of immobilizing C to enhance corrosion resistance, especially intergranular corrosion resistance, and therefore Ti may be contained as needed. However, if its content is more than 0.5%, its nitride forms even with the content of N set at the content described above, which rather results in deterioration in corrosion resistance, and its content being more than 0.5% also leads to deterioration in hot workability. Accordingly, a content of Ti is set at 0.5% or less. To obtain the above effect, it is preferable to set the content of Ti at 0.01% or more.

W: 0 to 5.0%

[0041] W (tungsten) has an action of enhancing corrosion resistance in the environment where high-concentration sulfuric acid condenses, and therefore W may be contained as needed. However, if its content is more than 5.0%, the above effect is saturated, resulting only in higher costs. Accordingly, a content of W is set at 5.0% or less. To obtain the above effect, it is preferable to set the content of W at 0.1% or more.

Zr: 0 to 1.0%

[0042] Zr (zirconium) has an action of enhancing corrosion resistance in the environment where high-concentration sulfuric acid condenses, and therefore Zr may be contained as needed. However, if its content is more than 1.0%, the above effect is saturated, resulting only in higher costs. Accordingly, a content of Zr is set at 1.0% or less. To obtain the above effect, it is preferable to set the content of Zr at 0.02% or more.

Al: 0 to 0.5%

[0043] Al has a deoxidation action, and therefore in a case where the content of Si is set to be extremely low, Al may be contained. However, when its content is more than 0.5%, even an austenitic stainless steel with N at the content described above deteriorates in its hot workability. Accordingly, a content of Al is set at 0.5% or less. A lower limit of the content of Al is not particularly limited and may be within an impurity range. In the case where the content of Si is set to be extremely low, however, it is preferable to add Al positively to make Al contained at 0.02% or more, so as to exert the deoxidation action sufficiently. Even with 0.05% or more of Si contained, it is preferable to set the content of Al at 0.01% or more so as to exert the deoxidation action sufficiently.

Ca: 0 to 0.01%

[0044] Combining with S, Ca (calcium) has an effect of preventing deterioration in hot workability, and therefore Ca may be contained as needed. However, a Ca content more than 0.01% results in deterioration in cleanliness of the steel, causing a defect to occur in production performed as a hot processing. Accordingly, a content of Ca is set at 0.01% or less. To obtain the above effect, the content of Ca is preferably set at 0.0005% or more, more preferably 0.001% or more.

B: 0 to 0.01%

[0045] B (boron) has an effect of improving hot workability, and therefore B may be contained as needed. However, adding B in an excessive amount promotes precipitation of Cr-B compound in grain boundaries, leading to deterioration in corrosion resistance. In particular, a content of B more than 0.01% results in a significant deterioration in corrosion resistance. Accordingly, a content of B is set at 0.01% or less. To obtain the above effect, the content of B is preferably set at 0.0005% or more, more preferably 0.001% or more.

REM: 0 to 0.01%

[0046] REMs (rare earth metals) have an action of enhancing hot workability, and therefore REM may be contained as needed. However, an REM content more than 0.01% results in deterioration in cleanliness of the steel, causing a defect to occur in production performed as a hot processing. Accordingly, a content of REM is set at 0.01% or less. To obtain the above effect, it is preferable to set the content of REM at 0.0005% or more.

[0047] Here, REM refers to Sc (scandium), Y (yttrium), and lanthanoids, 17 elements in total, and the content of REM refers to the total content of these elements.

[0048] In the chemical composition of the base metal of the austenitic stainless steel according to the present invention, the balance is Fe and impurities. The term "impurities" used herein means components that are mixed in steel in producing the steel industrially, owing to various factors including raw materials such as ores and scraps, and a producing process, and are allowed to be mixed in the steel within ranges in which the impurities have no adverse effect on the present invention.

3. Coating Film

[0049] As described above, on at least part of a surface of the base metal, a coating film is formed. In the coating film, by making a total content of Cr, Ni, Cu, and Mo relatively higher than that of Fe, acid resistance is greatly improved.

