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(54) MARTENSITIC STAINLESS STEEL FOR HYDROGEN GAS ENVIRONMENT AND MANUFACTURING METHOD THEREFOR

(57) Disclosed is a martensitic stainless steel for a hydrogen gas environment, having a composition consisting of: 0.02 mass% ≤ C ≤ 0.30 mass%, Si ≤ 1.50 mass%, Mn ≤ 1.50 mass%, P ≤ 0.150 mass%, S ≤ 0.150 mass%, 8.0 mass% ≤ Cr ≤ 22.0 mass%, 1.0 mass% ≤ Ni ≤ 6.0 mass%, 0.01 mass% ≤ Nb ≤ 1.0 mass%, and N ≤ 0.12 mass%, and optionally at least one selected from the group consisting of: Cu ≤ 6.00 mass%, Mo ≤ 3.00 mass%, V ≤ 1.50 mass%, and B ≤ 0.0500 mass%, with the balance being Fe and inevitable impurities; having: a crystal grain size number of prior austenite grains of 2.0 or more, an amount of retained austenite of 40 vol% or less, a tensile strength of 1,500 MPa or less, and satisfying $D_{H2(0.7)}/D_{air} \geq 0.8$.

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Description

TECHNICAL FIELD

[0001] The present invention relates to martensitic stainless steel for a hydrogen gas environment and a manufacturing method therefor. More particularly, the present invention relates to martensitic stainless steel for a hydrogen gas environment, having appropriate strength and high hydrogen embrittlement resistance, and to a manufacturing method therefor.

BACKGROUND ART

[0002] As one of methods for achieving carbon neutrality, use of hydrogen is exemplified. For example, in the case of a fuel cell vehicle (FCV), which is a typical example of the use of hydrogen, since high-pressure hydrogen gas is used, a problem of hydrogen embrittlement of a steel material exposed to a hydrogen gas environment arises. As the steel material exposed to such a hydrogen gas environment, austenitic stainless steel excellent in hydrogen embrittlement resistance has been used in the related art. The austenitic stainless steel has both the hydrogen embrittlement resistance and corrosion resistance. However, it is difficult to achieve weight reduction because strength of the austenitic stainless steel is lower than that of martensitic stainless steel and the like. In addition, since expensive elements such as Ni are used, the cost is high.

[0003] In order to solve these problems, various proposals have been made in the related art.

[0004] For example, Patent Literature 1 discloses a substrate for hydrogen equipment including

a base material made of carbon steel, low alloy steel, ferritic stainless steel, or martensitic stainless steel, and
a hydrogen permeation resistance film formed on a surface of the base material, in which
the hydrogen permeation resistance film includes a three-layered structure film of an aluminum-based intermetallic compound layer, an aluminum layer, and an alumina layer, and has an average thickness of 3 μm or more and less than 35 μm.

[0005] Patent Literature 1 discloses that (A) when molten aluminum plating is applied on the surface of the substrate by using an Al-Si aluminum alloy, the three-layered structure film can be formed on the surface of the substrate, and (B) both the three-layered structure film and a two-layered structure film of an aluminum-based intermetallic compound layer and an alumina layer have a function of preventing hydrogen penetration, but the three-layered structure film is superior to the two-layered structure film in this function.

[0006] Patent Literature 2 discloses a manufacturing method for a martensitic stainless steel billet, although the manufacturing method is not intended to improve hydrogen embrittlement resistance in a high-pressure hydrogen gas environment. In the method, (a) in the case where steel containing predetermined amounts of C, N, Si, Mn, Cr, P, S, N, Al, H, Ti, V, and Nb is refined and melted by an argon-oxygen decarburization refining method (AOD method) and subjected to a hot working, (b) the steel is cooled at an average cooling rate of 15°C/min or less in a temperature range from 400°C to 150°C in cooling after finishing, to form retained austenite.

[0007] Patent Literature 2 discloses that (A) when a small amount of hydrogen is contained in the melted martensitic stainless steel, the small amount of hydrogen may cause delayed fracture after the hot working or cold working, (B) when the martensitic stainless steel having a predetermined composition is subjected to the hot working and then is slowly cooled in a predetermined temperature range, a structure in which fine austenite retains in a martensite phase is obtained, and the delayed fracture is prevented without performing a process of reducing the amount of hydrogen in the steel, and (C) it is presumed that the delayed fracture is prevented because the fine retained austenite functions as a hydrogen trap site and aggregation of hydrogen near fine defects is prevented.

[0008] Further, Patent Literature 3 discloses a manufacturing method for martensitic stainless steel, although the manufacturing method is not intended to improve hydrogen embrittlement resistance. In the method, (a) martensitic stainless steel containing 0.01 mass% to 0.1 mass% of C and 9 mass% to 15 mass% of Cr is heated to an A_{c3} point or higher, then (b) the martensitic stainless steel is cooled from 800°C to 400°C at a cooling rate of 0.08°C/sec or more, and (c) the martensitic stainless steel is cooled to 150°C at a cooling rate of 1°C/sec or less.

[0009] Patent Literature 3 discloses that (A) when heating in a two-phase region of A_{c1} to A_{c3} is performed for a long time, austenite-forming elements are concentrated in reverse-transformed austenite, and an Ms point and an Mf point are significantly reduced, whereby coarse reverse-transformed austenite is formed, and thus yield stress is reduced, and (B) when martensitic stainless steel containing 0.1 mass% or more of C is heated to an austenite region of the A_{c3} point or higher, then is cooled relatively rapidly in a high temperature region, and is cooled from the Ms point to room temperature without being subjected to rapid cooling, very thin plate-shaped retained austenite is formed at a lath interface of martensite, and thus high strength and high toughness are obtained.

[0010] As described above, although the austenitic stainless steel is excellent in the hydrogen embrittlement resistance, it is difficult to enhance the strength thereof. Therefore, the austenitic stainless steel is not suitable for a structural member requiring weight reduction and size reduction, for example, a vehicle component. In addition, since a large amounts of expensive elements such as Ni and Mo are used, the cost is high.

[0011] On the other hand, since the martensitic stainless steel is high in corrosion resistance and has high strength as compared to the austenitic stainless steel, the weight reduction and size reduction of the component can be achieved. However, since the martensitic stainless steel is inferior in hydrogen embrittlement resistance, it is necessary to apply a special plating treatment to a surface thereof in order to use the martensitic stainless steel for a component exposed to a hydrogen gas environment (see Patent Literature 1). In addition to the cost of the plating treatment, even in the case where a small fraction of defects, scratches, or the like is present on the surface of the steel material due to the plating treatment, there is a concern of causing hydrogen embrittlement, and there is a problem in terms of safety assurance.

[0012] Further, some kinds of low alloy steel are recognized to be used in a high-pressure hydrogen gas environment, but these cannot be applied to structural members used in a specific corrosive environment due to insufficient corrosion resistance of any of those.

CITATION LIST

PATENT LITERATURE

[0013]

Patent Literature 1: WO2015/098981
Patent Literature 2: JP2003-253333A
Patent Literature 3: JP2003-129190A

SUMMARY OF INVENTION

[0014] An object of the present invention is to provide martensitic stainless steel for a hydrogen gas environment having appropriate strength and high hydrogen embrittlement resistance, and a manufacturing method therefor.

[0015] In order to achieve the above object, a martensitic stainless steel for a hydrogen gas environment according to the present invention,

has a composition consisting of:

$$0.02\ \text{mass\%} \leq \text{C} \leq 0.30\ \text{mass\%},$$

$$\text{Si} \leq 1.50\ \text{mass\%},$$

$$\text{Mn} \leq 1.50\ \text{mass\%},$$

$$\text{P} \leq 0.150\ \text{mass\%},$$

$$\text{S} \leq 0.150\ \text{mass\%},$$

$$8.0\ \text{mass\%} \leq \text{Cr} \leq 22.0\ \text{mass\%},$$

$$1.0\ \text{mass\%} \leq \text{Ni} \leq 6.0\ \text{mass\%},$$

$$0.01\ \text{mass\%} \leq \text{Nb} \leq 1.0\ \text{mass\%},$$

and

$$N \leq 0.12 \text{ mass\%},$$

and

optionally at least one selected from the group consisting of:

$$Cu \leq 6.00 \text{ mass\%},$$

$$Mo \leq 3.00 \text{ mass\%},$$

$$V \leq 1.50 \text{ mass\%},$$

and

$$B \leq 0.0500 \text{ mass\%},$$

with the balance being Fe and inevitable impurities;

has:

a crystal grain size number of prior austenite grains of 2.0 or more,
an amount of retained austenite of 40 vol% or less,
a tensile strength of 1,500 MPa or less, and

satisfies the following formula (1):

$$D_{H2(0.7)}/D_{air} \geq 0.8 \qquad (1)$$

here, D_{air} represents a displacement at a time point when stress shows a local maximum in a stress-displacement curve obtained by performing a tensile test under a condition of a strain rate of 5×10^{-5}/s in the atmosphere at normal temperature (25°C), and
$D_{H2(0.7)}$ represents a displacement at a time point when stress shows a local maximum or a maximum value in a stress-displacement curve obtained by performing a tensile test under a condition of a strain rate of 5×10^{-5}/s in hydrogen gas of 0.7 MPa at normal temperature (25°C).

