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(54) **AUSTENITIC STAINLESS STEEL**

(57) Provided is an austenitic stainless steel having excellent anti-carburizing properties even in a high temperature carburizing environment, and an excellent hot workability in its production. The austenitic stainless steel according to the present embodiment includes a chemical composition consisting of, in mass percent, C: 0.03 to less than 0.25%, Si: 0.01 to 2.0%, Mn: 2.0% or less, Cr: 10 to less than 22%, Ni: more than 30.0% to 40.0%, Al: more than 2.5% to less than 4.5%, Nb: 0.01 to 3.5%, Ca: 0.0005 to 0.05%, Mg: 0.0005 to 0.05%, and N: 0.03% or less, with the balance being Fe and impurities. In the

austenitic stainless steel, a Cr concentration  $C_{Cr}'$  in its outer layer and an Al concentration  $C_{Al}'$  in the outer layer satisfy Formula (1) for a Cr concentration  $C_{Cr}$  in an other-than-outer-layer region and an Al concentration  $C_{Al}$  in the other-than-outer-layer region.

$$0.40 \leq (C_{Cr}'/C_{Al}')/(C_{Cr}/C_{Al}) \leq 0.80 \quad (1)$$

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## Description

## TECHNICAL FIELD

**[0001]** The present invention relates to a stainless steel, more particularly to an austenitic stainless steel.

## BACKGROUND ART

**[0002]** In facilities used under high temperature carburizing environment, such as thermal power generation boilers and chemical plants, austenitic stainless steels containing increased contents of Cr and increased contents of Ni, or Ni-based alloys containing increased contents of Cr have been used as heat resistant steels. These heat resistant steels are austenitic stainless steels or Ni-based alloys each containing about 20 to 30% by mass of Cr and about 20 to 70% by mass of Ni.

**[0003]** Pipes of the facilities such as thermal power generation boilers and chemical plants are produced from steel material pipes. The steel material pipe is produced by melting and thereafter performing hot working on the above austenitic stainless steel or Ni-based alloy. Therefore, heat resistant steels are requested to have high hot workabilities. However, austenitic stainless steels typically have high deformation resistances and low ductilities at high temperature. For that reason, there is a demand for austenitic stainless steels having excellent hot workabilities.

**[0004]** In what is called the shale gas revolution, inexpensive shale gas has been produced in recent years. As compared with conventional raw materials such as naphtha, use of shale gas as source gas in facilities such as chemical plants is likely to cause carburization, which is a corrosion phenomenon of a metallic tube (e.g., reaction tube) used in the facilities such as chemical plants due to carbon (C) derived from the source gas. Therefore, steels used in facilities such as chemical plants are requested to have excellent anti-carburizing properties.

**[0005]** Stainless steels having increased anti-carburizing properties and anti-coking properties are proposed in, for example, Japanese Patent Application Publication No. 2005-48284 (Patent Literature 1).

**[0006]** A stainless steel disclosed in Patent Literature 1 is made of a base material including a chemical composition consisting of, in mass percent, C: 0.01 to 0.6%, Si: 0.1 to 5%, Mn: 0.1 to 10%, P: 0.08% or less, S: 0.05% or less, Cr: 20 to 55%, Ni: 10 to 70%, N: 0.001 to 0.25%, O (oxygen): 0.02% or less, with the balance being Fe and unavoidable impurities. This stainless steel includes a Cr depleted zone in its near-surface portion, a Cr concentration in the Cr depleted zone is 10% or more and less than a Cr concentration in the base material, and a thickness of the Cr depleted zone is within 20  $\mu\text{m}$ . Patent Literature 1 states that the anti-carburizing properties and the anti-coking properties are increased by forming a protection film mainly made of  $\text{Cr}_2\text{O}_3$  coating film.

**[0007]** However, in the stainless steel of Patent Literature 1, the protection film mainly includes the  $\text{Cr}_2\text{O}_3$  coating film. Therefore, the stainless steel suffers from an insufficient function of preventing oxygen and carbon from entering from an external atmosphere, in particular, under a high temperature carburizing environment. As a result, internal oxidation and carburizing may occur in the material.

**[0008]** Hence, International Application Publication No. WO2010/113830 (Patent Literature 2), International Application Publication No. WO2004/067788 (Patent Literature 3), and Japanese Patent Application Publication No. 10-140296 (Patent Literature 4) disclose techniques relating to protection films that are alternatives to  $\text{Cr}_2\text{O}_3$  coating films. Specifically, according to these literatures, a protection film mainly containing  $\text{Al}_2\text{O}_3$ , which is thermodynamically stable, is formed on a surface of heat resistant steel, as a protection film that is an alternative to the  $\text{Cr}_2\text{O}_3$  coating films.

**[0009]** A cast product disclosed in Patent Literature 2 includes a casting made of a heat resistant alloy that consists of, in mass percent, C: 0.05 to 0.7%, Si: more than 0% to 2.5% or less, Mn: more than 0% to 3.0% or less, Cr: 15 to 50%, Ni: 18 to 70%, Al: 2 to 4 %, and rare earth metals: 0.005 to 0.4 %, as well as W: 0.5 to 10% and/or Mo: 0.1 to 5%, with the balance being Fe and unavoidable impurities. The casting includes a barrier layer formed on its surface that is to be brought into contact with a high-temperature atmosphere, the barrier layer is an  $\text{Al}_2\text{O}_3$  layer having a thickness of 0.5  $\mu\text{m}$  or more, 80% by area or more of an outermost surface of the barrier layer is  $\text{Al}_2\text{O}_3$ , and Cr-based particles disperse in an interface between the  $\text{Al}_2\text{O}_3$  layer and the casting, the Cr-based particles having a Cr concentration higher than that of a base of the alloy. Patent Literature 2 states that with added Al, a protection film mainly including an  $\text{Al}_2\text{O}_3$  protection film is formed, and anti-carburizing properties are increased.

**[0010]** A nickel-chromium casting alloy disclosed in Patent Literature 3 consists of, up to 0.8 % of Carbon, up to 1% of silicon, up to 0.2% of manganese, 15% to 40% of chromium, 0.5% to 13% of iron, 1.5% to 7% of aluminum, up to 2.5% of niobium, up to 1.5% of titanium, 0.01% to 0.4% of zirconium, up to 0.06% of nitrogen, up to 12% of cobalt, up to 5% of molybdenum, up to 6% of tungsten, and 0.019 % to 0.089% of yttrium, with the rest being nickel. Patent Literature 3 states that with added REM as well as Al, the nickel-chromium casting alloy including  $\text{Al}_2\text{O}_3$ , which serves as a protection film, with enhanced anti-peeling properties can be provided.

**[0011]** An austenitic stainless steel disclosed in Patent Literature 4 consists of, in mass percent, C: 0.15% or less, Si: 0.9% or less, Mn: 0.2 to 2%, P: 0.04% or less, S: 0.005% or less, S(%) and O(%) at 0.015% or less in total, Cr: 12 to

30%, Ni: 10 to 35%, Al: 1.5 to 5.5%, B: 0.001 to 0.01%, N: 0.025% or less, Ca: 0 to 0.008%, Cu: 0 to 2%, one or more elements of Ti, Nb, Zr, V, and Hf at 0 to 2% in total, one or more elements of W, Mo, Co, and Re at 0 to 3% in total, and one or more elements of rare earth metals at 0 to 0.05% in total, with the balance being Fe and unavoidable impurities. Patent Literature 4 states that with added Al, a protection film mainly including an  $\text{Al}_2\text{O}_3$  protection film is formed, and an oxidation resistance is increased.