[0050] Specifically, the coating film includes a maximum-Cr depth where a concentration of Cr reaches its maximum, and at the maximum-Cr depth, the chemical composition needs to satisfy the following formula (i). Note that a position of the maximum-Cr depth is not particularly limited, and the maximum-Cr depth may lie in an outermost layer of the coating film.

$$(\mathrm{Cr} + \mathrm{Ni} + \mathrm{Cu} + \mathrm{Mo}) / \mathrm{Fe} \geq 1.0 \ldots \qquad \text{(i)}$$

Each symbol of element in the above formula denotes a content (at%) of a corresponding element in the surface of the steel.

[0051] The coating film according to the present invention generally has a structure including a layer on an outer layer side in which Cr is relatively concentrated, and a layer on a base metal side in which Ni and the like are relatively concentrated. That is, on a base metal side of the maximum-Cr depth, there is a minimum-Cr depth where the concentration of Cr reaches its minimum.

[0052] In addition, at the maximum-Cr depth, the chemical composition preferably satisfies the following formula (ii), and at the minimum-Cr depth, the chemical composition preferably satisfies the following formula (iii):

$$\mathrm{Cr} / (\mathrm{Ni} + \mathrm{Cu} + \mathrm{Mo}) \geq 1.0 \ldots \qquad \text{(ii)}$$

$$\mathrm{Cr} / (\mathrm{Ni} + \mathrm{Cu} + \mathrm{Mo}) < 1.0 \ldots \qquad \text{(iii)}$$

where each symbol of element in the formulas denotes a content (at%) of a corresponding element.

[0053] A thickness of the coating film is not particularly limited but is preferably within a range of, for example, from 2 to 10 nm. This is because if the thickness of the coating film is less than 2 nm, there is a risk that corrosion resistance against sulfuric acid cannot be obtained sufficiently, and at the same time, if the thickness of the coating film is more than 10 nm, there is a risk that a nonuniform composition of the coating film and peeling of the coating film is likely to occur.

[0054] In the present invention, the chemical composition of the coating film is assumed to be measured by depth profile analysis with the X-ray photoelectron spectroscopy (XPS). By the depth profile analysis, a concentration profile of each element is derived in a form of a ratio (at%) to components except for O, C, and N. In addition, after identifying the maximum-Cr depth and the minimum-Cr depth, concentrations of the elements at the depths are determined, and from values of the concentrations, the above formulas (i) to (iii) are calculated.

[0055] The thickness of the coating film is determined from the concentration profile of O (oxygen). Specifically, a position where a concentration of O is 1/3 of its maximum is determined as a boundary portion between the coating film and the base metal, and a length from a surface of the coating film to the above boundary portion is determined as the thickness of the coating film. It is desirable to make measurements of the composition and the thickness of the coating film at a plurality of points and to adopt average values of the measurements.

4. Producing Method

[0056] Although there is no particular limit to conditions for producing the austenitic stainless steel according to the present invention, but the austenitic stainless steel can be produced by, for example, performing heat treatment and acid treatment on a starting steel material having the chemical composition described above under the following conditions.

<Heat Treatment Process>

[0057] The starting steel material is subjected to heat treatment in which the starting steel material is held at a temperature within a range of from 1060 to 1140°C, for 60 to 600 seconds. On a surface of the starting steel material, an oxide film mainly containing Fe is thereby formed. If the temperature of the heat treatment is less than 1060°C, the formation of the Fe oxide film becomes insufficient. In contrast, if the temperature of the heat treatment is more than 1140°C, grains in the base metal become coarse, causing Fe to less diffuse, which makes the Fe oxide film uneven and further causes coating film to easily separate. Consequently, the concentration of Cr, Ni, Cu, and Mo hardly occurs in any of the above cases.

<Acid Treatment Process>

[0058] Subsequently to the heat treatment described above, the starting steel material is subjected to acid treatment. In an acid treatment process, Cr, Ni, Cu, and Mo can be concentrated in the surface of the steel by dissolving an Fe component preferentially. To dissolve the Fe component preferentially, it is preferable to immerse the starting steel material in hydrofluoric and nitric acid containing 5 to 8 vol% of HNO_3 and 5 to 8 vol% of HF at 30 to 50°C, for 1 to 5 hours.

[0059] Hereunder, the present invention is more specifically described with reference to Examples, but the present invention is not limited to these Examples.