[0016] A manufacturing method for a martensitic stainless steel for a hydrogen gas environment according to the present invention, contains:

a first step of manufacturing a material consisting of:

$$0.02 \text{ mass\%} \leq C \leq 0.30 \text{ mass\%},$$

$$Si \leq 1.50 \text{ mass\%},$$

$$Mn \leq 1.50 \text{ mass\%},$$

$$P \leq 0.150 \text{ mass\%},$$

$$S \leq 0.150 \text{ mass\%},$$

$$8.0 \text{ mass\%} \leq Cr \leq 22.0 \text{ mass\%},$$

$$1.0 \text{ mass\%} \leq Ni \leq 6.0 \text{ mass\%},$$

$$0.01 \text{ mass\%} \leq Nb \leq 1.0 \text{ mass\%},$$

and

$$N \leq 0.12 \text{ mass\%},$$

and

optionally at least one selected from the group consisting of:

$$Cu \leq 6.00 \text{ mass\%},$$

$$Mo \leq 3.00 \text{ mass\%},$$

$$V \leq 1.50 \text{ mass\%},$$

and

$$B \leq 0.0500 \text{ mass\%},$$

with the balance being Fe and inevitable impurities;

a second step of subjecting the material to a quenching from a temperature equal to or higher than an A_{c3} point and lower than a solidus temperature, or further performing a sub-zero treatment on the material after the quenching, and a third step of subjecting the material after the quenching or after the sub-zero treatment to a tempering one or more times under conditions of a final tempering temperature of 200°C or higher and 800°C or lower and a final tempering time of 10 minutes or more and 24 hours or less to obtain the martensitic stainless steel for a hydrogen gas environment according to the present invention.

[0017] In the case where martensitic stainless steel having a predetermined composition is subjected to quenching and tempering, when the tempering is performed under conditions of low temperature and long time, martensitic stainless steel having excellent hydrogen embrittlement resistance can be obtained.

[0018] The reason for this is considered to be that due to the tempering under a low temperature for a long time, (a) a structure having retained austenite in which austenite stabilization elements are appropriately concentrated (austenite (initial retained austenite) remaining after the quenching, and reverse-transformed austenite) is obtained, and an amount of retained austenite in which austenite stabilization elements are not concentrated (that is, retained austenite having an adverse effect on the hydrogen embrittlement resistance) is reduced, and (b) an Ms point and an Mf point of the retained austenite are reduced, martensitic transformation of the retained austenite in a cooling process after the tempering is prevented, and an amount of fresh martensite having an adverse effect on the hydrogen embrittlement resistance is reduced.

BRIEF DESCRIPTION OF DRAWINGS

[0019]

FIG. 1 is a schematic diagram of a change in structure accompanying a heat treatment of a material in which only quenching was performed and tempering was not performed (Comparative Example 5);
FIG. 2 is a schematic diagram of a change in structure accompanying a heat treatment of a material with a high tempering temperature (Comparative Example 6);
FIG. 3 is a schematic diagram of a change in structure accompanying a heat treatment of a material with a short tempering time (Comparative Example 3);
FIG. 4 is a schematic diagram of a change in structure accompanying a heat treatment of a material in which tempering conditions were appropriate but components were inappropriate (Comparative Example 1);
FIG. 5 is a schematic diagram of a change in structure accompanying a heat treatment of a material in which tempering conditions and components were appropriate (Example 1);
FIG. 6A is an example of element mapping of Ni of a material in which Ni is concentrated, which was measured by using a STEM (Example 1);
FIG. 6B is an example of element mapping of Ni of a material in which Ni is not concentrated, which was measured by using a STEM (Comparative Example 5);
FIG. 7A is a diagram showing an example of a stress-displacement curve in a slow strain rate tensile (SSRT) test of a steel material having poor hydrogen embrittlement resistance; and
FIG. 7B is a diagram showing an example of a stress-displacement curve in a slow strain rate tensile (SSRT) test of a steel material having excellent hydrogen embrittlement resistance.

DESCRIPTION OF EMBODIMENTS

[0020] Hereinafter, an embodiment of the present invention will be described in detail.

[1. Martensitic Stainless Steel for Hydrogen Gas Environment]

[1.1. Main Constituent Elements]

[0021] The martensitic stainless steel for a hydrogen gas environment (hereinafter, also referred to as "martensitic stainless steel" or simply "steel") according to the present invention contains the following elements, with the balance being Fe and inevitable impurities. Types of additive elements, component ranges thereof, and reasons for limitation thereof are as follows.

(1) 0.02 mass% $\leq$ C $\leq$ 0.30 mass%:

[0022] C is an interstitial element and contributes to an improvement in strength. In addition, C bonds to Cr, Mo, V, Nb, and the like to be described later to form a carbonitride (containing carbide and nitride, and the same applies hereinafter), and improves tempering hardness. Further, C is an important element to form a carbonitride effective for exhibiting a pinning effect of preventing coarsening of crystal grains at the time of quenching. In order to achieve such an effect, the amount of C needs to be 0.02 mass% or more. The amount of C is preferably 0.03 mass% or more.
[0023] On the other hand, in the case where the amount of C is excessive, tensile strength becomes too high, and hydrogen embrittlement resistance may be reduced. Therefore, the amount of C needs to be 0.30 mass% or less. The amount of C is preferably 0.25 mass% or less, and more preferably 0.22 mass% or less.

(2) Si $\leq$ 1.50 mass%:

[0024] The martensitic stainless steel may contain Si. Si is a deoxidizing element and is effective for preventing formation of an oxide that causes reduction in toughness and ductility. In order to achieve such an effect, the amount of Si is preferably 0.005 mass % or more.
[0025] On the other hand, in the case where the amount of Si is excessive, deterioration of hydrogen embrittlement resistance or reduction of hot workability may be caused. Therefore, the amount of Si needs to be 1.50 mass% or less. The amount of Si is preferably 1.00 mass% or less, and more preferably 0.50 mass% or less.

(3) Mn $\leq$ 1.50 mass%:

[0026] The martensitic stainless steel may contain Mn. In the case where S is contained in the steel, Mn forms MnS and has an effect of enhancing hot workability and machinability. In addition, Mn is concentrated in retained austenite after final tempering, and has an effect of enhancing hydrogen embrittlement resistance.
[0027] In order to achieve such effects, the amount of Mn is preferably 0.005 mass % or more.
[0028] On the other hand, in the case where the amount of Mn is excessive, the amount of austenite remaining after quenching (initial amount of retained austenite) is increased, which may lead to a deterioration of hydrogen embrittlement resistance. Therefore, the amount of Mn needs to be 1.50 mass% or less. The amount of Mn is preferably 1.00 mass% or less, and more preferably 0.50 mass% or less.

(4) P $\leq$ 0.150 mass%:

[0029] P is an element that deteriorates hot workability, grain boundary strength, toughness and ductility, and hydrogen embrittlement resistance. Therefore, the amount of P is preferably reduced. In order to prevent the above-mentioned deterioration in the properties, the amount of P needs to be 0.150 mass% or less. The amount of P is preferably 0.100 mass% or less, and more preferably 0.040 mass% or less.
[0030] An excessive reduction in the amount of P causes an increase in cost. Therefore, it is preferable to select an optimum amount of P in consideration of these points.

(5) S $\leq$ 0.150 mass%:

[0031] The martensitic stainless steel may contain S. S has an effect of promoting the formation of MnS and enhancing machinability.
[0032] On the other hand, in the case where the amount of S is excessive, corrosion resistance and toughness and ductility may be reduced, or hot workability may be reduced. Therefore, the amount of S needs to be 0.150 mass% or less. The amount of S is preferably 0.100 mass% or less, and more preferably 0.030 mass% or less.
[0033] In the case where it is not necessary to improve machinability, an excessive reduction in the amount of S causes an increase in cost. Therefore, it is preferable to select an optimum amount of S in consideration of these points.