## CITATION LIST

## PATENT LITERATURE

## [0012]

Patent Literature 1: Japanese Patent Application Publication No. 2005-48284

Patent Literature 2: International Application Publication No. WO2010/113830

Patent Literature 3: International Application Publication No. WO2004/067788

Patent Literature 4: Japanese Patent Application Publication No. 10-140296

## SUMMARY OF INVENTION

## TECHNICAL PROBLEM

[0013] However, in Patent Literature 2, the heat resistant alloy contains Cr at 50% at the maximum. Therefore, in a high temperature carburizing environment such as a hydrocarbon gas atmosphere, Cr may form its carbide on a steel surface. In this case,  $\text{Al}_2\text{O}_3$ , which serves as a protection film, is not formed uniformly. As a result, carburizing may occur.

[0014] In addition, the casting item and the nickel-chromium casting alloy disclosed in Patent Literatures 2 and 3 each have a high content of C, which significantly decreases their hot workabilities.

[0015] Furthermore, in Patent Literature 3, a content of Ni is high, which significantly increases a raw-material cost.

[0016] In Patent Literature 4, anti-carburizing properties are not considered. As a result, its anti-carburizing properties may be low.

[0017] An objective of the present invention is to provide an austenitic stainless steel that has excellent anti-carburizing properties even in a high temperature carburizing environment such as a hydrocarbon gas atmosphere, and provides an excellent hot workability in its production.

## SOLUTION TO PROBLEM

[0018] An austenitic stainless steel according to the present embodiment includes a chemical composition consisting of, in mass percent, C: 0.03 to less than 0.25%, Si: 0.01 to 2.0%, Mn: 2.0% or less, P: 0.04% or less, S: 0.01% or less, Cr: 10 to less than 22%, Ni: more than 30.0% to 40.0%, Al: more than 2.5% to less than 4.5%, Nb: 0.01 to 3.5%, N: 0.03% or less, Ca: 0.0005 to 0.05%, Mg: 0.0005 to 0.05%, Ti: 0 to less than 0.2%, Mo: 0 to 0.5%, W: 0 to 0.5%, Cu: 0 to 0.5%, V: 0 to 0.2%, and B: 0 to 0.01%, with the balance being Fe and impurities, and satisfying Formula (1).

$$0.40 \leq (\text{C}_{\text{Cr}}'/\text{C}_{\text{Al}}')/(\text{C}_{\text{Cr}}/\text{C}_{\text{Al}}) \leq 0.80 \quad (1)$$

[0019] Here, a Cr concentration (mass percent) in an outer layer of the austenitic stainless steel is substituted for  $\text{C}_{\text{Cr}}'$  in Formula (1). An Al concentration (mass percent) in the outer layer of the austenitic stainless steel is substituted for  $\text{C}_{\text{Al}}'$ . A Cr concentration (mass percent) in an other-than-outer-layer region of the austenitic stainless steel is substituted for  $\text{C}_{\text{Cr}}$ . An Al concentration (mass percent) in the other-than-outer-layer region of the austenitic stainless steel is substituted for  $\text{C}_{\text{Al}}$ .

## ADVANTAGEOUS EFFECTS OF INVENTION

[0020] The austenitic stainless steel according to the present embodiment has excellent anti-carburizing properties even in a high temperature carburizing environment such as a hydrocarbon gas atmosphere, and provides an excellent hot workability in its production.

## DESCRIPTION OF EMBODIMENTS

[0021] The present inventors conducted investigations and studies about anti-carburizing properties of the austenitic stainless steel in a high temperature carburizing environment and a hot workability in its production, and obtained the following findings. The high temperature carburizing environment refers to an environment in a hydrocarbon gas atmosphere at 1000°C or more.

(A) When an austenitic stainless steel or a Ni-based alloy is made to contain Cr, Cr<sub>2</sub>O<sub>3</sub> that is a protection film is formed on its steel surface, increasing its anti-carburizing properties. However, as described above, Cr<sub>2</sub>O<sub>3</sub> is thermodynamically unstable. Hence, in the present invention, an Al<sub>2</sub>O<sub>3</sub> coating film is formed on a surface of the steel. Al<sub>2</sub>O<sub>3</sub> acts as a protection film. Al<sub>2</sub>O<sub>3</sub> is thermodynamically more stable than Cr<sub>2</sub>O<sub>3</sub> in the high temperature carburizing environment. That is, the Al<sub>2</sub>O<sub>3</sub> coating film can increase the anti-carburizing properties of austenitic stainless steel even in an environment at 1000°C or more.

(B) When Cr is excessively contained in Al-containing austenitic stainless steel or Ni-based alloy, Cr binds with C derived from atmospheric gas in the high temperature carburizing environment. Cr binding with C forms a Cr carbide on the steel surface. The Cr carbide physically inhibits uniform formation of the Al<sub>2</sub>O<sub>3</sub> coating film on the steel surface. As a result, the anti-carburizing properties of steel are decreased. Therefore, the content of Cr needs to be limited to a certain content.

Meanwhile, Cr promotes uniform formation of the Al<sub>2</sub>O<sub>3</sub> coating film. Hereafter, this effect is called a Third Element Effect of Cr (referred to as a TEE effect below). A mechanism of the TEE effect is as follows. At the very beginning of a heat treatment process to be described later, Cr is preferentially oxidized first in the steel surface, and Cr<sub>2</sub>O<sub>3</sub> is formed. Therefore, an oxygen partial pressure in the steel surface locally decreases. As a result, Al does not undergo the inside oxidation but forms a uniform Al<sub>2</sub>O<sub>3</sub> coating film in proximity to the surface. Afterward, oxygen used in a form of Cr<sub>2</sub>O<sub>3</sub> is incorporated into Al<sub>2</sub>O<sub>3</sub>. Then, at the end of the heat treatment process, a protection film made only of Al<sub>2</sub>O<sub>3</sub> is formed. Likewise, Cr has the TEE effect even under the high temperature carburizing environment. That is, Cr promotes the uniform formation of the Al<sub>2</sub>O<sub>3</sub> coating film even under the high temperature carburizing environment. Therefore, to form a uniform Al<sub>2</sub>O<sub>3</sub> coating film, Cr needs to be contained at a certain content or more.

Accordingly, in order to promote inhibition of the production of a Cr carbide and promote the formation of the Al<sub>2</sub>O<sub>3</sub> coating film under the high temperature carburizing environment, a content of Cr is set at 10 to less than 22% in the present invention.

(C) For austenitic stainless steel, it is effective to make a ratio of a Cr concentration in an outer layer to an Al concentration in the outer layer moderately lower than a ratio of a Cr concentration in an other-than-outer-layer region to an Al concentration in the other-than-outer-layer region. That is, when an austenitic stainless steel satisfies Formula (1), the anti-carburizing properties in the high temperature carburizing environment is increased.

$$0.40 \leq (C_{Cr'}/C_{Al'})/(C_{Cr}/C_{Al}) \leq 0.80 \quad (1)$$

Here, a Cr concentration (mass percent) in an outer layer of the austenitic stainless steel is substituted for C<sub>Cr'</sub> in Formula (1). An Al concentration (mass percent) in the outer layer of the austenitic stainless steel is substituted for C<sub>Al'</sub>. A Cr concentration (mass percent) in an other-than-outer-layer region of the austenitic stainless steel is substituted for C<sub>Cr</sub>. An Al concentration (mass percent) in the other-than-outer-layer region of the austenitic stainless steel is substituted for C<sub>Al</sub>.

Define F1 as  $F1 = (C_{Cr'}/C_{Al'})/(C_{Cr}/C_{Al})$ . When F1 is 0.40 or more, the TEE effect by Cr is sufficiently provided on the steel surface in the high temperature carburizing environment. In this case, the formation of the Al<sub>2</sub>O<sub>3</sub> coating film is promoted. When F1 is 0.80 or less, the formation of the Cr carbide on the steel surface is inhibited in the high temperature carburizing environment. Therefore, the uniform Al<sub>2</sub>O<sub>3</sub> coating film is formed. As a result, the anti-carburizing properties are increased.