EXAMPLES

[0060] Steels having chemical compositions shown in Table 1 (steel Nos. 1 to 11) were melted in a 3.5 t VIM melting furnace, and subjected to hot forging, hot extrusion, and cold drawing using normal methods, so as to be produced into steel pipe starting materials each having an outer diameter of 75 mm and a wall thickness of 3 mm. Thereafter, for test Nos. 1 to 17 and 19 to 28, the steel pipe starting materials were subjected to the heat treatment and the acid treatment under conditions shown in Table 2, thereby formed into austenitic stainless steel pipes. For a test No. 18, the steel pipe starting material was subjected to the heat treatment and the acid treatment under the same conditions as those for a test No. 3, and its surface was polished.

[Table 1]

Table 1

Steel No.	Chemical composition (in mass%, balance: Fe and impurities)																				
	C	Si	Mn	P	S	O	N	Ni	Cr	Cu	Mo	Co	Sn	V	Nb	Ti	W	Zr	Al	Ca	B	REM
1	0.02	0.48	1.01	0.006	0.001	0.003	0.037	15.51	17.97	4.23	3.23	0.02	0.002	0.02	0.012	0.008	-	-	0.022	-	0.0035	-
2	0.02	0.51	1.15	0.012	0.001	0.003	0.030	15.42	18.01	4.21	3.20	0.02	0.01	-	-	-	-	-	-	-	-	-
3	0.02	0.46	0.98	0.010	0.001	0.005	0.032	15.68	17.94	4.20	3.26	0.02	0.01	0.02	0.030	-	-	-	-	-	-	-
4	0.02	0.45	1.05	0.011	0.001	0.006	0.038	15.67	17.95	4.31	3.27	0.02	0.01	0.02	-	0.020	-	-	-	-	-	-
5	0.02	0.52	1.06	0.013	0.001	0.005	0.025	15.32	18.12	4.24	3.19	0.02	0.01	0.02	-	-	0.20	-	-	-	-	-
6	0.02	0.49	1.12	0.012	0.001	0.008	0.031	15.79	18.06	4.18	3.21	0.02	0.01	0.02	-	-	-	0.03	-	-	-	-
7	0.02	0.55	0.96	0.015	0.001	0.010	0.039	15.61	18.09	4.17	3.27	0.02	0.01	0.02	-	-	-	-	0.030	-	-	-
8	0.02	0.53	0.95	0.014	0.001	0.008	0.034	15.55	17.99	4.23	3.26	0.02	0.01	0.02	-	-	-	-	-	0.002	-	-
9	0.02	0.57	1.01	0.016	0.001	0.011	0.032	15.43	17.96	4.19	3.24	0.02	0.01	0.02	-	-	-	-	-	-	0.0030	-
10	0.02	0.48	1.08	0.012	0.001	0.005	0.030	15.38	17.90	4.25	3.22	0.02	0.01	0.02	-	-	-	-	-	-	-	0.005
11	0.01	0.26	1.57	<0.002	0.001	0.006	0.095 *	14.51	17.41	0.08 *	3.73	-	-	-	0.30	-	-	-	0.014	-	0.0015	-

* indicates that conditions do not satisfy those defined by the present invention.

[Table 2]

[0061]

Table 2

Test No.	Steel No.	Heat treatment conditions		Acid treatment conditions			
		Temperature (°C)	Time (s)	HNO_3 (vol.%)	HF (vol.%)	Temperature (°C)	Time (h)
1	1	1040	60	5	5	30	1
2	1	1040	180	5	5	30	1
3	1	1060	60	5	5	30	1
4	1	1060	180	5	5	30	1
5	1	1080	60	5	5	30	1
6	1	1080	180	5	5	30	1
7	1	1100	60	5	5	30	1
8	1	1100	180	5	5	30	1
9	1	1100	600	5	5	30	1
10	1	1120	60	5	5	30	1
11	1	1120	180	5	5	30	1
12	1	1140	60	5	5	30	1
13	1	1140	180	5	5	30	1
14	1	1160	180	5	5	30	1
15	1	1100	180	10	10	40	2
16	1	1100	180	5	5	60	2
17	1	1100	180	5	5	40	0.5
18	1	Polished surface					
19	2	1100	180	5	5	40	2
20	3	1100	180	5	5	40	2
21	4	1100	180	5	5	40	2
22	5	1100	180	5	5	40	2
23	6	1100	180	5	5	40	2
24	7	1100	180	5	5	40	2
25	8	1100	180	5	5	40	2
26	9	1100	180	5	5	40	2
27	10	1100	180	5	5	40	2
28	11	1100	180	5	5	40	2