(6) 8.0 mass% $\leq$ Cr $\leq$ 22.0 mass%:

[0034] Cr forms a carbonitride and contributes to an improvement in strength. In addition, Cr is an element effective in improving corrosion resistance. In order to achieve such effects, the amount of Cr needs to be 8.0 mass% or more. The amount of Cr is preferably 10.0 mass% or more, and more preferably 11.5 mass% or more.
[0035] On the other hand, in the case where the amount of Cr is excessive, formation of δ ferrite is promoted, and toughness and ductility may be reduced. Therefore, the amount of Cr needs to be 22.0 mass% or less. The amount of Cr is preferably 19.0 mass% or less, and more preferably 18.0 mass% or less.

(7) 1.0 mass% $\leq$ Ni $\leq$ 6.0 mass%:

[0036] Ni is an austenite stabilization element and is an element required for martensitic transformation at the time of quenching. In addition, Ni is an important element that has an effect of enhancing hydrogen embrittlement resistance by improving mobility of dislocation. Further, Ni is concentrated in the retained austenite after final tempering, and has an effect of enhancing hydrogen embrittlement resistance. In order to achieve such effects, the amount of Ni needs to be 1.0 mass% or more. The amount of Ni is preferably 1.1 mass% or more, and more preferably 1.2 mass% or more.
[0037] On the other hand, in the case where the amount of Ni is excessive, the amount of retained austenite after final tempering is increased, and hydrogen embrittlement resistance may be reduced. Therefore, the amount of Ni needs to be 6.0 mass% or less. The amount of Ni is preferably 5.5 mass% or less, and more preferably 5.0 mass% or less.

(8) 0.01 mass% $\leq$ Nb $\leq$ 1.0 mass%:

[0038] Nb bonds to C and/or N to form a carbonitride. The carbonitride pins crystal grains and contributes to refinement of the crystal grains. In order to achieve such an effect, the amount of Nb needs to be 0.01 mass% or more. The amount of Nb is preferably 0.05 mass% or more.
[0039] On the other hand, in the case where the amount of Nb is excessive, a coarse carbonitride is formed, and toughness and ductility may significantly deteriorate. Therefore, the amount of Nb needs to be 1.0 mass% or less. The amount of Nb is preferably 0.6 mass% or less.

(9) N $\leq$ 0.12 mass%:

[0040] The martensitic stainless steel may contain N. N is an interstitial element and contributes to an improvement in strength. In addition, N bonds to Cr, Mo, V, Nb, and the like to form a carbonitride. The carbonitride has an effect of improving tempering hardness and an effect of pinning crystal grains to prevent coarsening of the crystal grains. In order to achieve such effects, the amount of N is preferably 0.01 mass % or more.

[0041] On the other hand, in the case where the amount of N is excessive, tensile strength excessively increases, and hydrogen embrittlement resistance may be reduced. In addition, in the case where the amount of N is excessive, blowholes may be generated at the time of casting. Therefore, the amount of N needs to be 0.12 mass% or less.

[1.2. Sub-constituent Elements]

[0042] The martensitic stainless steel material according to the present invention may further contain one or two or more of the following elements in addition to the above-described main constituent elements. Types of additive elements, component ranges thereof, and reasons for limitation thereof are as follows.

(1) Cu $\leq$ 6.00 mass%:

[0043] The martensitic stainless steel may contain Cu. Cu forms a precipitate at the time of tempering and contributes to an improvement in strength. In addition, Cu has an effect of improving corrosion resistance. Further, Cu is concentrated in the retained austenite after final tempering, and has an effect of enhancing hydrogen embrittlement resistance. In order to achieve such effects, the amount of Cu is preferably 0.01 mass % or more.

[0044] On the other hand, in the case where the amount of Cu is excessive, hot workability may deteriorate. Therefore, the amount of Cu is preferably 6.00 mass% or less. The amount of Cu is more preferably 5.00 mass% or less, and further preferably 4.00 mass% or less.

(2) Mo $\leq$ 3.00 mass%:

[0045] The martensitic stainless steel may contain Mo. Mo has an effect of improving corrosion resistance. In addition, Mo has an effect of improving strength as a solid solution-strengthening element. Further, Mo bonds to C and/or N at the time of tempering to contribute to an improvement in hardness. In order to achieve such effects, the amount of Mo is preferably 0.01 mass % or more. The amount of Mo is more preferably 0.05 mass% or more.

[0046] On the other hand, in the case where the amount of Mo is excessive, formation of δ ferrite is promoted, and toughness and ductility may be reduced. Therefore, the amount of Mo is preferably 3.00 mass% or less. The amount of Mo is more preferably 2.00 mass% or less, and further preferably 1.00 mass% or less.

(3) V $\leq$ 1.50 mass%:

[0047] The martensitic stainless steel may contain V. V bonds to C and/or N at the time of tempering to contribute to an improvement in hardness. In order to achieve such an effect, the amount of V is preferably 0.01 mass % or more. The amount of V is more preferably 0.05 mass% or more.

[0048] On the other hand, in the case where the amount of V is excessive, a coarse carbonitride is formed, and toughness and ductility may be significantly reduced. Therefore, the amount of V is preferably 1.50 mass% or less. The amount of V is more preferably 1.00 mass% or less, and further preferably 0.6 mass% or less.

[0049] The martensitic stainless steel may contain any one of Mo and V, or may contain both of Mo and V.

(4) B $\leq$ 0.0500 mass%:

[0050] The martensitic stainless steel may contain B. B contributes to an improvement in toughness and ductility. In addition, B has an effect of improving hot workability. In order to achieve such effects, the amount of B is preferably 0.0001 mass % or more.

[0051] On the other hand, in the case where the amount of B is excessive, hot workability may be rather reduced. Therefore, the amount of B is preferably 0.0500 mass% or less. The amount of B is more preferably 0.0400 mass% or less, and further preferably 0.0300 mass% or less.

[0052] The martensitic stainless steel may contain any one of Mo, V, and B, or may contain two or more thereof.

[1.3. Properties]

[1.3.1. Crystal Grain Size Number of Prior Austenite]

[0053] The "crystal grain size number of prior austenite grain" refers to a value measured in accordance with JIS G 0551:2020.

in the case where the crystal grain size number of the steel after final tempering is small (= grain size is large), the resistances against cracks caused by hydrogen and spreading thereof become small. As a result, hydrogen embrittlement resistance deteriorates, and a result of unsuitable is obtained in a slow strain rate tensile (SSRT) test. In order to obtain excellent hydrogen embrittlement resistance, the crystal grain size number of the prior austenite grain needs to be 2.0 or more. The crystal grain size number is preferably 3.0 or more, and more preferably 4.0 or more.

[1.3.2. Amount of Retained Austenite]

[0054] The "amount of retained austenite (vol%)" refers to a value measured by using a method (so-called 5-peak method) using peak intensities of (200) and (211) of a ferrite phase and peak intensities of (200), (220), and (311) of an austenite layer, obtained by X-ray diffraction using a Mo tube.

[0055] In the present invention, the "retained austenite" refers to a combination of both (a) austenite remaining after quenching (initial retained austenite), and (b) austenite generated by reverse-transformation during tempering (reverse-transformed austenite).

[0056] In steel containing an austenite stabilization element such as Ni, austenite may be generated by reverse-transformation from martensite at the time of tempering, and the austenite may remain as it is after the tempering. In the retained austenite (initial retained austenite and reverse-transformed austenite), austenite stabilization elements such as C, N, Cu, and Mn, as well as Ni, are concentrated, and thus austenite stability is increased. It is considered that the retained austenite having high austenite stability hardly causes martensitic transformation due to a stress load, and thus does not adversely affect hydrogen embrittlement resistance.

[0057] On the other hand, in the case where a large amount of reverse-transformed austenite is generated at the time of tempering, an austenite stabilization element is hardly concentrated in the retained austenite, and as a result, hydrogen embrittlement resistance deteriorates.

[0058] In order to prevent deterioration of hydrogen embrittlement resistance, the amount of retained austenite needs to be 40 vol% or less. The amount of retained austenite is preferably 30.0 vol% or less, and more preferably 20.0 vol% or less.

