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(54) AUSTENITIC STAINLESS STEEL AND METHOD FOR MANUFACTURING AUSTENITIC STAINLESS STEEL

(57) An austenitic stainless steel with good strength and ductility is provided. An austenitic stainless steel has a chemical composition of, in mass %: 0.005 to 0.060 % C; 0.20 to 1.20 % Si; 4.0 to 8.0 % Mn; 12.0 to 15.0 % Ni; 19.0 to 24.0 % Cr; 1.0 to 4.0 % Mo; 0.05 to 0.40 % Nb; 0.05 to 0.40 % V; 0.20 to 0.50 % N; up to 0.050 % Al; and other elements, the tensile strength being not lower than 800 MPa, the braking elongation being not lower than 35 %, the steel satisfying the following expressions, (1) and (2): (1) $0.7 \times \mathrm{Nb} \leq [\mathrm{Nb}] \leq 0.30$; and (2) $20 \times [\mathrm{Nb}] / \mathrm{D} \geq 0.050$. In expressions (1) and (2), the Nb content in the chemical composition represented in mass %, the amount of Nb determined through analysis of an electrolytic extraction residue represented in mass %, and the crystal grain size represented in pm are substituted for "Nb", "[Nb]", and "D", respectively.

EP 4 495 274 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to an austenitic stainless steel and a method of manufacturing an austenitic stainless steel.

BACKGROUND ART

[0002] In recent years, research has been conducted on the commercialization of transportation equipment that uses hydrogen, instead of fossil fuels, as an energy source. For example, development is underway of fuel-cell vehicles that run on hydrogen and of hydrogen stations that supply hydrogen to fuel-cell vehicles.

[0003] When stainless steel is used in fuel-cell vehicles or hydrogen stations, the stainless steel is used in a high-pressure hydrogen-gas environment. In addition, there has been a demand to reduce the weight of fuel-cell vehicles, to make hydrogen stations more compact, and to operate hydrogen stations under high pressure. As such, a stainless steel used in fuel-cell vehicles and hydrogen stations is required to have high strength.

[0004] WO 2012/132992 A1 discloses a high-strength austenitic stainless steel for high-pressure hydrogen gas. WO 2017/056619 A1 discloses an austenitic stainless steel with good strength, ductility, and weldability. JP 2014-47420 A describes an austenitic stainless steel for nuclear reactors that exhibits good strength in the typical reactor water temperature range and also has good SCC resistance and weldability.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0005]

Patent Document 1: WO 2012/132992 A1
Patent Document 2: WO 2017/056619 A1
Patent Document 3: JP 2014-47420 A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006] A hydrogen station is made up of various kinds of members. Conventionally, among such members for hydrogen stations, piping is commonly produced from steel pipes as it is required to have high strength. However, in recent years, there has been a growing demand for various other kinds of members having high strength, which has prompted attempts to use austenitic stainless steel for members other than piping. Such members include solid members. This means that it is desirable that solid members provide both good strength and ductility equivalent to steel pipes.

[0007] WO 2012/132992 A1 discloses providing an austenitic stainless steel with a tensile strength not lower than 800 MPa by performing solution heat treatment and then cold working with a reduction in area not lower than 20 % before performing heat treatment once again. However, during manufacture of solid members, it is difficult to perform cold working with high reduction in area.

[0008] A problem to be solved by the present invention is to provide an austenitic stainless steel with good strength and ductility and a method of manufacturing an austenitic stainless steel.

MEANS FOR SOLVING THE PROBLEMS

[0009] An austenitic stainless steel according to one embodiment of the present invention has a chemical composition of, in mass %: 0.005 to 0.060 % C; 0.20 to 1.20 % Si; 4.0 to 8.0 % Mn; 12.0 to 15.0 % Ni; 19.0 to 24.0 % Cr; 1.0 to 4.0 % Mo; 0.05 to 0.40 % Nb; 0.05 to 0.40 % V; 0.20 to 0.50 % N; up to 0.050 % Al; 0 to 3.0 % Cu; 0 to 0.50 % Co; 0 to 0.0050 % Ca; 0 to 0.0050 % B; 0 to 0.10 % W; 0 to 0.10 % Ta; and balance Fe and impurities, the impurities including: up to 0.030 % P; up to 0.010 % S; and up to 0.015 % O, a tensile strength being not lower than 800 MPa, a braking elongation being not lower than 35 %, an amount of Nb determined through analysis of an electrolytic extraction residue satisfying expression (1) below, the amount of Nb determined through analysis of the electrolytic extraction residue and a crystal grain size satisfying expression (2) below:

$$0.7 \times \mathrm{Nb} \leq [\mathrm{Nb}] \leq 0.30 \qquad (1),$$

and

$$20 \times [\mathrm{Nb}] / \mathrm{D} \geq 0.050 \qquad (2),$$

in expressions (1) and (2), the Nb content in the chemical composition represented in mass %, the amount of Nb determined through analysis of the electrolytic extraction residue represented in mass %, and the crystal grain size represented in pm are substituted for "Nb", "[Nb]", and "D", respectively.

[0010] A method of manufacturing an austenitic stainless steel according to one embodiment of the present invention is a method of manufacturing the above-described austenitic stainless steel, including: performing a primary heat treatment on a steel material having said chemical composition at 1180 to 1280 °C; after the primary heat treatment, performing cold working on the steel material with a reduction in area not lower than 5 % and lower than 20 %; and, after the cold working, performing a secondary heat treatment on the steel material at a temperature of 1000 to 1180 °C.