(D) When a chemical composition of an austenitic stainless steel contains 0.0005% or more of calcium (Ca) and 0.0005% or more of magnesium (Mg), the hot workability is increased. In contrast, when contents of these elements are excessively high, a toughness and a ductility of an austenitic stainless steel at high temperature are decreased, resulting in a decrease in hot workability. For this reason, Ca: 0.0005 to 0.05%, and Mg: 0.0005 to 0.05% are contained.

[0022] An austenitic stainless steel according to the present embodiment that is made based on the above findings includes a chemical composition consisting of, in mass percent, C: 0.03 to less than 0.25%, Si: 0.01 to 2.0%, Mn: 2.0%

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or less, P: 0.04% or less, S: 0.01% or less, Cr: 10 to less than 22%, Ni: more than 30.0% to 40.0%, Al: more than 2.5% to less than 4.5%, Nb: 0.01 to 3.5%, N: 0.03% or less, Ca: 0.0005 to 0.05%, Mg: 0.0005 to 0.05%, Ti: 0 to less than 0.2%, Mo: 0 to 0.5%, W: 0 to 0.5%, Cu: 0 to 0.5%, V: 0 to 0.2%, and B: 0 to 0.01%, with the balance being Fe and impurities, and satisfying Formula (1).

$$0.40 \leq (C_{Cr'}/C_{Al'})/(C_{Cr}/C_{Al}) \leq 0.80 \quad (1)$$

Here, a Cr concentration (mass percent) in an outer layer of the austenitic stainless steel is substituted for  $C_{Cr'}$  in Formula (1). An Al concentration (mass percent) in the outer layer of the austenitic stainless steel is substituted for  $C_{Al'}$ . A Cr concentration (mass percent) in an other-than-outer-layer region of the austenitic stainless steel is substituted for  $C_{Cr}$ . An Al concentration (mass percent) in the other-than-outer-layer region of the austenitic stainless steel is substituted for  $C_{Al}$ .

**[0023]** The above chemical composition may contain one or two or more types selected from the group consisting of Ti: 0.005 to less than 0.2%, Mo: 0.01 to 0.5%, W: 0.01 to 0.5%, Cu: 0.005 to 0.5%, V: 0.005 to 0.2%, and B: 0.0001 to 0.01.

**[0024]** Hereafter, the austenitic stainless steel according to the present embodiment will be described in detail. The sign "%" following each element means mass percent unless otherwise noted.

[Chemical Composition]

**[0025]** A chemical composition of the austenitic stainless steel according to the present embodiment contains the following elements.

C: 0.03 to less than 0.25%

**[0026]** Carbon (C) binds mainly with Cr to form a Cr carbide in the steel, increasing a creep strength in use in the high temperature carburizing environment. An excessively low content of C results in failure to provide this effect. In contrast, an excessively high content of C causes a large number of coarse eutectic carbides to be formed in a solidification micro structure after the steel is cast, resulting in a decrease in a toughness of the steel. Consequently, a content of C is 0.03 to less than 0.25%. A lower limit of the content of C is preferably 0.05%, more preferably 0.08%. An upper limit of the content of C is preferably 0.23%, more preferably 0.20%.

Si: 0.01 to 2.0%

**[0027]** Silicon (Si) deoxidizes steel. If the deoxidation can be sufficiently performed using another element, a content of Si may be reduced as much as possible. In contrast, an excessively high content of Si results in a decrease in the hot workability. Consequently, the content of Si is 0.01 to 2.0%. A lower limit of the content of Si is preferably 0.02%, more preferably 0.03%. An upper limit of the content of Si is preferably 1.0%.

Mn: 2.0% or less

**[0028]** Manganese (Mn) is unavoidably contained. Mn binds with S contained in the steel to form MnS, increasing the hot workability of the steel. However, an excessively high content of Mn makes the steel too hard, resulting in decreases in the hot workability and weldability. Consequently, a content of Mn is 2.0% or less. A lower limit of the content of Mn is preferably 0.1%, more preferably 0.2%. An upper limit of the content of Mn is preferably 1.2%.

P: 0.04% or less

**[0029]** Phosphorus (P) is an impurity. P decreases the weldability and the hot workability of the steel. Consequently, a content of P is 0.04% or less. An upper limit of the content of P is preferably 0.03%. The content of P is preferably as low as possible. A lower limit of the content of P is, for example, 0.0005%.

S: 0.01% or less

**[0030]** Sulfur (S) is an impurity. S decreases the weldability and the hot workability of the steel. Consequently, a content of S is 0.01% or less. An upper limit of the content of S is preferably 0.008%. The content of S is preferably as low as possible. A lower limit of the content of S is, for example, 0.001%.

Cr: 10 to less than 22%

**[0031]** Chromium (Cr) exhibits the above TEE effect to promote the formation of the  $\text{Al}_2\text{O}_3$  coating film in the heat treatment process and under the high temperature carburizing environment. In addition, Cr binds with C in the steel to form a Cr carbide, increasing the creep strength. An excessively low content of Cr results in failure to provide these effects. In contrast, an excessively high content of Cr causes Cr to bind with C derived from atmospheric gas (hydrocarbon gas) under the high temperature carburizing environment and form a Cr carbide on the steel surface. The formation of the Cr carbide on the steel surface causes local depletion of Cr in the steel surface. This lessens the TEE effect, resulting in failure to form the uniform  $\text{Al}_2\text{O}_3$  coating film. An excessively high content of Cr further causes the Cr carbide on the steel surface to physically inhibit the formation of the uniform  $\text{Al}_2\text{O}_3$  coating film. Consequently, a content of Cr is 10 to less than 22%. A lower limit of the content of Cr is preferably 11%, more preferably 12%. An upper limit of the content of Cr is preferably 21%, more preferably 20%. In the present specification, the Cr carbide is divided into a Cr carbide formed in the steel and a Cr carbide formed on the steel surface. For the austenitic stainless steel according to the present embodiment, the Cr carbide in the steel is allowed to form, and the Cr carbide on the steel surface is inhibited.

Ni: more than 30.0% to 40.0%

**[0032]** Nickel (Ni) stabilizes an austenite, increasing the creep strength. In addition, Ni increases the anti-carburizing properties of the steel. An excessively low content of Ni results in failure to provide these effects. In contrast, an excessively high content of Ni results not only in saturation of these effects but also in an increase in raw-material costs. Consequently, a content of Ni is more than 30.0% to 40.0%. A lower limit of the content of Ni is preferably 31.0%, more preferably 32.0%. An upper limit of the content of Ni is preferably 39.0%, more preferably 38.0%.

Al: more than 2.5% to less than 4.5%

**[0033]** Aluminum (Al) forms the  $\text{Al}_2\text{O}_3$  coating film on the steel surface in the heat treatment process and under the high temperature carburizing environment, increasing the anti-carburizing properties of the steel. In particular, in the high temperature carburizing environment assumed in the present invention, the  $\text{Al}_2\text{O}_3$  coating film is thermodynamically stable as compared with  $\text{Cr}_2\text{O}_3$  coating films conventionally used. An excessively low content of Al results in failure to provide these effects. In contrast, an excessively high content of Al leads to a decrease in structural stability, resulting in a significant decrease in the creep strength. Consequently, a content of Al is more than 2.5% to less than 4.5%. A lower limit of the content of Al is preferably 2.55%, more preferably 2.6%. An upper limit of the content of Al is preferably 4.2%, more preferably 4.0%. In the austenitic stainless steel according to the present invention, the content of Al means a total amount of Al contained in the steel material.