[1.3.3. Tensile Strength]

[0059] The "tensile strength" refers to a value obtained by (a) performing a tensile test (slow strain rate tensile test) under a condition of a strain rate of 5×10^{-5}/s in the atmosphere at normal temperature (25°C), and (b) dividing the maximum value of stress in the slow strain rate tensile test by an area of a parallel portion of a tensile test piece.

[0060] In the case where a component used in a hydrogen gas environment is manufactured by using the martensitic stainless steel according to the present invention, in order to reduce the weight of the component, the tensile strength of the martensitic stainless steel is preferably as high as possible. However, in the case where the tensile strength becomes too high, toughness is reduced, and a brittle fracture easily occurs. In order to prevent the brittle fracture, the tensile strength needs to be 1,500 MPa or less. The tensile strength is preferably 1,400 MPa or less, and more preferably 1,300 MPa or less.

[0061] However, in the case where the tensile strength becomes too low, it may be difficult to reduce the weight of the component. Therefore, the tensile strength is preferably 540 MPa or more. The tensile strength is more preferably 600 MPa or more, and still more preferably 700 MPa or more.

[1.3.4. D_{H2}/D_{air}]

[0062] The martensitic stainless steel needs to satisfy the following formula (1):

$$D_{H2(0.7)}/D_{air} \geq 0.8 \qquad (1)$$

here,

D_{air} represents a displacement at a time point when stress shows a local maximum in a stress-displacement curve obtained by performing a tensile test under a condition of a strain rate of 5×10^{-5}/s in the atmosphere at normal temperature (25°C), and

$D_{H2(0.7)}$ represents a displacement at a time point when stress shows a local maximum or a maximum value in a stress-displacement curve obtained by performing a tensile test under a condition of a strain rate of 5×10^{-5}/s in hydrogen gas of 0.7 MPa at normal temperature (25°C).

[0063] In addition, the martensitic stainless steel preferably satisfies the following formula (2) in addition to the formula (1):

$$D_{H2(90)}/D_{air} \geq 0.8 \qquad (2)$$

here,

D_{air} represents a displacement at a time point when stress shows a local maximum in the stress-displacement curve obtained by performing the tensile test under a condition of a strain rate of 5×10^{-5}/s in the atmosphere at normal temperature (25°C), and

$D_{H2(90)}$ represents a displacement at a time point when stress shows a local maximum or a maximum value in a stress-displacement curve obtained by performing a tensile test under a condition of a strain rate of 5×10^{-5}/s in hydrogen gas of 90.0 MPa at normal temperature (25°C).

In the case where the tensile test is performed in a hydrogen atmosphere, when the test piece is broken before the stress reaches a local maximum or when whether the stress shows a local maximum cannot be clearly determined, a "displacement at the time when the stress shows the maximum value" is regarded as the "displacement at the time when the stress shows a local maximum", and values of the formulae (1) and (2) are calculated based thereon.

$D_{H2(0.7)}/D_{air}$ and $D_{H2(90)}/D_{air}$ (hereinafter, also collectively referred to as "D_{H2}/D_{air}") represent indices of hydrogen embrittlement resistance. D_{H2}/D_{air} being large indicates that a deformation amount under a hydrogen atmosphere is large, that is, the material is excellent in the hydrogen embrittlement resistance. The martensitic stainless steel according to the present invention is excellent in hydrogen embrittlement resistance since the composition and structure thereof are optimized. Specifically, by optimizing the composition and structure, $D_{H2(0.7)}/D_{air}$ becomes 0.8 or more. In the case where the composition and structure are further optimized, $D_{H2(0.7)}/D_{air}$ becomes 0.9 or more.

[0064] In the case where the composition and structure are further optimized, $D_{H2(90)}/D_{air}$ becomes 0.8 or more or 0.9 or more in addition to $D_{H2(0.7)}/D_{air}$ satisfying the above-described conditions.

[1.4. Application]

[0065] The martensitic stainless steel according to the present invention can be used for various members used in a hydrogen gas environment. Examples of such members include (a) a valve, pipe, and pressure-reducing valve for high-pressure hydrogen gas used in a hydrogen station or an FCV, and (b) a member for a compressor used to increase a pressure of hydrogen gas.

[2. Manufacturing Method for Martensitic Stainless Steel for Hydrogen Gas Environment]

[0066] A manufacturing method for martensitic stainless steel for a hydrogen gas environment, according to the present invention, includes:

a first step of manufacturing a material containing

$$0.02 \text{ mass\%} \leq C \leq 0.30 \text{ mass\%},$$

$$Si \leq 1.50 \text{ mass\%},$$

$$Mn \leq 1.50 \text{ mass\%},$$

$$P \leq 0.150 \text{ mass\%},$$

$$S \leq 0.150 \text{ mass\%},$$

$$8.0 \text{ mass\%} \leq Cr \leq 22.0 \text{ mass\%},$$

$$1.0 \text{ mass\%} \leq Ni \leq 6.0 \text{ mass\%},$$

$$0.01 \text{ mass\%} \leq Nb \leq 1.0 \text{ mass\%},$$

$$N \leq 0.12 \text{ mass\%},$$

$$Cu \leq 6.00 \text{ mass\%},$$

$$Mo \leq 3.00 \text{ mass\%},$$

$$V \leq 1.50 \text{ mass\%},$$

and

$$B \leq 0.0500 \text{ mass\%},$$

with the balance being Fe and inevitable impurities,
a second step of subjecting the material to a quenching from a temperature equal to or higher than an A_{c3} point and lower than a solidus temperature, or further performing a sub-zero treatment on the material after the quenching, and
a third step of subjecting the material after the quenching or after the sub-zero treatment to a tempering one or more times under conditions of a final tempering temperature of 200°C or higher and 800°C or lower and a final tempering time of 10 minutes or more and 24 hours or less, to obtain the martensitic stainless steel for a hydrogen gas environment according to the present invention.

[2.1. First Step]

[0067] First, a material containing predetermined elements and the balance being Fe and inevitable impurities is manufactured (first step).

[0068] The manufacturing method for the material is not particularly limited, and an optimum method can be selected according to a purpose thereof. The material is generally obtained by (a) melting and casting raw materials blended to have a predetermined composition, to obtain an ingot, and (b) subjecting the ingot to hot working.

[0069] The composition of the material is as described above, and descriptions thereof are omitted.

[2.2. Second Step]

[0070] Next, the material is subjected to a quenching from a temperature equal to or higher than an A_{c3} point and lower than a solidus temperature (second step). The solidus temperature is a temperature at which the material starts to melt. The solidus temperature varies depending on the composition, and for example, is 1300°C or higher.

[0071] The second step may include a step of performing only the quenching, or may further include a step of performing a sub-zero treatment on the material after the quenching.

[2.2.1. Quenching Step]

[0072] The quenching is generally a process of heating the material to a temperature equal to or higher than the A_{c3} point and cooling the material to around room temperature. The quenching temperature may be lower than the solidus temperature. However, in the case where the quenching temperature is too high, coarsening of crystal grains may occur, and hydrogen embrittlement resistance may deteriorate. Therefore, as the quenching temperature, it is preferable to select an optimum temperature in consideration of this point.

[0073] As a holding time at the quenching temperature, an optimum time is selected according to the quenching temperature. In general, as the quenching temperature increases, an austenite single phase state is obtained in a short time. The holding time at the quenching temperature depends on a dimension of the material, and is usually about 10 minutes to 2 hours.

[0074] A cooling method at the time of quenching is not particularly limited, and an optimum method can be selected according to a purpose thereof. Specific examples of the cooling method include water cooling, oil cooling, blast cooling, and air cooling.

[2.2.2. Sub-zero Treatment Step]

[0075] The sub-zero treatment is a treatment for cooling the material after quenching to a temperature of 0°C or lower. In the case where a large amount of initial retained austenite remains after the quenching alone, it is preferable to further perform the sub-zero treatment on the material after quenching. By reducing the initial retained austenite by the sub-zero treatment, stable strength characteristics can be exhibited at the time of tempering. The sub-zero treatment is usually performed at -30°C to -196°C.

[2.3. Third Step]

[0076] Next, the material after the quenching or after the sub-zero treatment is subjected to a tempering one or more times under conditions of a final tempering temperature of 200°C or higher and 800°C or lower and a final tempering time of 10 minutes or more and 24 hours or less (third step). As a result, the martensitic stainless steel for a hydrogen gas environment according to the present invention can be obtained.