EFFECTS OF THE INVENTION

[0011] The present invention provides an austenitic stainless steel with good strength and ductility.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0012] To solve the above-identified problem, the present inventors conducted various research and obtained the following discoveries, (a) to (f).

(a) The strength of steel material may be increased by solid solution strengthening and grain refining by means of N. 0.20 to 0.50 mass % N is contained in the austenitic stainless steel of the present embodiment to effect solid solution strengthening, thereby increasing its strength. Rendering the crystal grains finer further increases the strength.

(b) The crystal grains may be rendered finer by causing precipitation of fine alloy carbonitrides or nitrides during the final solution heat treatment to prevent growth of the crystal grains by means of the pinning effect. The addition of Nb is effective to produce fine carbonitrides or nitrides to provide finer crystal grains in high-nitrogen steel. However, while the conventional methods may cause precipitation of Nb carbonitrides and/or Nb nitrides, the particles are course, which prevents the pinning effect from sufficiently being produced.

(c) To solve this, WO 2012/132992 A1 proposes a method that involves performing solution heat treatment, cold working and a secondary heat treatment in this order. However, such a method cannot ensure that a solid member, on which it is difficult to perform cold working with high reduction in area, provides strength and ductility.

(d) In view of this, as a primary heat treatment, a heat treatment prior to cold working is performed at a temperature higher than conventional solution heat treatment temperatures. This allows more of the alloy elements to dissolve, which increases precipitation nuclei for Nb carbonitrides and Nb nitrides that are to precipitate during the secondary heat treatment, even with strain from cold working with low reduction in area. Thus, even cold working with low reduction in area can cause precipitation of finer and more Nb carbonitrides and/or Nb nitrides.

(e) With the same magnitude of pinning's effect of preventing growth of the crystal grains, higher temperatures for the primary and secondary heat treatments lead to relatively large crystal grains. However, even with crystal grains larger than those disclosed in WO 2012/132992 A1, both high strength and ductility will be provided if the amounts of Nb carbonitrides and Nb nitrides and the size of crystal grains satisfy a predetermined relationship. Specifically, if the amount of Nb determined through analysis of an electrolytic extraction residue satisfies expression (1) provided below and the amount of Nb determined through analysis of the electrolytic extraction residue and the crystal grain size satisfy expression (2) provided below, the synergetic effects of finer crystal grains and strengthened precipitation will provide both high strength and ductility:

$$0.7 \times \mathrm{Nb} \leq [\mathrm{Nb}] \leq 0.30 \qquad (1),$$

and

$$20 \times [\mathrm{Nb}] / \mathrm{D} \geq 0.050 \qquad (2).$$

In expressions (1) and (2), the Nb content represented in mass %, the amount of Nb determined through analysis of the

electrolytic extraction residue represented in mass %, and the crystal grain size represented in pm are substituted for "Nb", "[Nb]", and "D", respectively.
(f) More preferably, the secondary heat treatment is performed at a temperature of 1050 to 1160 °C. If the secondary heat treatment is performed in a temperature range that is found near the precipitation nose for Nb carbonitrides and Nb nitrides, larger amounts of Nb carbonitrides and Nb nitrides can be precipitated in a reduced period of time.

[0013] The present invention was made based on these discoveries. Now, an austenitic stainless steel and a method of manufacturing an austenitic stainless steel according to one embodiment of the present invention will be described in detail.

[Chemical Composition]

[0014] An austenitic stainless steel according to one embodiment of the present invention has such a chemical composition as specified below. In the description below, "%" for the content of an element means mass %.

C: 0.005 to 0.060 %

[0015] Carbon (C) is effective to stabilize austenite. Further, C produces carbonitrides of Nb, thus also contributing to providing sufficient strength. To sufficiently produce these effects, C content must be not lower than 0.005 %. However, if C content is too high, this produces excessive amounts of Nb carbonitrides, which decreases the ductility of the steel. In view of this, C content must be not higher than 0.060 %. A lower limit of C content is preferably 0.010 %, and more preferably 0.020 %. An upper limit of C content is preferably 0.050 %, and more preferably 0.040 %.

Si: 0.20 to 1.20 %

[0016] Silicon (Si) is effective as a deoxidizer and also effective to improve corrosion resistance. To sufficiently produce these effects, Si content must be not lower than 0.20 %. However, if Si content is too high, this decreases the stability of the austenitic structure, and also decreases the ductility of the steel. In view of this, Si content is to be 0.20 to 1.20 %. A lower limit of Si content is preferably 0.25 %, and more preferably 0.30 %. An upper limit of Si content is preferably 1.10 %, and more preferably 1.00 %.

Mn: 4.0 to 8.0 %

[0017] Manganese (Mn) contributes to deoxidation during manufacture and is also effective to stabilize austenite. Mn also indirectly contributes to increasing strength by increasing the solubility of N. These effects are not produced if Mn content is too low. On the other hand, if Mn content is too high, this decreases the ductility and hot workability of the steel. In view of this, Mn content is to be 4.0 to 8.0 %. A lower limit of Mn content is preferably 4.5 %, and more preferably 5.0 %. An upper limit of Mn content is preferably 7.5 %, and more preferably 7.0 %.

Ni: 12.0 to 15.0 %

[0018] Nickel (Ni) is indispensable for providing stable austenite; it increases stacking fault energy and reduces embrittlement susceptibility in a hydrogen environment. To sufficiently produce these effects, Ni content must be not lower than 12.0 %. However, Ni is an expensive element, and higher content leads to increased costs. In view of this, Ni content is to be 12.0 to 15.0 %. A lower limit of Ni content is preferably 12.3 %, and more preferably 12.5 %. An upper limit of Ni content is preferably 14.8 %, and more preferably 14.5 %.