[0062] Next, a chemical composition and a thickness of a coating film formed on a surface of each steel pipe were measured by the depth profile analysis using the XPS. Specifically, a concentration profile of each element was derived in a form of a ratio (at%) to components except for O, C, and N, the maximum-Cr depth and the minimum-Cr depth were identified, and then a concentration of each element at the depths was determined. Then, from values of the concentration, the formulas (i) to (iii) were calculated. In the present Example, the maximum-Cr depth laid in an outermost layer of the coating film in all of the Examples except for the test No. 18, and the minimum-Cr depth laid closer to the base metal side than the maximum-Cr depth in all of the Examples.

[0063] The thickness of the coating film was determined from the concentration profile of O (oxygen). Specifically, a position where a concentration of O was 1/3 of its maximum was determined as a boundary portion between the coating film and the base metal, and a length from a surface of the coating film to the above boundary portion was determined as the thickness of the coating film.

[0064] In addition, to evaluate the corrosion resistance against sulfuric acid, a corrosion test in a sulfuric acid environment was conducted. The corrosion test was conducted by immersing each steel pipe in a solution with a sulfuric acid concentration of 70% at a temperature of 100°C. Then, a corrosion loss after the immersion for 8 hours was measured, and a corrosion rate per unit area was calculated. In the present invention, cases where the above corrosion rate was equal to or less than 1.00 g/(m^2 h) were determined to be excellent in the corrosion resistance against sulfuric acid.

[0065] The results are shown in Table 3 altogether.

[Table 3]

[0066]

Table 3

Test No.	Steel No.	Maximum-Cr depth							Minimum-Cr depth						Thickness of coating film (nm)	Corrosion rate (g/m^2/h)	
		Chemical composition (at%)					Left side value of formula (i)#1	Left side value of formula (ii)#2	Chemical composition (at%)					Left side value of formula (iii)#3			
		Cr	Fe	Ni	Cu	Mo			Cr	Fe	Ni	Cu	Mo				
1	1	28.2	52.0	14.5	2.0	3.2	0.9*	1.4	12.7	63.3	18.0	3.1	2.9	0.5	2.6	1.02	Comparative example
2	1	28.9	51.5	14.5	1.7	3.4	0.9*	1.5	12.8	63.7	17.8	2.8	2.9	0.5	3.0	1.05	
3	1	29.3	49.6	15.7	1.7	3.7	1.0	1.4	13.3	60.7	20.1	2.8	3.1	0.5	3.4	0.92	Inventive example
4	1	29.1	49.4	15.9	2.4	3.2	1.0	1.4	13.2	60.6	20.1	3.2	2.9	0.5	3.1	0.90	
5	1	32.2	46.4	15.3	2.3	3.8	1.2	1.5	14.9	58.8	19.8	3.3	3.2	0.6	2.8	0.71	
6	1	33.3	46.1	14.0	2.3	4.3	1.2	1.6	14.5	59.5	19.4	3.2	3.4	0.6	3.7	0.76	
7	1	28.4	49.8	15.6	2.5	3.7	1.0	1.3	12.9	60.6	20.3	3.2	3.0	0.5	3.4	0.82	
8	1	31.7	45.8	15.3	2.4	4.8	1.2	1.4	13.0	60.0	18.5	5.0	3.5	0.5	3.5	0.85	
9	1	33.3	46.7	14.2	2.0	3.7	1.1	1.7	14.7	60.2	18.2	3.5	3.4	0.6	3.9	0.93	
10	1	33.6	45.1	15.3	2.1	3.8	1.2	1.6	15.4	58.6	18.7	3.8	3.5	0.6	4.1	0.65	
11	1	33.9	45.7	14.7	2.0	3.7	1.2	1.7	16.0	58.0	19.0	4.0	3.0	0.6	3.8	0.75	
12	1	34.8	45.8	13.6	2.2	3.7	1.2	1.8	16.5	58.5	18.1	3.7	3.2	0.7	4.2	0.81	
13	1	33.2	47.3	13.7	2.1	3.8	1.1	1.7	15.3	58.1	19.6	3.9	3.1	0.6	3.7	0.87	
14	1	29.9	52.1	13.0	1.9	3.1	0.9*	1.7	12.4	63.2	19.0	2.8	2.6	0.5	3.3	1.06	Comparative example
15	1	27.4	54.8	13.5	1.5	2.8	0.8*	1.5	12.8	62.5	18.7	2.9	3.1	0.5	3.4	1.15	
16	1	24.5	57.0	13.7	1.8	3.0	0.8*	1.3	13.4	62.2	18.5	3.1	2.8	0.5	3.2	1.21	
17	1	23.7	58.2	12.7	2.1	3.3	0.7*	1.3	14.6	61.0	18.9	3.1	2.4	0.6	3.1	1.42	
18	1	27.5	58.4	9.6	2.4	2.1	0.7*	2.0	14.0	63.5	18.0	2.0	2.5	0.6	2.8	1.50	