[2.3.1. Number of Times of Tempering]

[0077] The tempering is performed on the material that has subjected to the quenching or the sub-zero treatment. The tempering is performed in order to (a) appropriately reduce strength of a martensite structure generated by the quenching or the sub-zero treatment, and strength of a martensite structure generated in a cooling process of the immediately preceding tempering in the case where the tempering is performed a plurality of times, and to recover toughness and ductility, or (b) promote precipitation of a carbonitride, Cu, and the like and increase strength.

[0078] Therefore, in the case where the strength and the amount of retained austenite are not sufficiently adjusted by one time of tempering, the tempering may be performed twice or more.

[2.3.2. Tempering Conditions Other than Final Tempering]

[0079] In the case where the tempering is performed twice or more, the tempering conditions other than the final tempering are not particularly limited, and it is preferable to select optimum conditions according to a purpose thereof.

[0080] Generally, in the case where the tempering temperature is too low, recovery of toughness and ductility may be insufficient. On the other hand, in the case where the tempering temperature is too high, reverse-transformed austenite may be excessively generated. As a result, concentrating of austenite stabilization elements in the retained austenite becomes insufficient, and hydrogen embrittlement resistance may deteriorate. In addition, a large amount of martensite (fresh martensite) may be generated in a cooling process after tempering, and toughness and ductility may deteriorate. Therefore, as the tempering temperature in other than the final tempering, it is preferable to select an optimum temperature in consideration of these points. For example, the tempering temperature in other than the final tempering may be 600°C to 850°C.

[0081] The tempering time depends on the dimension of the material, and may be 10 minutes to 24 hours. The cooling method is not particularly limited, and an optimum method can be selected according to a purpose thereof. Examples of the cooling method include water cooling, oil cooling, blast cooling, and air cooling.

[2.3.3. Final Tempering Conditions]

[0082] The "final tempering" refers to a first tempering in the case where the tempering is performed only once, and refers to the finally performed tempering in the case where the tempering is performed twice or more.

[0083] In the present invention, the final tempering conditions are important. As a tempering temperature during the final tempering (final tempering temperature), it is preferable to select a temperature at which strength, toughness and ductility, and hydrogen embrittlement resistance after final tempering are appropriate. In the case where the final tempering temperature is too low, the recovery of toughness and ductility may be insufficient. Therefore, the final tempering temperature needs to be 200°C or higher. The final tempering temperature is more preferably 300°C or higher, and still preferably 400°C or higher.

[0084] On the other hand, in the case where the final tempering temperature is too high, a large amount of reverse-transformed austenite is generated during tempering. As a result, the retained austenite may undergo martensitic transformation in the cooling process after tempering, and a large amount of fresh martensite may be generated.

[0085] In addition, in the case where a large amount of reverse-transformed austenite is generated, concentrating of austenite stabilization elements in the retained austenite becomes insufficient. The retained austenite in which the concentrating of the austenite stabilization elements is insufficient is easily transformed into fresh martensite when stress acts thereon.

[0086] Therefore, the retained austenite in which the concentrating of the austenite stabilization elements is insufficient may cause deterioration of hydrogen embrittlement resistance. Therefore, the final tempering temperature needs to be 800°C or lower. The final tempering temperature is preferably 750°C or lower.

[0087] As a tempering time during the final tempering (final tempering time), it is preferable to select a time with which the austenite stabilization elements can be diffused and concentrated in the retained austenite and hydrogen embrittlement resistance can be increased. In the case where the final tempering time is too short, the concentrating of the austenite stabilization elements becomes insufficient. Therefore, the final tempering time needs to be 10 minutes or more. The final tempering time is preferably 20 minutes or more, more preferably 30 minutes or more.

[0088] On the other hand, in the case where the final tempering time is increased more than necessary, the cost increases. Therefore, the final tempering time needs to be 24 hours or less.

[3. Effects]

[3.1. Change in Structure of Material Subjected to Only Quenching and not Subjected to Tempering]

[0089] FIG. 1 illustrates a schematic diagram of a change in structure accompanying a heat treatment of a material in which only quenching was performed and tempering was not performed (Comparative Example 5). When a martensitic stainless steel having a predetermined composition is heated to a temperature higher than the A_{c3} point (about 800°C to 900°C), an austenite γ_0 single phase is obtained. When the quenching is performed from this state to a temperature lower than an A_{c1} point, γ_0 is transformed into martensite (fresh martensite) α_1', but a part of γ_0 remains as initial retained austenite γ_1. The A_{c1} point is a temperature at which a structural transformation from a body center cubic (BCC) structure (martensite, ferrite, etc.) to a face center cubic (FCC) starts in a course of heating. The A_{c3} point is a temperature at which the structural transformation from the BCC structure to the FCC is completed in the course of heating. The A_{c1} point and A_{c3} point can be determined by measuring the change in volume caused by the change in structure in the course of heating.

[0090] In the case where the tempering is not performed, (a) the austenite stabilization elements are not concentrated in γ_1, (b) α_1' is excessively generated, and (c) strength of the steel becomes excessively high.

[0091] All of the above-mentioned (a) to (c) cause a decrease in hydrogen embrittlement resistance. Therefore, in order to prevent the decrease in hydrogen embrittlement resistance, tempering needs to be performed after quenching.

[3.2. Change in Structure of Material Subjected to Tempering at High Temperature]

[0092] FIG. 2 illustrates a schematic diagram of a change in structure accompanying a heat treatment of a material with a high tempering temperature (Comparative Example 6).

[0093] In the case where the material after quenching is subjected to tempering, the tempering is performed at a temperature of the A_{c1} point or higher and the A_{c3} point or lower. In this temperature range, an austenite phase (γ) and a ferrite phase (α) become stable. Therefore, in the case where the tempering is performed in this temperature range, a part of the fresh martensite α_1' is tempered to be tempered-martensite α_T', and at the same time, another part of α_1' is reverse transformed to be reverse-transformed austenite γ_2.

[0094] In this case, when the tempering temperature becomes too high, a relatively large amount of γ_2 is generated.

[0095] In the retained austenite (γ_1 and γ_2), the austenite stabilization elements such as Ni tends to be concentrated due to diffusion of elements during tempering. However, in the case where a large amount of γ_2 is generated at the time of tempering, the concentrating of the austenite stabilization elements in each retained austenite (γ_1 and γ_2) becomes insufficient.

[0096] As a result, a part of the retained austenite (γ_1 and γ_2) undergoes the martensitic transformation in the cooling process after tempering, and martensite (fresh martensite) α_2' is newly generated. α_2' has high strength but low toughness because α_2' has not undergone tempering. Both the retained austenite (γ_1 and γ_2) in which the austenite stabilization elements are not concentrated and excessive α_2' cause deterioration of hydrogen embrittlement resistance.

[3.3. Change in Structure of Material Subjected to Tempering in Short Time]

[0097] FIG. 3 illustrates a schematic diagram of a change in structure accompanying a heat treatment of a material with a short tempering time (Comparative Example 3).

[0098] In the case where the tempering temperature is relatively low, the generation amount of the reverse-transformed austenite γ_2 is reduced. Accordingly, the generation amount of the fresh martensite α_2' generated in the cooling process after tempering is also reduced. However, in the case where the tempering time is short, the concentrating of the austenite stabilization elements in the retained austenite (γ_1 and γ_2) becomes insufficient. The retained austenite (γ_1 and γ_2) in which the austenite stabilization elements are not concentrated causes deterioration of hydrogen embrittlement resistance.

[3.4. Change in Structure of Material having Inappropriate Components]

[0099] FIG. 4 illustrates a schematic diagram of a change in structure accompanying a heat treatment of a material in which tempering conditions are appropriate but components are inappropriate (Comparative Example 1). Even when the tempering temperature is relatively low, in the case where the austenite stabilization elements (for example, Ni) are excessively contained, a relatively large amount of the reverse-transformed austenite γ_2 is generated during tempering. As a result, even in the case where the tempering is performed for a long time, the concentrating of the austenite stabilization elements in γ_2 becomes insufficient. The retained austenite (γ_1 and γ_2) in which the austenite stabilization elements are not concentrated causes deterioration of hydrogen embrittlement resistance.