Cr: 19.0 to 24.0 %

[0019] Chromium (Cr) is indispensable for providing sufficient corrosion resistance in the use environment. Cr also indirectly contributes to increasing strength by increasing the solubility of N during manufacture. To sufficiently produce these effects, Cr content must be not lower than 19.0 %. However, if Cr content is too high, this renders the austenitic structure unstable. In view of this, Cr content is to be 19.0 to 24.0 %. A lower limit of Cr content is preferably 19.5 %, and more preferably 20.0 %. An upper limit of Cr content is preferably 23.5 %, and more preferably 23.0 %.

Mo: 1.0 to 4.0 %

[0020] Molybdenum (Mo) is effective to improve corrosion resistance in the use environment and to increase strength.

To sufficiently produce these effects, Mo content must be not lower than 1.0 %. However, Mo is an expensive element, and higher content leads to increased costs. Further, if Mo content is too high, this renders the austenitic structure unstable. In view of this, Mo content is to be 1.0 to 4.0 %. A lower limit of Mo content is preferably 1.2 %, and more preferably 1.5 %. An upper limit of Mo content is preferably 3.8 %, and more preferably 3.5 %.

Nb: 0.05 to 0.40 %

[0021] Niobium (Nb) is effective to increase strength by precipitating in the matrix in the form of fine carbonitrides and nitrides. To sufficiently produce this effect, Nb content must be not lower than 0.05 %. However, if Nb content is too high, this decreases the ductility of the steel. In view of this, Nb content is to be 0.05 to 0.40 %. A lower limit of Nb content is preferably 0.10 %, and more preferably 0.15 %. An upper limit of Nb content is preferably 0.35 %, and more preferably 0.30 %.

[0022] As used herein, Nb content means the total amount of Nb contained in the austenitic stainless steel. Specifically, it means the sum of the amount of Nb dissolved in the matrix and the amount of Nb present in the form of precipitates. According to the present embodiment, not only the Nb content, but also the amount of Nb present in the form of precipitates, i.e., the amount of Nb determined through analysis of the electrolytic extraction residue, must be in a prescribed range.

V: 0.05 to 0.40 %

[0023] Vanadium (V) is effective to increase strength by precipitating in the matrix in the form of fine carbonitrides and nitrides. To sufficiently produce this effect, V content must be not lower than 0.05 %. However, if V content is too high, this decreases the ductility of the steel. In view of this, V content is to be 0.05 to 0.40 %. A lower limit of V content is preferably 0.10 %, and more preferably 0.15 %. An upper limit of V content is preferably 0.35 %, and more preferably 0.30 %.

N: 0.20 to 0.50 %

[0024] Nitrogen (N) contributes to increasing strength by dissolving in the matrix, and also contributes to increasing strength by combining with Nb or other elements to form fine carbonitrides and nitrides. N is also effective to stabilize the austenitic structure. To sufficiently produce these effects, N content must be not lower than 0.20 %. However, if N content is too high, this decreases hot workability during manufacture, and also leads to precipitation of excessive amounts of precipitates of Nb, thus decreasing the ductility of the steel. In view of this, N content is to be 0.20 to 0.50 %. A lower limit of N content is preferably 0.23 %, and more preferably 0.25 %. An upper limit of N content is preferably 0.48 %, and more preferably 0.45 %.

Al: up to 0.050 %

[0025] Similar to Si, aluminum (Al) is contained in steel as a deoxidizer. However, if Al content is too high, this decreases the cleanliness of the steel and thus decreases hot workability. In view of this, Al content is to be not higher than 0.050 %. Al content is preferably not higher than 0.040 %, and more preferably not higher than 0.030 %. Although no particular lower limit of Al content needs to be specified, excessive reduction leads to increased steel-manufacturing costs. In view of this, a lower limit of Al content is preferably 0.005 %, and more preferably 0.010 %.

Cu: 0 to 3.0%

[0026] Copper (Cu) is an optionally added element, and need not be contained. Cu stabilizes the austenitic structure. Cu also increases the strength of steel through solid solution strengthening. These effects are produced to some degree if a small amount of Cu is contained. However, Cu is an expensive element, and higher content leads to increased costs. Also, if Cu content is too high, this decreases the ductility of the steel. In view of this, Cu content is to be 0 to 3.0 %. A lower limit of Cu content is preferably 0.01 %, and more preferably 0.10 %. An upper limit of Cu content is preferably 2.5 %, and more preferably 2.0 %.

Co: 0 to 0.50 %

[0027] Cobalt (Co) is an optionally added element, and need not be contained. Co stabilizes the austenitic structure. Co also increases the strength of steel through solid solution strengthening. These effects are produced to some degree if a small amount of Co is contained. However, Co is an expensive element, and higher content leads to increased costs. In view of this, Co content is to be 0 to 0.50 %. A lower limit of Co content is preferably 0.01 %, and more preferably 0.10 %. An upper limit of Co content is preferably 0.30 %, and more preferably 0.20 %.

Ca: 0 to 0.0050 %

[0028] Calcium (Ca) is an optionally added element, and need not be contained. Ca prevents solidification cracking during casting of the steel. This effect is produced to some degree if a small amount of Ca is contained. However, an excessive Ca content decreases the hot workability of the steel. In view of this, Ca content is to be 0 to 0.0050 %. A lower limit of Ca content is preferably 0.0001 %, and more preferably 0.0005 %. An upper limit of Ca content is preferably 0.0040 %, and more preferably 0.0030 %.