(continued)

Test No.	Steel No.	Maximum-Cr depth							Minimum-Cr depth						Thickness of coating film (nm)	Corrosion rate ($g/m^2/h$)	
		Chemical composition (at%)					Left side value of formula (i)[#1]	Left side value of formula (ii)[#2]	Chemical composition (at%)					Left side value of formula (iii)[#3]			
		Cr	Fe	Ni	Cu	Mo			Cr	Fe	Ni	Cu	Mo				
19	2	29.8	49.3	15.4	1.8	3.7	1.0	1.4	14.4	58.8	20.8	3.4	2.6	0.5	3.0	0.68	Inventive example
20	3	29.1	49.5	16.0	2.2	3.2	1.0	1.4	13.2	60.1	20.7	3.6	2.4	0.5	2.7	0.72	
21	4	32.3	46.2	15.5	2.1	3.9	1.2	1.5	14.3	58.5	20.8	3.3	3.1	0.5	2.8	0.91	
22	5	33.5	46.1	13.9	2.2	4.3	1.2	1.6	15.3	57.7	20.7	3.7	2.6	0.6	3.1	0.83	
23	6	31.3	48.8	14.4	2.2	3.3	1.0	1.6	15.1	58.4	20.7	3.6	2.2	0.6	3.3	0.67	
24	7	31.8	45.9	15.2	2.3	4.8	1.2	1.4	13.8	58.9	20.4	3.7	3.2	0.5	3.9	0.84	
25	8	33.6	45.1	15.3	2.3	3.7	1.2	1.6	15.8	58.1	20.1	3.8	2.2	0.6	4.5	0.79	
26	9	34.1	45.7	14.7	1.9	3.6	1.2	1.7	17.6	56.4	19.6	4.0	2.4	0.7	4.0	0.64	
27	10	32.6	49.3	13.3	1.8	3.0	1.0	1.8	16.4	57.9	18.6	4.0	3.1	0.6	3.8	0.91	
28	11*	29.2	51.3	15.7	0.1	3.7	0.9*	1.5	14.9	61.3	21.6	0.1	2.1	0.6	3.5	25.64	Comp. ex.

* indicates that conditions do not satisfy those defined by the present invention.

[#1]

$$(Cr+Ni+Cu+Mo)Fe \geq 1.0 \quad (i)$$

[#2]

$$Cr/(Ni+Cu+Mo) \geq 1.0 \quad (ii)$$

[#3]

$$Cr/(Ni+Cu+Mo) < 1.0 \quad (iii)$$

[0067] As seen from Table 3, as to test Nos. 1, 2, and 14 to 17, and the test No. 18 with the polished surface, in which the production conditions were inappropriate, their corrosion rates were high because the concentration of Cr, Ni, Cu, and Mo did not occur in their coating films, resulting in their poor corrosion resistances against sulfuric acid. Similarly, as to a test No. 28, in which a content of Cu in its base metal fell out of the regulation in the present invention, acid resistance brought by Cu was not obtained, and in addition, the concentration of Cr, Ni, Cu, and Mo in its coating film was insufficient, resulting in its poor corrosion resistance against sulfuric acid.

[0068] In contrast to them, as to test Nos. 3 to 13 and 19 to 27, which satisfied the regulations in the present invention, and in which Cr, Ni, Cu, and Mo were concentrated in their coating films, their corrosion rates were 1.00 g/(m^2 h) or less, resulting in their excellent corrosion resistances against sulfuric acid.