[3.5. Change in Structure of Material having Appropriate Tempering Conditions and Components]

[0100] FIG. 5 illustrates a schematic diagram of a change in structure accompanying a heat treatment of a material in which tempering conditions and components are appropriate (Example 1). In the case where the material having appropriate components is subjected to a tempering at a relatively low temperature for a long time, the generation amount of the reverse-transformed austenite γ_2 at the time of tempering can be reduced. In addition, by performing the tempering for a long time, concentrating of austenite stabilization elements in the retained austenite (γ_1 and γ_2) is promoted. As a result, an Ms point and an Mf point of the retained austenite (γ_1 and γ_2) are lowered. Accordingly, the generation amount of the fresh martensite α_2' in the cooling process after tempering is reduced. Further, the strength can be adjusted to 1,500 MPa or less by the tempering, and deterioration of hydrogen embrittlement resistance can be prevented. The Ms point is a temperature at which a martensitic transformation starts in a course of cooling after heat treatment. The Mf point is a temperature at which the martensitic transformation is completed in the course of cooling after heat treatment. The Ms point and Mf point can be determined by measuring the change in volume caused by the change in structure in the course of cooling.

EXAMPLES

(Examples 1 to 19 and Comparative Examples 1 to 7)

[1. Preparation of Sample]

[0101] In a vacuum induction furnace, 50 kg of steel having a composition shown in Table 1 was melted and cast into an ingot. Then, the ingot was subjected to a hot forging, hot rolling, and machining to manufacture a steel bar having a diameter of 30 mm.

[0102] Next, the steel bar was subjected to a quenching, sub-zero treatment, and tempering.

[0103] The quenching was performed by holding the steel bar at 980°C to 1,220°C for 30 minutes, followed by oil cooling. The sub-zero treatment was performed by further holding the quenched steel bar at -30°C for 3 hours.

[0104] Further, the tempering was performed by holding the steel bar after the quenching or after the sub-zero treatment at 300°C to 850°C for 1 minute to 6 hours, followed by water cooling or air cooling. In addition, the tempering was performed twice on some samples.

[Table 1]

	Component (mass%)												
	C	Si	Mn	P	S	Ni	Cr	Nb	N	Mo	Cu	V	B
Ex. 1	0.03	0.18	0.98	0.031	0.016	4.8	15.1	0.05	0.06	0.95	0.21	-	-
Ex. 2	0.03	0.18	0.98	0.031	0.016	4.8	15.1	0.05	0.06	0.95	0.21	-	-
Ex. 3	0.16	0.48	0.72	0.023	0.001	1.8	15.3	0.08	0.04	0.07	0.06	0.09	-
Ex. 4	0.16	0.48	0.72	0.023	0.001	1.8	15.3	0.08	0.04	0.07	0.06	0.09	-
Ex. 5	0.16	0.48	0.72	0.023	0.001	1.8	15.3	0.08	0.04	0.07	0.06	0.09	-
Ex. 6	0.04	0.27	0.87	0.035	0.001	4.3	16.2	0.25	0.03	0.21	3.62	-	0.0016
Ex. 7	0.04	0.27	0.87	0.035	0.001	4.3	16.2	0.25	0.03	0.21	3.62	-	0.0016
Ex. 8	0.04	0.27	0.87	0.035	0.001	4.3	16.2	0.25	0.03	0.21	3.62	-	0.0016
Ex. 9	0.04	0.27	0.87	0.035	0.001	4.3	16.2	0.25	0.03	0.21	3.62	-	0.0016
Ex. 10	0.04	0.27	0.87	0.035	0.001	4.3	16.2	0.25	0.03	0.21	3.62	-	0.0016
Ex. 11	0.04	0.27	0.87	0.035	0.001	4.3	16.2	0.25	0.03	0.21	3.62	-	0.0016
Ex. 12	0.05	0.21	0.21	0.021	0.002	3.1	15.1	0.31	0.04	0.07	3.06	-	0.0009
Ex. 13	0.05	0.21	0.21	0.021	0.002	3.1	15.1	0.31	0.04	0.07	3.06	-	0.0009
Ex. 14	0.05	0.21	0.21	0.021	0.002	3.1	15.1	0.31	0.04	0.07	3.06	-	0.0009
Ex. 15	0.05	0.21	0.21	0.021	0.002	3.1	15.1	0.31	0.04	0.07	3.06	-	0.0009
Ex. 16	0.05	0.21	0.21	0.021	0.002	3.1	15.1	0.31	0.04	0.07	3.06	-	0.0009
Ex. 17	0.10	0.31	0.91	0.015	0.006	5.8	16.3	0.06	0.03	0.81	0.21	-	-
Ex. 18	0.10	0.31	0.91	0.015	0.006	5.8	16.3	0.06	0.03	0.81	0.21	-	-
Ex. 19	0.13	0.42	0.58	0.032	0.025	2.6	16.8	0.08	0.05	-	-	-	-
Comp. Ex. 1	0.05	0.24	0.51	0.012	0.005	6.8	12.8	-	0.03	0.31	0.13	-	0.0005
Comp. Ex. 2	0.24	0.41	0.72	0.034	0.018	0.5	16.4	0.10	0.05	0.11	0.15	0.06	0.0018
Comp. Ex. 3	0.04	0.27	0.87	0.035	0.001	4.3	16.2	0.25	0.03	0.21	3.62	-	0.0016
Comp. Ex. 4	0.04	0.27	0.87	0.035	0.001	4.3	16.2	0.25	0.03	0.21	3.62	-	0.0016
Comp. Ex. 5	0.16	0.48	0.72	0.023	0.001	1.8	15.3	0.08	0.04	0.07	0.06	0.09	-

(continued)

	Component (mass%)												
	C	Si	Mn	P	S	Ni	Cr	Nb	N	Mo	Cu	V	B
Comp. Ex. 6	0.16	0.48	0.72	0.023	0.001	1.8	15.3	0.08	0.04	0.07	0.06	0.09	-
Comp. Ex. 7	0.01	0.42	0.68	0.011	0.004	4.5	14.8	<0.003	0.01	0.87	0.03	0.01	-

	Heat treatment			
	Quenching treatment	Sub-zero treatment	Tempering treatment (1)	Tempering treatment (2)
Ex. 1	980°C/oil cooling	None	600°C × 2h/air cooling	None
Ex. 2	980°C/oil cooling	None	300°C × 6h/air cooling	None
Ex. 3	1,000°C/oil cooling	None	700°C × 30 min/water cooling	None
Ex. 4	1,000°C/oil cooling	None	600°C × 3h/water cooling	None
Ex. 5	1,000°C/oil cooling	None	750°C × 1h/air cooling	600°C × 4h /air cooling
Ex. 6	1,040°C/oil cooling	None	620°C × 4h/air cooling	None
Ex. 7	1,040°C/oil cooling	-30°C	550°C × 4h/air cooling	None
Ex. 8	1,040°C/oil cooling	None	480°C × 1h/air cooling	None
Ex. 9	1,040°C/oil cooling	None	760°C × 30 min/air cooling	625°C × 4h /air cooling
Ex. 10	1,150°C/oil cooling	None	550°C × 4h/air cooling	None
Ex. 11	1,100°C/oil cooling	None	550°C × 4h/air cooling	None
Ex. 12	1,040°C/oil cooling	None	620°C × 4h/air cooling	None
Ex. 13	1,040°C/oil cooling	None	580°C × 4h/air cooling	None
Ex. 14	1,040°C/oil cooling	None	550°C × 4h/air cooling	None
Ex. 15	1,040°C/oil cooling	None	480°C × 1h/air cooling	None
Ex. 16	1,040°C/oil cooling	None	760°C × 1h/air cooling	625°C × 4h /air cooling
Ex. 17	1,000°C/oil cooling	None	630°C × 2h/air cooling	None
Ex. 18	1,000°C/oil cooling	None	800°C × 30 min/air cooling	600°C × 4h /air cooling
Ex. 19	1,000°C/oil cooling	None	750°C × 1h/air cooling	None

(continued)

	Heat treatment			
	Quenching treatment	Sub-zero treatment	Tempering treatment (1)	Tempering treatment (2)
Comp. Ex. 1	1,000°C/oil cooling	None	700°C × 4h/water cooling	None
Comp. Ex. 2	1,000°C/oil cooling	None	500°C/water cooling	None
Comp. Ex. 3	1,040°C/oil cooling	None	650°C × 1 min/air cooling	None
Comp. Ex. 4	1,220°C/oil cooling	None	550°C × 4h/air cooling	None
Comp. Ex. 5	1,000°C/oil cooling	None	None	None
Comp. Ex. 6	1,000°C/oil cooling	None	850°C × 1h/air cooling	None
Comp. Ex. 7	1,000°C/oil cooling	None	600°C × 3h/water cooling	None

[2. Test Method]

[2.1. Amount of Retained Austenite]

[0105] The steel bar after the quenching or after the sub-zero treatment was subjected to an X-ray diffraction measurement using a Mo tube. Next, the amount of retained austenite (vol%) was calculated by using a "5-peak method". The "5-peak method" refers to a method of calculating the amount of retained austenite (vol%) by using peak intensities of (200) and (211) of a ferrite phase and peak intensities of (200), (220), and (311) of an austenite phase, appearing in an X-ray profile.