B: 0 to 0.0050 %

[0029] Boron (B) is an optionally added element, and need not be contained. B renders precipitates finer, thus providing finer crystal grains and thereby increasing the strength of the steel. This effect is produced to some degree if a small amount of B is contained. However, an excessive B content decreases the hot workability of the steel. In view of this, B content is to be 0 to 0.0050 %. A lower limit of B content is preferably 0.0001 %, and more preferably 0.0005 %. An upper limit of B content is preferably 0.0030 %, and more preferably 0.0020 %.

W: 0 to 0.10%

[0030] Tungsten (W) is an optionally added element, and need not be contained. W increases the strength of the steel. This effect is produced to some degree if a small amount of W is contained. However, if an excessive amount is contained, saturation is reached in terms of effect. In view of this, W content is to be 0 to 0.10 %. A lower limit of W content is preferably 0.01 %, and more preferably 0.02 %. An upper limit of W content is preferably 0.08 %, and more preferably 0.06 %.

Ta: 0 to 0.10%

[0031] Tantalum (Ta) is an optionally added element, and need not be contained. Ta increases the strength of the steel. This effect is produced to some degree if a small amount of Ta is contained. However, if an excessive amount is contained, saturation is reached in terms of effect. In view of this, Ta content is to be 0 to 0.10 %. A lower limit of Ta content is preferably 0.001 %, and more preferably 0.002 %. An upper limit of Ta content is preferably 0.08 %, and more preferably 0.06 %.

[0032] The balance of the chemical composition of the austenitic stainless steel according to the present embodiment is Fe and impurities. Impurity as used herein means an element originating from ore or scrap used as raw material for steel or an element that has entered from the environment or the like during the manufacturing process. Among the impurities, according to the present embodiment, P, S and O in particular are limited to the following content ranges.

P: up to 0.030 %

[0033] Phosphorus (P) is contained in steel as an impurity. If P content is too high, this decreases hot workability during manufacture. In view of this, P content is to be not higher than 0.030 %. P content is preferably not higher than 0.025 %, and more preferably not higher than 0.020 %.

S: up to 0.010 %

[0034] Sulfur (S) is contained in steel as an impurity. If S content is too high, this decreases hot workability during manufacture. In view of this, S content is to be not higher than 0.010 %. S content is preferably not higher than 0.005 %, and more preferably not higher than 0.002 %.

O: up to 0.015 %

[0035] Oxygen (O) is contained in steel as an impurity. If O content is too high, this decreases hot workability during manufacture, and also deteriorates the cleanliness of the steel and thus decreases ductility. In view of this, O content is to be not higher than 0.015 %. O content is preferably not higher than 0.010 %, and more preferably not higher than 0.005 %.

[Amount of Nb Determined through Analysis of Electrolytic extraction Residue and Steel Microstructure]

[0036] In the austenitic stainless steel according to the present embodiment, the amount of Nb determined through analysis of an electrolytic extraction residue satisfies expression (1) provided below, and the amount of Nb determined through analysis of the electrolytic extraction residue and the crystal grain size satisfy expression (2) provided below:

$$0.7 \times \mathrm{Nb} \leq [\mathrm{Nb}] \leq 0.30 \quad (1),$$

and

$$20 \times [\mathrm{Nb}] / \mathrm{D} \geq 0.050 \quad (2).$$

In expressions (1) and (2), the Nb content represented in mass %, the amount of Nb determined through analysis of the electrolytic extraction residue represented in mass %, and the crystal grain size represented in pm are substituted for "Nb", "[Nb]", and "D", respectively.

[0037] In the austenitic stainless steel according to the present embodiment, the amount of Nb determined through analysis of the electrolytic extraction residue is not smaller than 0.7 times the Nb content of the material, and not larger than 0.30 mass %. During the process of solution heat treatment, Nb contained in the material precipitates in the form of fine carbonitrides and nitrides. The fine precipitated Nb carbonitrides and Nb nitrides improve the strength of the steel. To produce this effect, the amount of Nb precipitated in the form of carbonitrides and nitrides, i.e., the amount of Nb determined through analysis of the electrolytic extraction residue must be not smaller than 0.7 times the Nb content of the base material. However, an excessive amount of Nb determined through analysis of the electrolytic extraction residue decreases the ductility of the steel. In view of this, an upper limit of the amount of Nb determined through analysis of the electrolytic extraction residue is to be 0.30 mass %. A lower limit of the amount of Nb determined through analysis of the electrolytic extraction residue is more preferably 0.8 times the amount of Nb of the material. An upper limit of the amount of Nb determined through analysis of the electrolytic extraction residue is more preferably 0.28 mass %, and yet more preferably 0.25 mass %.

[0038] To provide both strength and good ductility, it is effective to utilize Nb carbonitrides and Nb nitrides to provide finer crystal grains. To provide both strength and ductility, the amount of Nb determined through analysis of the extraction residue and the crystal grain size must satisfy expression (2). The value of the left side of expression (2) is more preferably not lower than 0.060, and yet more preferably not lower than 0.080.

[0039] The amount of Nb determined through analysis of the electrolytic extraction residue may be adjusted by changing the Nb content and N content of the material as well as production conditions such as heat treatment. Specifically, the higher the Nb content and N content of the material, the larger the amount of Nb determined through analysis of the electrolytic extraction residue. Description of the production conditions will be given further below.