Nb: 0.01 to 3.5%

**[0034]** Niobium (Nb) forms intermetallic compounds to be precipitation strengthening phases (Laves phase and  $\text{Ni}_3\text{Nb}$  phase) to cause precipitation strengthening in crystal grain boundaries and in grains, increasing the creep strength of the steel. In contrast, an excessively high content of Nb causes the intermetallic compounds to be produced excessively, resulting in a decrease in the toughness of the steel. In addition, an excessively high content of Nb also results in a decrease in the toughness after long-time aging. Consequently, a content of Nb is 0.01 to 3.5%. A lower limit of the content of Nb is preferably 0.05%, more preferably 0.1%. An upper limit of the content of Nb is preferably less than 3.2%, more preferably 3.0%.

N: 0.03% or less,

**[0035]** Nitrogen (N) stabilizes austenite and is unavoidably contained. In contrast, an excessively high content of N causes coarse nitride and/or carbo-nitride, which remains undissolved even after heat treatment, to be produced. The coarse nitride and/or carbo-nitride decreases the toughness of the steel. Consequently, a content of N is 0.03% or less. An upper limit of the content of N is preferably 0.01%. A lower limit of the content of N is, for example, 0.0005%.

Ca: 0.0005 to 0.05%

**[0036]** Calcium (Ca) immobilizes S in a form of its sulfide, increasing the hot workability. In contrast, an excessively high content of Ca results in a decrease in the toughness and the ductility. As a result, the hot workability decreases. In addition, an excessively high content of Ca results in a decrease in cleanliness. Consequently, a content of Ca is 0.0005 to 0.05%. A lower limit of the content of Ca is preferably 0.0006%, more preferably 0.0008%. An upper limit of the content

of Ca is preferably 0.01%, more preferably 0.008%.

Mg: 0.0005 to 0.05%

5 **[0037]** Magnesium (Mg) immobilizes S in a form of its sulfide, increasing the hot workability of the steel. In contrast, an excessively high content of Mg results in a decrease in the toughness and the ductility. As a result, the hot workability decreases. In addition, an excessively high content of Mg results in a decrease in cleanliness. Consequently, a content of Mg is 0.0005 to 0.05%. A lower limit of the content of Mg is preferably 0.0006%, more preferably 0.0008%. An upper limit of the content of Mg is preferably 0.01%, more preferably 0.008%.

10 **[0038]** The balance of the chemical composition of the austenitic stainless steel according to the present embodiment is Fe and impurities. Here, the impurities mean elements that are mixed from ores and scraps used as raw material, a producing environment, or the like when the austenitic stainless steel is produced in an industrial manner, and are allowed to be mixed within ranges in which the impurities have no adverse effect on the present invention.

15 [Optional Elements]

**[0039]** The above chemical composition of the austenitic stainless steel may further contain Ti in lieu of a part of Fe.

Ti: 0 to less than 0.2%

20 **[0040]** Titanium (Ti) is an optional element and need not be contained. If contained, Ti forms intermetallic compounds to be precipitation strengthening phases (Laves phase and  $\text{Ni}_3\text{Ti}$  phase) to cause precipitation strengthening, increasing the creep strength. In contrast, an excessively high content of Ti causes the intermetallic compounds to be produced excessively, resulting in a decrease in high-temperature ductility and the hot workability. In addition, an excessively high content of Ti results in a decrease in the toughness after long-time aging. Consequently, a content of Ti is 0 to less than 0.2%. A lower limit of the content of Ti is preferably 0.005%, more preferably 0.01%. An upper limit of the content of Ti is preferably 0.15%, more preferably 0.1%.

25 **[0041]** The above chemical composition of the austenitic stainless steel may further contain, in lieu of a part of Fe, one or two elements selected from the group consisting of Mo and W. All of these elements are optional elements and increase the creep strength of the steel.

Mo: 0 to 0.5%

35 **[0042]** Molybdenum (Mo) is an optional element and need not be contained. If contained, Mo is dissolved in the austenite, a parent phase. The dissolved Mo causes solid-solution strengthening, increasing the creep strength. In contrast, an excessively high content of Mo results in a decrease in the hot workability. Consequently, a content of Mo is 0 to 0.5%. A lower limit of the content of Mo is preferably 0.01%, more preferably 0.05%. An upper limit of the content of Mo is preferably 0.4%, more preferably 0.3%.

40 W: 0 to 0.5%

**[0043]** Tungsten (W) is an optional element and need not be contained. If contained, W is dissolved in the austenite, the parent phase. The dissolved W causes solid-solution strengthening, increasing the creep strength. In contrast, an excessively high content of W results in a decrease in the hot workability. Consequently, a content of W is 0 to 0.5%. A lower limit of the content of W is preferably 0.01%, more preferably 0.05%. An upper limit of the content of W is preferably 0.4%, more preferably 0.3%.

**[0044]** The above chemical composition of the austenitic stainless steel may further contain Cu in lieu of a part of Fe.

Cu: 0 to 0.5%

50 **[0045]** Copper (Cu) is an optional element and need not be contained. If contained, Cu stabilizes the austenite. In addition, Cu causes precipitation strengthening, increasing a strength of the steel. In contrast, an excessively high content of Cu results in a decrease in the ductility and the hot workability of the steel. Consequently, a content of Cu is 0 to 0.5%. A lower limit of the content of Cu is preferably 0.005%, more preferably 0.01%. An upper limit of the content of Cu is preferably 0.3%, more preferably 0.1%.

**[0046]** The above chemical composition of the austenitic stainless steel may further contain V in lieu of a part of Fe.

V: 0 to 0.2%

**[0047]** Vanadium (V) is an optional element and need not be contained. If contained, V forms intermetallic compounds, as with Ti, increasing the creep strength of the steel. In contrast, an excessively high content of V makes a volume ratio of the intermetallic compounds in the steel excessively high, resulting in a decrease in the hot workability. Consequently, a content of V is 0 to 0.2%. A lower limit of the content of V is preferably 0.005%, more preferably 0.01%. An upper limit of the content of V is preferably 0.15%, more preferably 0.1%.

**[0048]** The above chemical composition of the austenitic stainless steel may further contain B in lieu of a part of Fe.

B: 0 to 0.01%

**[0049]** Boron (B) is an optional element and need not be contained. If contained, B segregates in grain boundaries, promoting precipitation of intermetallic compounds in the grain boundaries. This increases the creep strength of the steel. In contrast, an excessively high content of B results in decreases in the weldability and the hot workability of the steel. Consequently, the content of B is 0 to 0.01%. A lower limit of the content of B is preferably 0.0001%, more preferably 0.0005%. An upper limit of the content of B is preferably 0.008%, more preferably 0.006%.

[Formula (1)]

**[0050]** The austenitic stainless steel according to the present embodiment further satisfies Formula (1).

$$0.40 \leq (C_{Cr}'/C_{Al}')/(C_{Cr}/C_{Al}) \leq 0.80 \quad (1)$$

Here, a Cr concentration (mass percent) in an outer layer of the austenitic stainless steel is substituted for  $C_{Cr}'$  in Formula (1). An Al concentration (mass percent) in the outer layer of the austenitic stainless steel is substituted for  $C_{Al}'$ . A Cr concentration (mass percent) in an other-than-outer-layer region of the austenitic stainless steel is substituted for  $C_{Cr}$ . An Al concentration (mass percent) in the other-than-outer-layer region of the austenitic stainless steel is substituted for  $C_{Al}$ .