INDUSTRIAL APPLICABILITY

[0069] According to the present invention, an austenitic stainless steel having an excellent acid resistance in the environment where high-concentration sulfuric acid condenses can be obtained. Therefore, the austenitic stainless steel according to the present invention can be applied to various members such as a heat exchanger used in thermal power generation or industrial boilers, members for a flue gas desulfurization facility used in a smoke flue, chimney, and various industrial fields, and structure members used in a facility operating in a sulfuric acid environment.

Claims

1. An austenitic stainless steel comprising base metal and a coating film formed on at least part of a surface of the base metal,
   a chemical composition of the base metal consisting of, in mass percent:

   C: 0.05% or less;
   Si: 1.0% or less;
   Mn: 2.0% or less;
   P: 0.040% or less;
   S: 0.010% or less;
   O: 0.020% or less;
   N: less than 0.050%;
   Ni: 12.0 to 27.0%;
   Cr: 15.0% or more to less than 20.0%;
   Cu: more than 3.5% to 8.0% or less;
   Mo: more than 2.0% to 5.0% or less;
   Co: 0.05% or less;
   Sn: 0.05% or less;
   V: 0 to 0.5%;
   Nb: 0 to 1.0%;
   Ti: 0 to 0.5%;
   W: 0 to 5.0%;
   Zr: 0 to 1.0%;
   Al: 0 to 0.5%;
   Ca: 0 to 0.01%;
   B: 0 to 0.01%;
   REM: 0 to 0.01%, and
   the balance: Fe and impurities, wherein

   a chemical composition at a maximum-Cr depth where a concentration of Cr in the coating film reaches a maximum satisfies a following formula (i):

   $$(Cr + Ni + Cu + Mo) / Fe \geq 1.0 \ldots \qquad (i)$$

   where each symbol of element in the formula denotes a content (at%) of a corresponding element.

2. The austenitic stainless steel according to claim 1, wherein
   the chemical composition of the base metal containing one or more elements selected from, in mass percent:

V: 0.01 to 0.5%;
Nb: 0.02 to 1.0%;
Ti: 0.01 to 0.5%;
W: 0.1 to 5.0%;
Zr: 0.02 to 1.0%;
Al: 0.01 to 0.5%;
Ca: 0.0005 to 0.01%;
B: 0.0005 to 0.01%; and
REM: 0.0005 to 0.01%.

3. The austenitic stainless steel according to claim 1 or claim 2, wherein
a minimum-Cr depth where the concentration of Cr in the coating film falls to a minimum lies closer to the base metal than the maximum-Cr depth, and
a chemical composition at the maximum-Cr depth satisfies a following formula (ii), and a chemical composition at the minimum-Cr depth satisfies a following formula (iii):

$$Cr / (Ni + Cu + Mo) \geq 1.0 \ldots \qquad (ii)$$

$$Cr / (Ni + Cu + Mo) < 1.0 \ldots \qquad (iii)$$

where each symbol of element in the formulas denotes a content (at%) of a corresponding element.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/028146

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/58*(2006.01)i, *C21D1/76*(2006.01)n, *C21D6/00*(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00-38/60, C21D1/76, C21D6/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-189848 A (Sumitomo Metal Industries, Ltd.), 13 July 1999 (13.07.1999), (Family: none)	1-3
A	JP 11-158584 A (Sumitomo Metal Industries, Ltd.), 15 June 1999 (15.06.1999), (Family: none)	1-3
A	JP 2002-241900 A (Sumitomo Metal Industries, Ltd.), 28 August 2002 (28.08.2002), & US 6171547 B1 & EP 971045 A1	1-3

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

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"&" document member of the same patent family

Date of the actual completion of the international search 26 September 2017 (26.09.17)	Date of mailing of the international search report 10 October 2017 (10.10.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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International application No.
PCT/JP2017/028146

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2002-121655 A (Nippon Steel Corp.), 26 April 2002 (26.04.2002), (Family: none)	1-3
A	JP 2001-181800 A (Sumitomo Metal Industries, Ltd.), 03 July 2001 (03.07.2001), (Family: none)	1-3

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Non-patent literature cited in the description

- **HIROO NAGANO.** Sulfur Dewpoint Corrosion. *Corrosion engineering,* 1977, vol. 26 (12), 731-740 **[0011]**