[0040] The amount of Nb determined through analysis of the electrolytic extraction residue is measured in the following manner: from an austenitic stainless steel is taken a test specimen with a predetermined size; the test specimen is anodically dissolved by the constant current electrolysis method using a 10 % acetylacetone - 1 % tetramethylammonium chloride / methanol solution as the electrolytic solution, at a current density of 20 to 25 mA/cm^2, and the carbonitrides and nitrides are extracted in the form of residues. After acid decomposition of the extracted residues, inductively coupled plasma (ICP) emission analysis is performed to measure the mass of Nb in the residues.

[0041] The crystal grain size may be measured by the intercept method.

[0042] In the austenitic stainless steel according to the present embodiment, the crystal grain size is preferably not smaller than 20.0 pm. The austenitic stainless steel according to the present embodiment is capable of providing both strength and ductility even in implementations where it is difficult to reduce the crystal grain size to below 20.0 pm. A lower limit of the crystal grain size is more preferably 25.0 pm, and more preferably 30.0 pm. An upper limit of the crystal grain size is preferably 60.0 pm.

[Mechanical Properties]

[0043] In the austenitic stainless steel according to the present embodiment, the tensile strength is not lower than 800 MPa. The tensile strength of the austenitic stainless steel according to the present embodiment is preferably not lower than 830 MPa, and more preferably not lower than 850 MPa.

[0044] In the austenitic stainless steel according to the present embodiment, the breaking elongation is not lower than 35 %. The breaking elongation of the austenitic stainless steel according to the present embodiment is preferably not lower than 38 %, and more preferably not lower than 40 %.

[0045] The austenitic stainless steel according to the present embodiment is preferably a solid member (i.e., solid steel). As used herein, "solid member" means any member that is not a hollow member such as a steel pipe. The austenitic stainless steel according to the present embodiment is more preferably a round bar, and yet more preferably a round bar with an outer diameter not smaller than 25 mm. A solid member, in particular a round bar with an outer diameter not smaller than 25 mm, is difficult to produce with cold working with high reduction in area. The austenitic stainless steel according to the present embodiment provides both strength and ductility even in implementations where it is difficult to perform cold working with high reduction in area. In implementations where the austenitic stainless steel according to the present embodiment is a round bar, a lower limit of the outer diameter is still more preferably 28 mm, yet more preferably 30 mm, still more preferably 33 mm.

[0046] The austenitic stainless steel according to the present embodiment is preferably used as a material for equipment for storing or transporting high-pressure hydrogen gas or liquid hydrogen.

[Manufacturing Method]

[0047] According to the present embodiment, to cause precipitation of fine Nb carbonitrides and Nb nitrides, the primary heat treatment, cold working and secondary heat treatment described below are performed in this order.

[0048] The primary heat treatment is performed at a temperature not lower than 1180 °C to achieve sufficient dissolution of Nb carbonitrides and Nb nitrides produced in steps preceding the primary heat treatment, such as hot working. On the other hand, if the temperature for the primary heat treatment is higher than 1280 °C, the crystal grains coarsen excessively. A lower limit of the temperature for the primary heat treatment is preferably 1200 °C. An upper limit of the temperature for the primary heat treatment is preferably 1260 °C. For convenience, the temperature for the primary heat treatment will be hereinafter referred to as "T1 (°C)". The holding time for the primary heat treatment is preferably 1 to 20 minutes, and more preferably 1 to 10 minutes. It is desirable that the steel material after the primary heat treatment be rapidly cooled, desirably water cooled.

[0049] After sufficient dissolution of Nb carbonitrides and Nb nitrides by the primary heat treatment, cold working and the secondary heat treatment are performed to cause fine Nb carbonitrides and Nb nitrides to precipitate. Since the reduction in area during cold working is low according to the present embodiment, larger amounts of Nb carbonitrides and Nb nitrides must be dissolved during the primary heat treatment. Nb carbonitrides and Nb nitrides produced by hot working and similar processes are coarse, and thus do not contribute to providing finer crystal grains by means of the pinning effect. Further, if the dissolution of Nb carbonitrides and Nb nitrides produced by hot working and other processes is not sufficient, i.e., some of them remain, this makes it difficult to introduce strain through cold working.

[0050] Next, to increase precipitation nuclei for Nb carbonitrides and Nb nitrides, cold working is performed with a reduction in area not lower than 5 % and lower than 20 %. The higher the reduction in area, the more precipitation nuclei are produced, causing finer Nb carbonitrides and Nb nitrides to precipitate during the secondary heat treatment. If the reduction in area during cold working is too low, fine Nb carbonitrides and Nb nitrides do not precipitate during the secondary heat treatment, and the pinning effect's effect of rendering the crystal grains finer is not sufficiently produced. On the other hand, if the austenitic stainless steel is a thick solid member, it is difficult to perform cold working with a reduction in area not lower than 20 %. A lower limit of the reduction in area during cold working is preferably 8 %, and more preferably 10 %. An upper limit of the reduction in area during cold working is preferably 18 %, and more preferably 15 %.

[0051] Lastly, to remove the strain introduced through cold working and cause fine Nb carbonitrides and Nb nitrides to precipitate, the secondary heat treatment is performed at a temperature of 1000 to 1180 °C. For convenience, the heat treatment temperature for the secondary heat treatment will be hereinafter referred to as "T2 (°C)".

[0052] T2 is preferably 1050 to 1160 °C. The secondary heat treatment is performed in a temperature range that is found near the precipitation nose for Nb carbonitrides and Nb nitrides to cause larger amounts of Nb carbonitrides and Nb nitrides to precipitate in a reduced period of time. A lower limit of T2 is more preferably 1080 °C. An upper limit of T2 is more preferably 1120 °C. The holding time for the secondary heat treatment is preferably 1 to 20 minutes, and more preferably 1 to 15 minutes. The steel material after the secondary heat treatment is preferably rapidly cooled, and more preferably water cooled.