**[0051]** In the present specification, the outer layer of the austenitic stainless steel means a range of 2  $\mu\text{m}$  depth from the surface of the austenitic stainless steel. The 2  $\mu\text{m}$  depth from the surface means 2  $\mu\text{m}$  depth from a surface of the base metal. When the austenitic stainless steel includes the  $\text{Al}_2\text{O}_3$  coating film on its surface, the 2  $\mu\text{m}$  depth from the surface of the base metal means 2  $\mu\text{m}$  depth from the surface of the base metal after the  $\text{Al}_2\text{O}_3$  coating film is removed by descaling treatment. That is, the Cr concentration (mass percent) in the range of 2  $\mu\text{m}$  depth from the surface of the austenitic stainless steel (when the austenitic stainless steel includes the  $\text{Al}_2\text{O}_3$  coating film on its surface, it is the surface of the base metal after the  $\text{Al}_2\text{O}_3$  coating film is removed by the descaling treatment) is substituted for  $C_{Cr}'$  in Formula (1). The Al concentration (mass percent) in the range of 2  $\mu\text{m}$  depth from the surface of the austenitic stainless steel (when the austenitic stainless steel includes the  $\text{Al}_2\text{O}_3$  coating film on its surface, it is the surface of the base metal after the  $\text{Al}_2\text{O}_3$  coating film is removed by the descaling treatment) is substituted for  $C_{Al}'$  in Formula (1). The Cr concentration of the other-than-outer-layer region (mass percent) means an average Cr concentration (mass percent) in a region of the base material other than the outer layer. The Al concentration of the other-than-outer-layer region (mass percent) means an average Al concentration (mass percent) in the region of the base material other than the outer layer.

**[0052]** As shown in Formula (1), in the austenitic stainless steel according to the present embodiment, the ratio of the Cr concentration in the outer layer to the Al concentration in the outer layer is made moderately lower than the ratio of the Cr concentration of the base material to the Al concentration of the base material. In this case, the formation of the  $\text{Al}_2\text{O}_3$  coating film is promoted as described above. As a result, the anti-carburizing properties are increased in the high temperature carburizing environment.

Define F1 as  $F1 = (C_{Cr}'/C_{Al}')/(C_{Cr}/C_{Al})$ . F1 is an index of Cr behavior.

**[0053]** When F1 is more than 0.80, the ratio of the Cr concentration of the outer layer to the Al concentration of the outer layer is excessively higher than the ratio of the Cr concentration of the base material to the Al concentration of the base material. That is,  $C_{Cr}'$ , the Cr concentration of the outer layer, is excessively high. In this case, in the high temperature carburizing environment, a Cr carbide is formed on the steel surface, physically inhibiting the formation of the uniform  $\text{Al}_2\text{O}_3$  coating film.

**[0054]** When F1 is less than 0.40, the ratio of the Cr concentration of the outer layer to the Al concentration of the outer layer is excessively lower than the ratio of the Cr concentration of the base material to the Al concentration of the



base material. That is,  $C_{Cr'}$  which is the Cr concentration of the outer layer, is excessively low. In this case, the TEE effect by Cr is not provided in the high temperature carburizing environment. Therefore, the uniform  $Al_2O_3$  coating film is not formed on the steel surface.

**[0055]** Consequently, F1 is 0.40 to 0.80. A lower limit of F1 is preferably 0.42, more preferably 0.44. An upper limit of F1 is preferably 0.79, more preferably 0.78.

**[0056]** The Cr concentration  $C_{Cr'}$  in the outer layer and the Al concentration  $C_{Al'}$  in the outer layer described above are determined by the following method. The austenitic stainless steel is cut perpendicularly to its surface. In the range of 2  $\mu m$  depth from the surface of the cut austenitic stainless steel (when the austenitic stainless steel includes the  $Al_2O_3$  coating film on its surface, it is the surface of the base metal after the  $Al_2O_3$  coating film is removed by the descaling treatment), any five points (measurement points) are selected. The Cr concentrations and the Al concentrations at the measurement points are measured by EDX (Energy Dispersive X-ray Spectroscopy). Values determined by averaging the measured values are defined as  $C_{Cr'}$  (%) and  $C_{Al'}$  (%).

**[0057]** When the austenitic stainless steel includes the  $Al_2O_3$  coating film on its surface, the Cr concentration  $C_{Cr'}$  in the outer layer and the Al concentration  $C_{Al'}$  in the outer layer are measured after the descaling treatment is performed. Conditions for descaling the austenitic stainless steels conform to JIS Z 2290(2004).

**[0058]** Analysis of the Cr concentration  $C_{Cr}$  in the other-than-outer-layer region and the Al concentration  $C_{Al}$  in the other-than-outer-layer region described above can be conducted by a well-known component analysis method. Specifically, they are determined by the following method. The austenitic stainless steel is cut perpendicularly to its longitudinal direction (in a case of a steel pipe, it is its axis direction), and a measurement surface is prepared. A wall-thickness center portion of the measurement surface is pierced with a drill. By the piercing, machined chips are produced, and the machined chips are collected. The machined chips are collected at four spots of the same measurement surface. When the austenitic stainless steel is a steel pipe, the machined chips are collected at four spots provided at 45° pitches. The collected machined chips are subjected to ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) to conduct an elemental analysis of its chemical composition. A procedure of the analysis according to the ICP-OES conforms to JIS G 1258(2007). Averages of the measured values for the four spots are defined as the Cr concentration  $C_{Cr}$  in the other-than-outer-layer region (%) and the Al concentration  $C_{Al}$  in the other-than-outer-layer region (%).

**[0059]** The austenitic stainless steel according to the present embodiment includes the  $Al_2O_3$  coating film on its surface after the heat treatment process to be described later. Therefore, the austenitic stainless steel of the present embodiment may include the  $Al_2O_3$  coating film on its surface. However, the  $Al_2O_3$  coating film can be removed by a well-known method such as pickling treatment and shotpeening performed after the heat treatment process. Therefore, in the austenitic stainless steel of the present embodiment, the  $Al_2O_3$  coating film may be removed from its surface.

#### [Grain Size]

**[0060]** The austenitic stainless steel according to the present embodiment preferably has a grain size of 30 to 80  $\mu m$ . When the grain size is 30  $\mu m$  or more, the creep strength of the steel further increases. When the grain size is 80  $\mu m$  or less, grain boundary diffusion of Al is promoted, which further promotes the formation of the  $Al_2O_3$  coating film. The grain size is determined by the microscopic test method for a grain size specified in JIS G 0551(2013).

**[0061]** A shape of the austenitic stainless steel according to the present embodiment is not limited to a particular shape. The austenitic stainless steel is, for example, a steel pipe. An austenitic stainless steel pipe is used as a reaction tube for a chemical plant. The austenitic stainless steel may be a plate material, a bar material, a wire rod, or the like.

#### [Producing Method]

**[0062]** As an example of a method for producing the austenitic stainless steel of the present embodiment, description will be made about a method for producing a steel pipe.

#### [Preparation Process]

**[0063]** A molten steel having the chemical composition described above is produced. The molten steel is subjected to a well-known degassing treatment as necessary. The molten steel is cast to produce a starting material. The starting material may be an ingot made by an ingot-making process, or a cast piece such as a slab, bloom, and billet made by a continuous casting process. Alternatively, a tube-shaped casting may be produced by a centrifugal casting process.

#### [Hot Forging Process]

**[0064]** Hot forging may be performed on the produced starting material to produce a cylindrical starting material. By performing the hot forging, an interior structure of the molten steel produced in the preparation process can be modified

from a solidification micro structure to a regulated-grain-sized structure, which is formed by homogeneous grains. A temperature of the hot forging is, for example, 900 to 1200°C.

#### [Hot Working Process]

**[0065]** Hot working is performed on the starting material produced through the preparation process or the starting material produced by the hot forging (cylindrical starting material) to produce a steel material pipe. For example, a through hole is formed at a center of the cylindrical starting material by machining. The cylindrical starting material with the through hole formed is subjected to hot extrusion to produce the steel material pipe. A machining temperature of the hot extrusion is, for example, 900 to 1200°C. The steel material pipe may be produced by performing piercing-rolling (the Mannesmann process etc.) on the cylindrical starting material.