[2.2. Crystal Grain Size of Prior Austenite Grain]

[0106] The crystal grain size of a prior austenite grain of the steel bar after the tempering was measured. The crystal grain size was measured in accordance with JIS G 0551:2020.

[2.3. Presence or Absence of Concentrating of Ni]

[0107] Element mapping was performed by using a STEM to evaluate presence or absence of the concentrating of Ni. FIG. 6A and FIG. 6B show examples of element mapping of Ni.

[2.4. Slow Strain Rate Tensile (SSRT) Test]

[0108] A tensile test piece was sampled from the steel bar after the tempering and subjected to a slow strain rate tensile (SSRT) test. A round bar test piece having a parallel portion diameter of 6 mm was used as the tensile test piece. The strain rate thereof was 5×10^{-5}/s. The test temperature thereof was normal temperature (25°C). The test atmosphere thereof was the atmosphere, hydrogen gas of 0.7 MPa, or hydrogen gas of 90 MPa. Based on the obtained stress-displacement diagram, presence or absence of a local maximum was evaluated, and $D_{H2(0.7)}/D_{air}$ and $D_{H2(90)}/D_{air}$ were calculated.

[0109] FIG. 7A shows an example of a stress-displacement curve in a slow strain rate tensile (SSRT) test of a steel material having a poor hydrogen embrittlement resistance. FIG. 7B shows an example of a stress-displacement curve in a slow strain rate tensile (SSRT) test of a steel material having an excellent hydrogen embrittlement resistance. The fact that stress does not show a local maximum in the stress-displacement curve indicates that the steel material has a poor ductility. On the other hand, the fact that stress shows a local maximum in the stress-displacement curve indicates that the steel material has a high ductility. Further, in the stress-displacement curve of the SSRT test performed in a hydrogen atmosphere, the fact that stress shows a local maximum indicates that the steel material is excellent in the hydrogen embrittlement resistance.

[2.5. Tensile Test]

[0110] A tensile test piece was sampled from the steel bar after the tempering and subjected to the slow strain rate tensile test. A round bar test piece having a parallel portion diameter of 6 mm was used as the tensile test piece. The strain rate thereof was 5×10^{-5}/s. The test temperature thereof was normal temperature (25°C). The test atmosphere thereof was the atmosphere. The tensile strength was calculated by dividing the maximum value of the stress by an area of the parallel portion.

[3. Results]

[0111] Results are shown in Table 2. The followings can be understood from Table 2.

[0112] Regarding the concentrating of Ni, "A" indicates that the concentrating of Ni was recognized, and "B" indicates that the concentrating of Ni was not recognized.

[0113] Regarding SSRT, "A" represents $D_{H2}/D_{air} \geq 0.9$, "B" represents $0.8 \leq D_{H2}/D_{air} < 0.9$, and "C" represents $D_{H2}/D_{air} < 0.8$.

[0114] Regarding the tensile strength, "A" indicates that the tensile strength was 540 MPa or more and 1,500 MPa or less, and "B" indicates that the tensile strength was more than 1,500 MPa.

(1) In Comparative Example 1, D_{H2}/D_{air} was less than 0.8. This is considered to be because Ni was excessive.
(2) In Comparative Example 2, D_{H2}/D_{air} was less than 0.8. This is considered to be because although the concentrating of Ni in the retained austenite (γ_1 and γ_2) was recognized, the concentrating of Ni was not sufficient since the

amount of Ni was small.

(3) In Comparative Example 3, D_{H2}/D_{air} was less than 0.8. This is considered to be because the final tempering time was too short, and thus the diffusion and concentrating of the austenite stabilization elements into the retained austenite (γ_1 and γ_2) were insufficient.

(4) In Comparative Example 4, D_{H2}/D_{air} was less than 0.8. This is considered to be because the quenching temperature was too high, and thus the crystal grains were coarsened.

(5) In Comparative Example 5, D_{H2}/D_{air} was less than 0.8. This is considered to be because the tempering was not performed.

(6) In Comparative Example 6, D_{H2}/D_{air} was less than 0.8. This is considered to be because the tempering temperature was too high, and thus a large amount of the fresh martensite α_2' was generated in the cooling process after tempering.

(7) In Comparative Example 7, D_{H2}/D_{air} was less than 0.8. This is considered to be because the amount of C and the amount of Nb were small, and thus pinning did not work and the crystal grains were coarsened.

(8) In each of Examples 1 to 9, $D_{H2(0.7)}/D_{air}$ was 0.9 or more.

(9) In Examples 6 and 9, $D_{H2(90)}/D_{air}$ was less than 0.8. This is considered to be because the amount of retained austenite was slightly large.

(10) In Examples 10 and 11, $D_{H2(90)}/D_{air}$ was less than 0.8. This is considered to be because the crystal grain size number of the prior austenite grain was slightly small (the crystal grain size of the prior austenite grain was slightly large).

[Table 2]

	Structure			Properties		
	Crystal grain size	Retained γ	Concentrating of Ni	SSRT (D_{H2}/D_{air})		Tensile strength
				In H_2 gas of 0.7 MPa	In H_2 gas of 90 MPa	
Ex. 1	#7.8	9.5%	A	A	A	A
Ex. 2	#6.4	5.4%	A	A	B	A
Ex. 3	#9.8	6.6%	A	A	A	A
Ex. 4	#8.9	5.8%	A	A	A	A
Ex. 5	#9.5	6.2%	A	A	A	A
Ex. 6	#4.8	28.9%	A	A	C	A
Ex. 7	#5.0	11.1%	A	A	B	A
Ex. 8	#5.2	8.4%	A	A	B	A
Ex. 9	#5.2	26.5%	A	A	C	A
Ex. 10	#2.5	12.1%	A	A	C	A
Ex. 11	#3.8	9.8%	A	A	C	A
Ex. 12	#5.8	7.3%	A	A	A	A
Ex. 13	#5.9	4.4%	A	A	A	A
Ex. 14	#5.3	1.6%	A	A	A	A
Ex. 15	#5.2	1.1%	A	A	A	A
Ex. 16	#5.6	7.7%	A	A	A	A
Ex. 17	#6.9	31.4%	A	A	C	A
Ex. 18	#7.0	6.4%	A	A	A	A
Ex. 19	#6.9	6.8%	A	A	A	A
Comp. Ex. 1	#4.2	42.4%	A	C	C	A

(continued)

	Structure			Properties		
				SSRT (D_{H2}/D_{air})		
	Crystal grain size	Retained γ	Concentrating of Ni	In H_2 gas of 0.7 MPa	In H_2 gas of 90 MPa	Tensile strength
Comp. Ex. 2	#8.6	0.8%	A	C	C	A
Comp. Ex. 3	#4.6	9.8%	B	C	C	A
Comp. Ex. 4	#1.8	11.7%	A	C	C	A
Comp. Ex. 5	#7.1	4.9%	B	C	C	B
Comp. Ex. 6	#7.3	2.3%	A	C	C	A
Comp. Ex. 7	#1.7	7.1%	A	C	C	A

[0115] Although the embodiments of the present invention have been described in detail above, the present invention is not limited to the above embodiments, and various modifications can be made without departing from the gist of the present invention.

[0116] The present application is based on Japanese patent application No. 2023-023052 filed on February 17, 2023, and the contents thereof are incorporated herein by reference.

INDUSTRIAL APPLICABILITY

[0117] The martensitic stainless steel for a hydrogen gas environment according to the present invention can be used as a structural member used in a high-pressure hydrogen gas device.