[0053] An austenitic stainless steel and a method of manufacturing an austenitic stainless steel according to one embodiment of the present invention have been described. The present embodiment provides an austenitic stainless steel with good strength and ductility.

EXAMPLES

[0054] The present invention will be described more specifically below by means of examples. The present invention is not limited to these examples.

[0055] Materials labeled Steel Types A to J having the chemical compositions shown in Table 1 were smelted in a laboratory and ingots were cast; each ingot was subjected to hot forging and hot rolling to produce a sheet with a sheet thickness of 20 mm. Thereafter, the sheet was subjected to the primary heat treatment at the relevant temperature T1 (°C) shown in Table 2. The cooling after the primary heat treatment was water cooling. Thereafter, cold working was performed with the relevant reduction in area shown in Table 2. Thereafter, the secondary heat treatment was performed at the relevant temperature T2 (°C) shown in Table 2. The holding time for the primary heat treatment was 1 to 10 minutes, and the holding time for the secondary heat treatment was 1 to 15 minutes.

[Residue Analysis]

[0056] From each sample was taken a 10 mm square test specimen with a length of 30 mm, and the above-described method was used to measure the amount of Nb determined through analysis of the electrolytic extraction residue.

[Crystal Grain Size]

[0057] 5 test specimens were cut out from each sample, where the observation surface of each test specimen was represented by a cut surface perpendicular to the direction of rolling (i.e., T-cut surface), and were mirror polished, etched and then observed by optical microscopy. For every one of the test specimens, three fields of view were observed with a magnification of 100 times; the average grain size for each of the 5 test specimens was determined by the intercept method and, then, their average was calculated to provide the crystal grain size of the sample.

[Tensile Testing]

[0058] From each sample was taken a round-bar tensile test specimen in accordance with JIS Z2241 (2011) with a parallel-portion diameter of 6 mm and a parallel-portion length of 30 mm, and tensile testing was conducted at room temperature. A tensile test specimen was taken from a sheet's middle portion as determined along the thickness direction such that the longitudinal direction of the test specimen was parallel to the direction of rolling. Tensile testing was conducted by the method in accordance with JIS Z2241 (2011) to determine tensile strength (MPa) and breaking elongation (%).

[0059] The results are shown in Table 2. In Table 2, "R" indicates the reduction in area during cold working, "[Nb]" the amount of Nb determined through analysis of the electrolytic extraction residue, "D" the crystal grain size, "TS" the tensile strength, "EL" the breaking elongation, F1 the value of the left side of expression (1) (i.e., 0.7 × Nb), and F2 the value of the left side of expression (2) (i.e., 20 × [Nb] / D).

[Table 1]

[0060]

TABLE 1

Steel Type	Chemical composition (in mass %, balance Fe and impurities)														
	C	Si	Mn	P	S	Ni	Cr	Mo	V	Nb	Al	Ca	Cu	N	O	Others
A	0.012	0.40	5.50	0.018	0.001	13.00	22.00	2.10	0.20	0.20	0.020	0.0015	-	0.32	0.014	
B	0.010	0.40	5.60	0.020	0.002	13.00	22.00	1.80	0.15	0.15	0.015	-	0.50	0.35	0.003	Ta:0.003
c	0.031	0.50	4.58	0.015	0.002	12.40	21,20	2.11	0.21	0.20	0.017	-	2.10	0.38	0.010	Co:0.11
D	0.060	0.4.4	5.88	0.016	0.003	13.31	22.00	1.82	0.30	0.29	0.038	0.0019	2.64	0.39	0.014	
B	0.010	0.38	5.41	0.014	0.002	13.05	20.96	1.61	0.12	0.13	0.014	0.0007	0.50	0.30	0.002	B : 0.0004
F	0.015	0.37	5.39	0.017	0.001	13.50	22.09	2.04	0.21	0.19	0.020	-	1.10	0.31	0.010	W:0.02
G	0.015	0.34	5.31	0.017	0.002	12.99	21.77	2.19	0.32	0.19	0.021	-	-	0.31	0.005	
H	0.014	0.40	5.26	0.016	0.002	13.00	22.30	2.09	0.17	0.31	0.015	0.0015	-	0.31	0.008	
I	0.015	0.40	5.39	0.017	0.001	13.50	22.09	2.04	0.21	0.02	0.020	-	0.10	0.33	0.010	
J	0.010	0.34	4.10	0.017	0.002	12.99	21.77	2.19	0.32	0.19	0.021	-	-	0.15	0.005	

[Table 2]

[0061]