#### [Cold Working Process]

**[0066]** Cold working is performed on the steel material pipe subjected to the hot working to produce an intermediate material. The cold working is, for example, cold drawing or the like. In the cold working process, giving strain to the steel surface allows elements such as Al and Cr to move to the steel surface easily. In this case, the TEE effect is provided sufficiently. It is thereby possible to obtain an austenitic stainless steel in which Cr is moderately depleted in an outer layer of the steel and that satisfies Formula (1). This effect cannot be provided when a working ratio of the cold working is excessively low. An upper limit of the working ratio of the cold working is not particularly specified, but cold working with an excessively high working ratio is practically difficult to perform. Consequently, the working ratio of the cold working is 10 to 90%.

#### [Heat Treatment Process]

**[0067]** Heat treatment is performed on the produced intermediate material in an air atmosphere. By performing the heat treatment in the air atmosphere, the uniform  $\text{Al}_2\text{O}_3$  coating film is formed on the steel surface. At that time, Cr in the outer layer of the steel is moderately depleted by the TEE effect. As a result, it is possible to obtain the austenitic stainless steel satisfying Formula (1).

**[0068]** A temperature of the heat treatment is 900 to less than 1100°C, and a duration of the heat treatment is 3.0 to 30.0 minutes.

**[0069]** If the temperature of the heat treatment is less than 900°C, or the duration of the heat treatment is less than 3.0 minutes, the TEE effect cannot be provided sufficiently. In this case, the Cr concentration  $C_{\text{Cr}}'$  in the outer layer of the steel becomes excessively high, failing to satisfy Formula (1). Accordingly, a Cr carbide is formed on the steel surface under the high temperature carburizing environment, and the uniform  $\text{Al}_2\text{O}_3$  coating film is not formed sufficiently. As a result, the anti-carburizing properties are decreased. Consequently, the temperature of the heat treatment is 900°C or more, and the duration of the heat treatment is 3.0 minutes or more. In addition, when the temperature of the heat treatment is 900°C or more, and the duration of the heat treatment is 3.0 minutes or more, a grain size becomes 30  $\mu\text{m}$  or more.

**[0070]** In contrast, if the temperature of the heat treatment is 1100°C or more, scales mainly made of  $\text{Cr}_2\text{O}_3$  are formed excessively on the steel surface. Therefore, Cr in the outer layer of the steel is excessively depleted. In this case, the Cr concentration  $C_{\text{Cr}}'$  in the outer layer of the steel becomes excessively low, failing to satisfy Formula (1). Accordingly, the TEE effect by Cr under the high temperature carburizing environment is lessened, and the uniform  $\text{Al}_2\text{O}_3$  coating film is not formed sufficiently. As a result, the anti-carburizing properties are decreased. If the duration of the heat treatment duration is more than 30.0 minutes, scales mainly made of  $\text{Al}_2\text{O}_3$  are formed excessively on the steel surface. Therefore, Al in the outer layer of the steel is excessively depleted. In this case, the Al concentration  $C_{\text{Al}}'$  in the outer layer of the steel becomes excessively low, failing to satisfy Formula (1). Accordingly, the uniform  $\text{Al}_2\text{O}_3$  coating film is not formed sufficiently under the high temperature carburizing environment. As a result, the anti-carburizing properties are decreased. Consequently, the temperature of the heat treatment is less than 1100°C, and the duration of the heat treatment is 30.0 minutes or less. In addition, when the temperature of the heat treatment is less than 1100°C, and the duration of the heat treatment is 30.0 minutes or less, a grain size becomes 80  $\mu\text{m}$  or less.

**[0071]** When the temperature of the heat treatment is 900 to less than 1100°C, and the duration of the heat treatment is 3.0 to 30.0 minutes, the TEE effect is provided sufficiently and appropriately, and the steel having a chemical composition satisfying Formula (1) is obtained. As a result, the anti-carburizing properties under the high temperature carburizing environment are increased.

**[0072]** For the purpose of removing the scales formed on the surface, pickling treatment may be performed on the intermediate material subjected to the heat treatment. For the pickling, for example, a mixed acid solution of nitric acid and hydrochloric acid is used. A duration of the pickling is, for example, 30 minutes to 60 minutes.

**[0073]** In addition, for the purpose of removing the scales on the steel surface and giving strain to the steel surface of the intermediate material subjected to the pickling treatment, shot peening may be performed on the steel surface. In the shot peening, a starting material and a shape of shot media, and treatment conditions are not specified, but the starting material and the shape, and the treatment conditions are set to be sufficient for peeling the scales on the steel surface and giving the strain to the steel surface. The scales refer to, for example,  $\text{Al}_2\text{O}_3$ . By well-known methods of the pickling treatment, shot peening, and the like, the  $\text{Al}_2\text{O}_3$  coating film can be removed.

**[0074]** By the above producing method, the austenitic stainless steel according to the present embodiment is produced. The above description is made about the method for producing a steel pipe. However, a plate material, bar material, wire rod, or the like may be produced by a similar producing method (preparation process, hot forging process, hot working process, cold working process, heat treatment process). It is particularly preferable to apply the austenitic stainless steel according to the present embodiment to steel pipes. Hence, the austenitic stainless steel according to the present embodiment is preferably an austenitic stainless steel pipe.

#### EXAMPLES

[Producing Method]

**[0075]** Molten steels having chemical compositions shown in Table 1 were produced using a vacuum furnace.

[Table 1]

[0076]

TABLE 1

STEEL TYPE	CHEMICAL COMPOSITION (mass%, BALANCE: Fe AND IMPURITIES)																	
	ESSENTIAL ELEMENT											OPTIONAL ELEMENT						
	C	Si	Mn	P	S	Cr	Ni	Al	Nb	N	Ca	Mg	Ti	Mo	W	Cu	V	B
A	0.112	1.20	1.85	0.038	0.004	14.6	38.5	2.54	2.29	0.0044	0.0114	0.0263	-	-	-	-	-	-
B	0.089	1.28	1.59	0.024	0.002	11.3	31.8	2.67	0.65	0.0270	0.0448	0.0381	-	-	-	-	-	-
C	0.136	2.00	1.44	0.001	0.001	11.8	34.9	3.44	0.11	0.0070	0.0323	0.0161	-	-	-	-	-	-
D	0.033	0.82	0.44	0.002	0.003	16.1	32.7	2.85	3.25	0.0185	0.0334	0.0098	-	-	-	-	-	-
E	0.205	0.15	1.43	0.002	0.008	20.3	35.3	2.76	0.28	0.0077	0.0481	0.0160	-	-	-	-	-	-
F	0.183	0.24	1.17	0.028	0.006	20.2	33.7	2.89	2.13	0.0002	0.0320	0.0410	-	-	-	-	-	-
G	0.210	1.51	0.84	0.027	0.002	12.1	30.4	4.22	0.36	0.0186	0.0323	0.0015	0.15	-	-	-	-	-
H	0.224	1.13	2.00	0.027	0.009	10.1	34.0	2.81	1.69	0.0118	0.0384	0.0185	-	0.09	-	-	-	-
I	0.091	1.30	1.61	0.024	0.002	11.4	31.9	2.69	0.68	0.0052	0.0453	0.0023	-	-	0.50	-	-	-
J	0.030	0.97	0.08	0.025	0.006	12.9	30.3	3.34	0.82	0.0156	0.0032	0.0164	-	-	-	0.15	-	-
K	0.221	0.83	1.57	0.016	0.009	12.4	36.4	2.90	0.54	0.0098	0.0021	0.0196	-	-	-	-	0.14	-
L	0.085	0.54	1.36	0.028	0.009	14.1	34.7	3.59	2.75	0.0271	0.0209	0.0269	-	-	-	-	-	0.0035
M	0.128	0.33	0.05	0.007	0.007	5.9	34.8	3.08	1.27	0.0221	0.0211	0.0131	-	-	-	-	-	-
N	0.166	1.34	1.02	0.040	0.003	32.8	32.5	3.47	1.86	0.0169	0.0463	0.0240	-	-	-	-	-	-
O	0.119	0.58	1.28	0.023	0.001	15.3	33.7	1.55	3.33	0.0157	0.0092	0.0123	-	-	-	-	-	-
P	0.137	0.62	1.15	0.031	0.004	15.2	19.2	4.36	1.59	0.0119	0.0441	0.0066	-	-	-	-	-	-
Q	0.039	0.81	1.57	0.006	0.001	20.1	36.8	3.75	2.23	0.0124	0.0305	0.0001	-	-	-	-	-	-
R	0.185	0.28	0.22	0.026	0.003	17.6	35.4	3.38	3.28	0.0162	0.0224	0.1485	-	-	-	-	-	-