TABLE 2

No.	Steel Type	T1 (°C)	R (%)	T2 (°C)	[Nb] (mass %)	TS (Mpa)	EL (%)	D (μm)	F1	F2	Class.
1	A	1220	12	1100	0.17	900	40	38	0.14	0.089	inv. ex.
2	A	1220	13	1100	0.18	902	42	as	0.14	0.095	
3	A	1220	12	1150	0.15	881	38	25	0.14	0.120	
4	A	1220	10	1000	0.18	850	40	50	0.14	0.072	
5	A	1250	11	1100	0.17	897	39	41	0.14	0.083	
6	A	1200	12	1100	0.17	897	38	12	0.14	0.081	
7	A	1220	8	1100	0.17	864	45	40	0.14	0.085	
8	A	1220	9	1100	0.19	879	44	41	0.14	0.093	
9	A	1250	9	1100	0.16	860	45	41	0.14	0.078	
10	A	1250	8	1100	0.17	857	47	40	0.14	0.085	
11	B	1220	11	1100	0.12	888	10	40	0.11	0.060	
12	B	1220	12	1100	0.13	878	41	43	0.11	0.060	
13	B	1220	12	1150	0.13	855	39	43	0.11	0.060	
14	C	1220	12	1100	0.18	911	39	Bi	0.14	0.097	
15	D	1 220	11	1100	0.21	920	36	32	0.20	0.131	
16	F	1220	11	1100	0.11	873	42	40	0.09	0.055	
17	F	1220	11	1100	0.17	890	42	38	0.13	0.089	
18	G	1220	11	1100	0.14	899	40	38	0.13	0.074	
19	G	1220	12	1100	0.15	890	41	40	0.13	0.075	
20	G	1220	12	1150	0.13	890	38	38	0.13	0.068	
21	G	1250	12	1100	0.14	895	42	41	0.13	0.068	
22	H	1220	9	1100	0.23	890	41	31	0.22	0.148	
23	H	1220	9	1100	0.24	900	39	29	0.22	0.166	
24	H	1280	8	1100	0.25	905	39	28	0.22	0.179	
25	H	1280	8	1100	0.24	896	40	29	0.22	0.166	

(continued)

No.	Steel Type	T1 (°C)	R (%)	T2 (°C)	[Nb] (mass %)	TS (Mpa)	EL (%)	D (μm)	F1	F2	Class.
26	A	-	11	1100	0.11	798	45	43	0.14	0.051	comp. ex.
27	A	-	7	1050	0.15	820	33	C1	0.14	0.049	
28	A	1100	8	1100	0.11	795	43	55	0.14	0.040	
29	A	1300	8	1100	0.16	770	34	113	0.14	0.028	
30	A	1250	8	1200	0.12	756	32	109	0.14	0.022	
31	H	1180	10	1100	0.31	919	30	30	0.22	0.207	
32	I	1220	12	1100	0.01	766	34	66	0.01	0.003	
33	J	1220	13	1100	0.14	777	31	40	0.13	0.070	
34	C	-	-	1100	0.10	786	39	75	0.14	0.027	
35	C	-	-	1200	0.09	732	47	154	0.14	0.012	
36	C	-	-	950	0.13	802	31	96	0.14	0.027	

[0062] As shown in Table 2, each of the samples labeled Test Nos. 1 to 25 had a tensile strength not lower than 800 MPa, and a breaking elongation not lower than 35 %.

[0063] Test Nos. 26 and 27 denote samples that were not subjected to the primary heat treatment. The sample labeled Test No. 26 had sufficient ductility but a tensile strength lower than 800 MPa. This is presumably because it did not satisfy expression (1). On the other hand, the sample labeled Test No. 27 had sufficient tensile strength, but had a breaking elongation lower than 35 %. This is presumably because it did not satisfy expression (2).

[0064] The sample labeled Test No. 28 had sufficient ductility but had a tensile strength lower than 800 MPa. This is presumably because it did not satisfy expression (1). It did not satisfy expression (1) presumably because the temperature for the primary heat treatment was too low. The sample labeled Test No. 29 had both low tensile strength and low ductility. This is presumably because it did not satisfy expression (2). It did not satisfy expression (2) presumably because the temperature for the primary heat treatment was too high.

[0065] The sample labeled Test No. 30 had both low tensile strength and low ductility. This is presumably because it did not satisfy expression (1) nor (2). It did not satisfy expression (1) nor (2) presumably because the temperature for the secondary heat that was too high.

[0066] The sample labeled Test No. 31 had sufficient tensile strength but a breaking elongation lower than 35 %. This is presumably because the amount of Nb determined through analysis of the electrolytic extraction residue was too large. The amount of Nb determined through analysis of the electrolytic extraction residue was too large presumably because the temperature for the primary heat treatment was too low to deal with the Nb content of the material and the dissolution of carbides and carbonitrides produced by hot working and other processes was not sufficient.

[0067] The sample labeled Test No. 32 had both low tensile strength and low ductility. This is presumably because the N content of the material was low. The sample labeled Test No. 33 had both low tensile strength and low ductility. This is presumably because the N content of the material was low.

[0068] Test Nos. 34 to 36 denote samples that were not subjected to the primary heat treatment nor cold working. The samples labeled Test Nos. 34 and 35 had low tensile strength. The sample labeled Test No. 36 had low ductility. These samples did not satisfy expression (1) nor (2).

[0069] Evaluation tests using sheets have been described; for Steel Type A, round-bar samples were produced and evaluated in the same manner. Specifically, an ingot with an outer diameter of 150 mm was subjected to hot extrusion to produce a round bar, which was subjected to the primary heat treatment at the relevant temperature T1 (°C) shown in Table 3. The cooling after the primary heat treatment was water cooling. Thereafter, the bar was subjected to cold tensile straightening to result in the relevant reduction in area shown in Table 3 to produce a solid member with the shape of a round bar with an outer diameter of 55 mm. Thereafter, the secondary heat treatment was performed at the relevant temperature T2 (°C) shown in Table 2. The holding time for the primary heat treatment was 1 to 10 minutes, and the holding time for the secondary heat treatment was 1 to 15 minutes. The results are shown in Table 3.