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**[0077]** Using the above molten steels, column-shaped ingots having an outer diameter of 120 mm (30 kg) were produced. The ingots were subjected to the hot forging and the hot rolling. After the hot rolling, the cold rolling was performed in conditions shown in Table 2 to produce intermediate materials having a thickness of 15 mm. From each of the intermediate materials of respective steel types, two 8 mm × 20 mm × 30 mm plate materials were produced by machining. The heat treatment was performed on the plate materials at temperatures and for durations shown in Table 2. After the heat treatment, the plate materials were water-cooled to produce test steel plates.

[Table 2]

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[0078]

TABLE 2

TEST NUMBER	STEEL TYPE	COLD ROLLING WORKING RATIO (%)	HEAT TREATMENT TEMPERATURE (°C)	HEAT TREATMENT DURATION (min)	GRAIN SIZE (μm)	Cr CONCENTRATION C <sub>Cr</sub> IN OUTER LAYER AFTER HEAT TREATMENT (%)	Al CONCENTRATION C <sub>Al</sub> IN OUTER LAYER AFTER HEAT TREATMENT (%)	C <sub>Cr</sub> / C <sub>Al</sub>	Cr CONCENTRATION C <sub>Cr</sub> IN OTHER-THAN-OUTER-LAYER REGION (%)	Al CONCENTRATION C <sub>Al</sub> IN OTHER-THAN-OUTER-LAYER REGION (%)	C <sub>Cr</sub> / C <sub>Al</sub>	F1	ENTERING QUANTITY (%)	REDUCTION OF AREA
1	A	36	1000	10	54	8.24	2.11	3.91	14.60	2.54	5.75	0.68	0.29	○
2	B	52	900	5	37	6.99	2.20	3.18	11.30	2.67	4.23	0.75	0.23	○
3	C	40	900	20	47	5.60	2.91	1.92	11.80	3.44	3.43	0.56	0.09	○
4	D	41	1050	10	60	10.01	2.28	4.39	16.10	2.85	5.65	0.78	0.18	○
5	E	62	1000	10	42	11.94	2.23	5.35	20.30	2.76	7.36	0.73	0.22	○
6	F	39	1000	5	54	13.22	2.54	5.20	20.20	2.89	6.99	0.74	0.14	○
7	G	62	1050	10	45	7.29	3.42	2.13	12.10	4.22	2.87	0.74	0.11	○
8	H	55	950	10	71	5.07	2.17	2.34	10.10	2.81	3.59	0.65	0.22	○
9	I	33	900	20	46	6.35	3.67	1.73	11.40	2.69	4.24	0.41	0.28	○
10	J	39	950	20	49	8.44	3.11	2.71	12.90	3.34	3.86	0.70	0.12	○
11	K	48	1000	10	40	7.78	3.65	2.13	12.40	2.90	4.28	0.50	0.17	○
12	L	49	1000	10	44	10.02	3.46	2.90	14.10	3.59	3.93	0.74	0.07	○
13	A	7	1050	5	76	4.25	2.11	2.01	14.60	2.54	5.75	0.35	0.51	○
14	B	32	700	5	21	9.36	2.21	4.24	11.30	2.67	4.23	1.00	0.65	○
15	C	57	1300	20	131	4.21	3.18	1.32	11.80	3.44	3.43	0.39	0.58	○
16	D	61	1000	0.5	22	14.29	2.38	6.00	16.10	2.85	5.65	1.06	0.69	○
17	E	50	1050	90	95	12.68	1.82	6.97	20.30	2.76	7.36	0.95	0.54	○
18	M	45	1000	10	58	1.92	2.35	0.82	5.90	3.08	1.92	0.43	0.75	○
19	N	47	900	20	43	15.89	3.06	5.19	32.80	3.47	9.45	0.55	0.60	○
20	O	64	900	5	35	9.34	1.23	7.59	15.30	1.55	9.87	0.77	0.83	○
21	P	34	1050	5	58	10.15	3.88	2.62	15.20	4.36	3.49	0.75	0.52	○

(continued)

TEST NUMBER	STEEL TYPE	COLD ROLLING WORKING RATIO (%)	HEAT TREATMENT TEMPERATURE (°C)	HEAT TREATMENT DURATION (min)	GRAIN SIZE (μm)	Cr CONCENTRATION $C_{Cr}$ IN OUTER LAYER AFTER HEAT TREATMENT (%)	Al CONCENTRATION $C_{Al}$ IN OUTER LAYER AFTER HEAT TREATMENT (%)	$C_{Cr}/C_{Al}$	Cr CONCENTRATION $C_{Cr}$ IN OTHER-THAN-OUTER-LAYER REGION (%)	Al CONCENTRATION $C_{Al}$ IN OTHER-THAN-OUTER-LAYER REGION (%)	$C_{Cr}/C_{Al}$	F1	ENTERING C QUANTITY (%)	REDUCTION OF AREA
22	Q	30	1050	20	67	12.78	3.31	3.86	20.10	3.75	5.36	0.72	0.14	×
23	R	31	1000	5	59	11.49	2.97	3.87	17.60	3.38	5.21	0.74	0.21	×

## [Measurement of Austenite Grain size]

**[0079]** For each of the steel plates of the respective test numbers, from a center portion of its cross section in a direction perpendicular to its rolling direction, a test specimen for microscopic observation was fabricated. Of the surfaces of the test specimen, a surface corresponding to the above cross section (referred to as an observation surface) was used, and the microscopic test method specified in ASTM E 112 was performed, and the grain size was measured. Specifically, the observation surface was subjected to mechanical polishing, and thereafter etched using etching reagent, and crystal grain boundaries in the observation surface were exposed. An average grain size of ten visual fields on the etched surface was determined. The area of each visual field was about 0.75 mm<sup>2</sup>.

[Measurement of Cr Concentration  $C_{Cr}'$  in Outer Layer and Al Concentration  $C_{Al}'$  in Outer Layer]

**[0080]** The steel plates of the respective test numbers were subjected to the descaling treatment under conditions conforming to JIS Z 2290(2004). Each of the steel plates subjected to the descaling treatment was cut perpendicularly to its rolling direction, and a sample including a surface of the steel plate was taken. Each of the samples was embedded in resin, and its observation surface including a cross section of the vicinity to the surface of the steel plate was polished. On the polished observation surface, the above method was used to determine  $C_{Cr}'$ , the Cr concentration and  $C_{Al}'$ , the Al concentration in the outer layer (range of 2 μm depth from the surface of the steel plate).

[Measurement of Cr Concentration  $C_{Cr}$  in Other-than-outer-layer region and Al Concentration  $C_{Al}$  in Other-than-outer-layer region]

**[0081]** The above method was used to determine the Cr concentration  $C_{Cr}$  in the other-than-outer-layer region and the Al concentration  $C_{Al}$  in the other-than-outer-layer region.

## [Carburizing Test]

**[0082]** The steel plates of the respective test numbers were retained in H<sub>2</sub>-CH<sub>4</sub>-CO<sub>2</sub> atmosphere at 1100°C × 96 hours. After the carburizing, scales and the like were removed from surfaces of the steel plates by performing manual dry polishing on the surfaces using #600 abrasive paper. From the surfaces of the steel plates, machined chips for analysis of four layers were taken at 0.5 mm pitches. On the taken machined chips for analysis, the C concentrations were measured by a high frequency combustion infrared absorption method. Values obtained by subtracting the C concentration originally contained in the steel from results of the measurement were determined as C concentration increase quantities. An average of C concentration increase quantities of the four layers was determined as an entering C quantity.

## [High-Temperature Tensile Test]

**[0083]** For each of the produced ingots, from its wall-thickness center portion, a column-shaped tensile test specimen having a diameter of 10 mm and a length of 130 mm was cut out. Each tensile test specimen was subjected to a tensile test at a tensile speed (strain rate) of 10/s, and its hot workability was evaluated. In the present invention, when a reduction of area of a test specimen after the tensile test at 900°C was 60% or more, the test specimen was determined as good (○), and when the reduction of area was less than 60%, the test specimen was determined as no good (×).

## [Test Results]

**[0084]** Results of the tests are shown in Table 2.

**[0085]** Referring to Table 2, as to a test number 1 to a test number 12, their chemical compositions were appropriate, their producing conditions were also appropriate, and F1 satisfied Formula (1). As a result, their entering C quantities were 0.4% or less, and they exhibited excellent anti-carburizing properties. In addition, their values of reduction of area in the high-temperature tensile test were 60 % or more, and they exhibited excellent hot workabilities.

**[0086]** In contrast, as to a test number 13, its working ratio of the cold rolling was excessively low. Accordingly, F1 was 0.35, failing to satisfy Formula (1). As a result, its entering C quantity was 0.51%, exhibiting poor anti-carburizing properties.

**[0087]** As to a test number 14, its temperature of the heat treatment was excessively low. Accordingly, F1 was 1.00, failing to satisfy Formula (1). As a result, its entering C quantity was 0.65%, exhibiting poor anti-carburizing properties. In addition, as to the test number 14, its grain size was 21 μm.

**[0088]** As to a test number 15, its temperature of the heat treatment was excessively high. Accordingly, F1 was 0.39,



failing to satisfy Formula (1). As a result, its entering C quantity was 0.58%, exhibiting poor anti-carburizing properties. In addition, as to the test number 15, its grain size was 131  $\mu\text{m}$ .

[0089] As to a test number 16, its duration of the heat treatment was excessively short. Accordingly, F1 was 1.06, failing to satisfy Formula (1). As a result, its entering C quantity was 0.69%, exhibiting poor anti-carburizing properties. In addition, as to the test number 16, its grain size was 22  $\mu\text{m}$ .

[0090] As to a test number 17, its duration of the heat treatment was excessively long. Accordingly, F1 was 0.95, failing to satisfy Formula (1). As a result, its entering C quantity was 0.54%, exhibiting poor anti-carburizing properties. In addition, as to the test number 17, its grain size was 95  $\mu\text{m}$ .

[0091] As to Test Number 18, its content of Cr was excessively low. Accordingly, the TEE effect by Cr was lessened. As a result, its entering C quantity was 0.75%, exhibiting poor anti-carburizing properties.

[0092] As to Test Number 19, its content of Cr was excessively high. Accordingly, its Cr carbide inhibited the formation of the  $\text{Al}_2\text{O}_3$  coating film. As a result, its entering C quantity was 0.60%, exhibiting poor anti-carburizing properties.

[0093] As to Test Number 20, its content of Al was excessively low. Accordingly, its  $\text{Al}_2\text{O}_3$  coating film was not formed sufficiently. As a result, its entering C quantity was 0.83%, exhibiting poor anti-carburizing properties.

[0094] As to Test Number 21, its content of Ni was excessively low. As a result, its entering C quantity was 0.52%, exhibiting poor anti-carburizing properties.

[0095] As to Test Number 22, its content of Mg was excessively low. As a result, its value of reduction of area was less than 60%, exhibiting a low hot workability.

[0096] As to Test Number 23, its content of Mg was excessively high. As a result, its value of reduction of area was less than 60%, exhibiting a low hot workability.

[0097] The embodiment according to the present invention has been described above. However, the aforementioned embodiment is merely an example for practicing the present invention. Therefore, the present invention is not limited to the aforementioned embodiment, and the aforementioned embodiment can be modified and implemented as appropriate without departing from the scope of the present invention.

## INDUSTRIAL APPLICABILITY

[0098] The austenitic stainless steel according to the present invention is available even in the high temperature carburizing environment such as a hydrocarbon gas atmosphere, in which there are concerns about carburizing and coking. In particular, the austenitic stainless steel is suitable for application to steel for reaction tube in chemical industry plants such as ethylene producing plants, and the like.

## Claims

1. An austenitic stainless steel comprising a chemical composition consisting of, in mass percent:

C: 0.03 to less than 0.25%;

Si: 0.01 to 2.0%;

Mn: 2.0% or less;

P: 0.04% or less;

S: 0.01% or less;

Cr: 10 to less than 22%;

Ni: more than 30.0% to 40.0%;

Al: more than 2.5% to less than 4.5%;

Nb: 0.01 to 3.5%;

N: 0.03% or less;

Ca: 0.0005 to 0.05%;

Mg: 0.0005 to 0.05%;

Ti: 0 to less than 0.2%;

Mo: 0 to 0.5%;

W: 0 to 0.5%;

Cu: 0 to 0.5%;

V: 0 to 0.2%; and

B: 0 to 0.01%,

with the balance being Fe and impurities, and satisfying Formula (1):

$$0.40 \leq (C_{Cr}'/C_{Al}')/(C_{Cr}/C_{Al}) \leq 0.80 \quad (1)$$

where, a Cr concentration (mass percent) in an outer layer of the austenitic stainless steel is substituted for  $C_{Cr}'$  in Formula (1), an Al concentration (mass percent) in the outer layer of the austenitic stainless steel is substituted for  $C_{Al}'$ , a Cr concentration (mass percent) in an other-than-outer-layer region of the austenitic stainless steel is substituted for  $C_{Cr}$ , and an Al concentration (mass percent) in the other-than-outer-layer region of the austenitic stainless steel is substituted for  $C_{Al}$ .

2. The austenitic stainless steel according to claim 1, wherein the chemical composition contains one or two or more elements selected from the group consisting of:

Ti: 0.005 to less than 0.2%;  
 Mo: 0.01 to 0.5%;  
 W: 0.01 to 0.5%;  
 Cu: 0.005 to 0.5%;  
 V: 0.005 to 0.2%; and  
 B: 0.0001 to 0.01%.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/023657

## A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D6/00(2006.01)i, C21D8/00(2006.01)i, C21D8/10  
(2006.01)i, C22C38/58(2006.01)i

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, C21D6/00, C21D8/00, C21D8/10

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 2015-190054 A (Nippon Steel & Sumitomo Metal Corp.), 02 November 2015 (02.11.2015), (Family: none)	1, 2
A	JP 02-115348 A (Nippon Steel Corp.), 27 April 1990 (27.04.1990), (Family: none)	1, 2
A	JP 61-243157 A (Nippon Steel Corp.), 29 October 1986 (29.10.1986), (Family: none)	1, 2

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

\* Special categories of cited documents:

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"&" document member of the same patent family

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**REFERENCES CITED IN THE DESCRIPTION**

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