[Table 3]

[0070]

TABLE 3

No.	Steel Type	T1 (°C)	R (%)	T2 (°C)	[Nb] (mass %)	TS (MPa)	EL (%)	D (μm)	F1	F2	Class.
51	A	1220	12	1100	0.19	841	41	38	0.14	0.100	inv. ex.
52	A	1220	13	1100	0.17	866	42	38	0.14	0.089	
53	A	1 220	12	1150	0.16	833	44	25	0.14	0.128	
54	A	1220	9	1000	0.18	841	40	50	0.11	0.072	
55	A	1250	8	1.100	0.18	832	39	41	0.14	0.088	
56	A	1200	9	1100	0.19	850	38	42	0.14	0.090	
57	A	-	9	1100	0.12	788	44	46	0.14	0.052	comp. ex.

[0071] As shown in Table 3, each of the samples labeled Test Nos. 51 to 56 had a tensile strength not lower than 800 MPa, and a breaking elongation not lower than 35 %. On the other hand, the sample labeled Test No. 57 had a tensile strength lower than 800 MPa. This is presumably because it did not satisfy expression (1). It did not satisfy expression (1) presumably because the primary heat treatment was not performed.

[0072] Although an embodiment of the present invention has been described, the above-described embodiment is merely an illustrative example useful for carrying out the present invention. Thus, the present invention is not limited to the above-described embodiment, and the above-described embodiment, when carried out, may be modified as appropriate within the scope of the invention.

Claims

1. An austenitic stainless steel having a chemical composition of, in mass %:

0.005 to 0.060 % C;
0.20 to 1.20 % Si;
4.0 to 8.0 % Mn;
12.0 to 15.0 % Ni;
19.0 to 24.0 % Cr;
1.0 to 4.0 % Mo;
0.05 to 0.40 % Nb;
0.05 to 0.40 % V;
0.20 to 0.50 % N;
up to 0.050 % Al;
0 to 3.0 % Cu;
0 to 0.50 % Co;
0 to 0.0050 % Ca;
0 to 0.0050 % B;
0 to 0.10 % W;
0 to 0.10 % Ta; and
balance Fe and impurities,
the impurities including:
up to 0.030 % P;
up to 0.010 % S; and
up to 0.015 % O,
a tensile strength being not lower than 800 MPa,
braking elongation being not lower than 35 %,
an amount of Nb determined through analysis of an electrolytic extraction residue satisfying expression (1) below,
the amount of Nb determined through analysis of the electrolytic extraction residue and a crystal grain size satisfying expression (2) below:

$$0.7 \times \mathrm{Nb} \leq [\mathrm{Nb}] \leq 0.30 \quad (1),$$

and

$$20 \times [\mathrm{Nb}] / \mathrm{D} \geq 0.050 \quad (2),$$

in expressions (1) and (2), the Nb content in the chemical composition represented in mass %, the amount of Nb determined through analysis of the electrolytic extraction residue represented in mass %, and the crystal grain size represented in pm are substituted for "Nb", "[Nb]", and "D", respectively.

2. The austenitic stainless steel according to claim 1, wherein the austenitic stainless steel is a solid member.

3. The austenitic stainless steel according to claim 2, wherein the solid member is a round bar.

4. The austenitic stainless steel according to claim 3, having an outer diameter not smaller than 25 mm.

5. The austenitic stainless steel according to any one of claims 1 to 4, wherein the chemical composition includes one or more elements selected from the group consisting of, in mass %:

0.01 to 3.0 % Cu;
0.01 to 0.50 % Co;
0.0001 to 0.0050 % Ca;
0.0001 to 0.0050 % B;
0.01 to 0.10 % W; and
0.001 to 0.10 % Ta.

6. The austenitic stainless steel according to any one of claims 1 to 4, used as a material in equipment for storing or transporting high-pressure hydrogen gas or liquid hydrogen.

7. A method of manufacturing the austenitic stainless steel according to any one of claims 1 to 4, comprising:

performing a primary heat treatment on a steel material having said chemical composition at 1180 to 1280 °C;
after the primary heat treatment, performing cold working on the steel material with a reduction in area not lower than 5 % and lower than 20 %; and,
after the cold working, performing a secondary heat treatment on the steel material at a temperature of 1000 to 1180 °C.

8. The method of manufacturing the austenitic stainless steel according to claim 7, wherein the temperature for the secondary heat treatment is 1050 to 1160 °C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/004210

A. CLASSIFICATION OF SUBJECT MATTER

C21D 8/02(2006.01)i; ***C21D 8/06***(2006.01)i; ***C21D 9/00***(2006.01)i; ***C21D 9/46***(2006.01)i; ***C22C 38/00***(2006.01)i; ***C22C 38/58***(2006.01)i
FI: C22C38/00 302Z; C22C38/58; C21D9/46 Q; C21D8/02 D; C21D8/06 B; C21D9/00 G

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)

C21D8/02; C21D8/06; C21D9/00; C21D9/46; C22C38/00; C22C38/58

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2020-132979 A (NIPPON STEEL CORP.) 31 August 2020 (2020-08-31)	1-8
A	JP 2017-008413 A (NIPPON STEEL & SUMITOMO METAL CORP.) 12 January 2017 (2017-01-12)	1-8
A	WO 2017/056619 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 06 April 2017 (2017-04-06)	1-8

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

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Date of the actual completion of the international search **23 March 2023**	Date of mailing of the international search report **04 April 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/004210

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2020-132979 A	31 August 2020	(Family: none)	
JP 2017-008413 A	12 January 2017	(Family: none)	
WO 2017/056619 A1	06 April 2017	US 2018/0258505 A1 EP 3358030 A1 KR 10-2018-0031753 A CN 108138280 A	

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2014047420 A **[0004] [0005]**