Claims

1. A martensitic stainless steel for a hydrogen gas environment,

having a composition consisting of:

$$0.02 \text{ mass\%} \leq C \leq 0.30 \text{ mass\%},$$

$$Si \leq 1.50 \text{ mass\%},$$

$$Mn \leq 1.50 \text{ mass\%},$$

$$P \leq 0.150 \text{ mass\%},$$

$$S \leq 0.150 \text{ mass\%},$$

$$8.0 \text{ mass\%} \leq Cr \leq 22.0 \text{ mass\%},$$

$$1.0 \text{ mass\%} \leq \text{Ni} \leq 6.0 \text{ mass\%},$$

$$0.01 \text{ mass\%} \leq \text{Nb} \leq 1.0 \text{ mass\%},$$

and

$$\text{N} \leq 0.12 \text{ mass\%},$$

and

optionally at least one selected from the group consisting of:

$$\text{Cu} \leq 6.00 \text{ mass\%},$$

$$\text{Mo} \leq 3.00 \text{ mass\%},$$

$$\text{V} \leq 1.50 \text{ mass\%},$$

and

$$\text{B} \leq 0.0500 \text{ mass\%},$$

with the balance being Fe and inevitable impurities;

having:

a crystal grain size number of prior austenite grains of 2.0 or more,
an amount of retained austenite of 40 vol% or less,
a tensile strength of 1,500 MPa or less, and

satisfying the following formula (1):

$$D_{H2(0.7)}/D_{air} \geq 0.8 \qquad (1)$$

here, D_{air} represents a displacement at a time point when stress shows a local maximum in a stress-displacement curve obtained by performing a tensile test under a condition of a strain rate of 5×10^{-5}/s in the atmosphere at normal temperature (25°C), and
$D_{H2(0.7)}$ represents a displacement at a time point when stress shows a local maximum or a maximum value in a stress-displacement curve obtained by performing a tensile test under a condition of a strain rate of 5×10^{-5}/s in hydrogen gas of 0.7 MPa at normal temperature (25°C).

2. The martensitic stainless steel for a hydrogen gas environment according to claim 1, wherein the composition further satisfies:

$$0.01 \text{ mass \%} \leq \text{Cu} \leq 6.00 \text{ mass\%}.$$

3. The martensitic stainless steel for a hydrogen gas environment according to claim 1 or 2, wherein the composition further satisfies at least one selected from the group consisting of:

$$0.01\ \text{mass\%} \leq \text{Mo} \leq 3.00\ \text{mass\%},$$

$$0.01\ \text{mass\%} \leq \text{V} \leq 1.50\ \text{mass\%},$$

and

$$0.0001\ \text{mass\%} \leq \text{B} \leq 0.0500\ \text{mass\%}.$$

4. A manufacturing method for a martensitic stainless steel for a hydrogen gas environment, comprising:

a first step of manufacturing a material consisting of:

$$0.02\ \text{mass\%} \leq \text{C} \leq 0.30\ \text{mass\%},$$

$$\text{Si} \leq 1.50\ \text{mass\%},$$

$$\text{Mn} \leq 1.50\ \text{mass\%},$$

$$\text{P} \leq 0.150\ \text{mass\%},$$

$$\text{S} \leq 0.150\ \text{mass\%},$$

$$8.0\ \text{mass\%} \leq \text{Cr} \leq 22.0\ \text{mass\%},$$

$$1.0\ \text{mass\%} \leq \text{Ni} \leq 6.0\ \text{mass\%},$$

$$0.01\ \text{mass\%} \leq \text{Nb} \leq 1.0\ \text{mass\%},$$

and

$$\text{N} \leq 0.12\ \text{mass\%},$$

and

optionally at least one selected from the group consisting of:

$$\text{Cu} \leq 6.00\ \text{mass\%},$$

$$\text{Mo} \leq 3.00\ \text{mass\%},$$

$$\text{V} \leq 1.50\ \text{mass\%},$$

and

$$B \leq 0.0500 \text{ mass\%},$$

with the balance being Fe and inevitable impurities;

a second step of subjecting the material to a quenching from a temperature equal to or higher than an A_{c3} point and lower than a solidus temperature, or further performing a sub-zero treatment on the material after the quenching, and
a third step of subjecting the material after the quenching or after the sub-zero treatment to a tempering one or more times under conditions of a final tempering temperature of 200°C or higher and 800°C or lower and a final tempering time of 10 minutes or more and 24 hours or less to obtain the martensitic stainless steel for a hydrogen gas environment according to any one of Claims 1 to 3.

5. Use of the martensitic stainless steel for a hydrogen gas environment according to any one of Claims 1 to 3, or of the martensitic stainless steel for a hydrogen gas environment manufactured according to Claim 4, for a structural member.

6. A structural member made of the martensitic stainless steel for a hydrogen gas environment according to any one of Claims 1 to 3, or of the martensitic stainless steel for a hydrogen gas environment manufactured according to Claim 4.

7. Use of the structural member according to claim 5 or 6 for a high-pressure hydrogen gas device.

8. A high-pressure hydrogen gas device comprising the structural member according to claim 6.

9. The high-pressure hydrogen gas device according to claim 8, being a fuel cell.

10. A fuel-cell vehicle, FCV, comprising the fuel cell according to claim 9.

FIG. 1

COMPARATIVE EXAMPLE 5

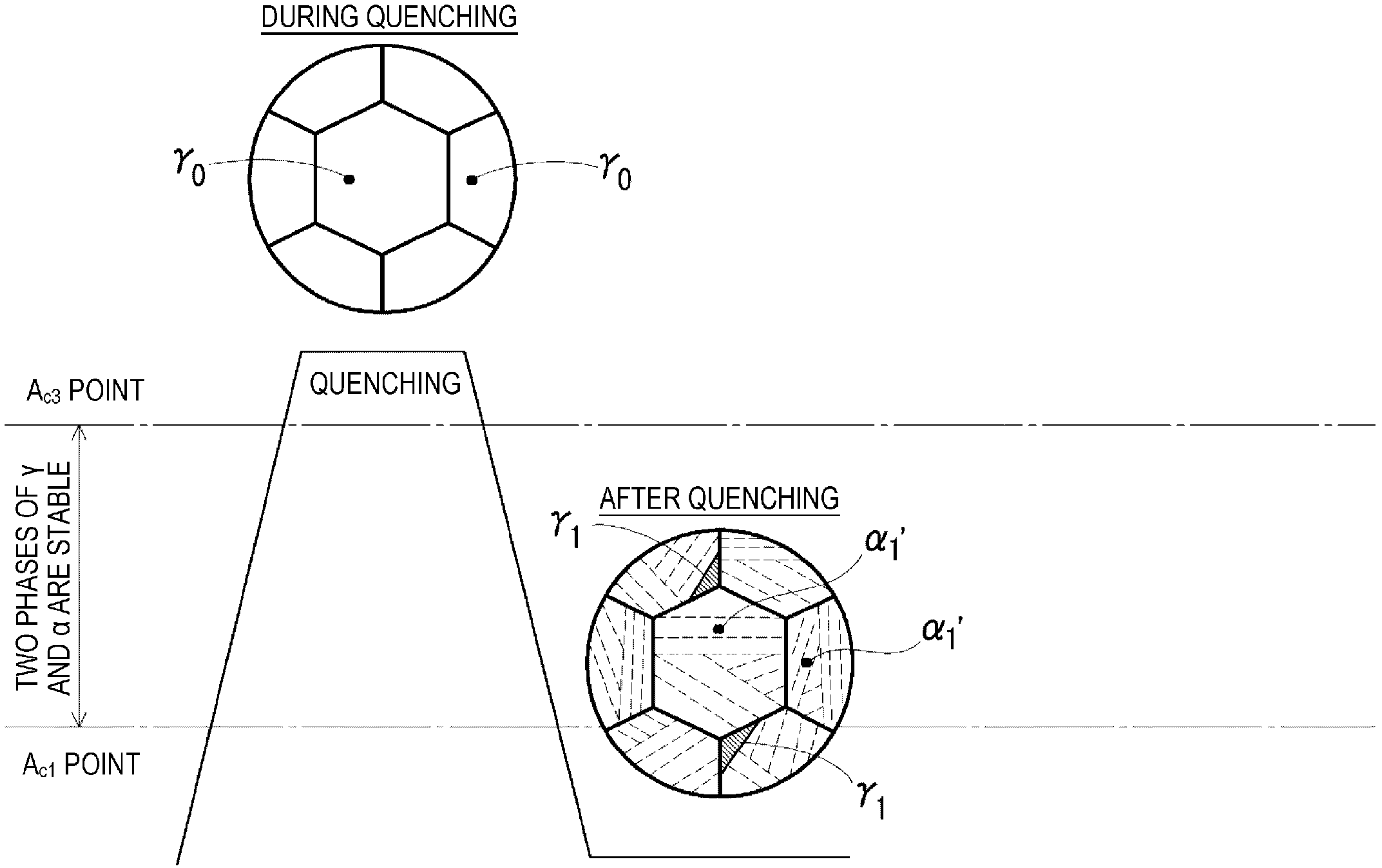


FIG. 2

COMPARATIVE EXAMPLE 6

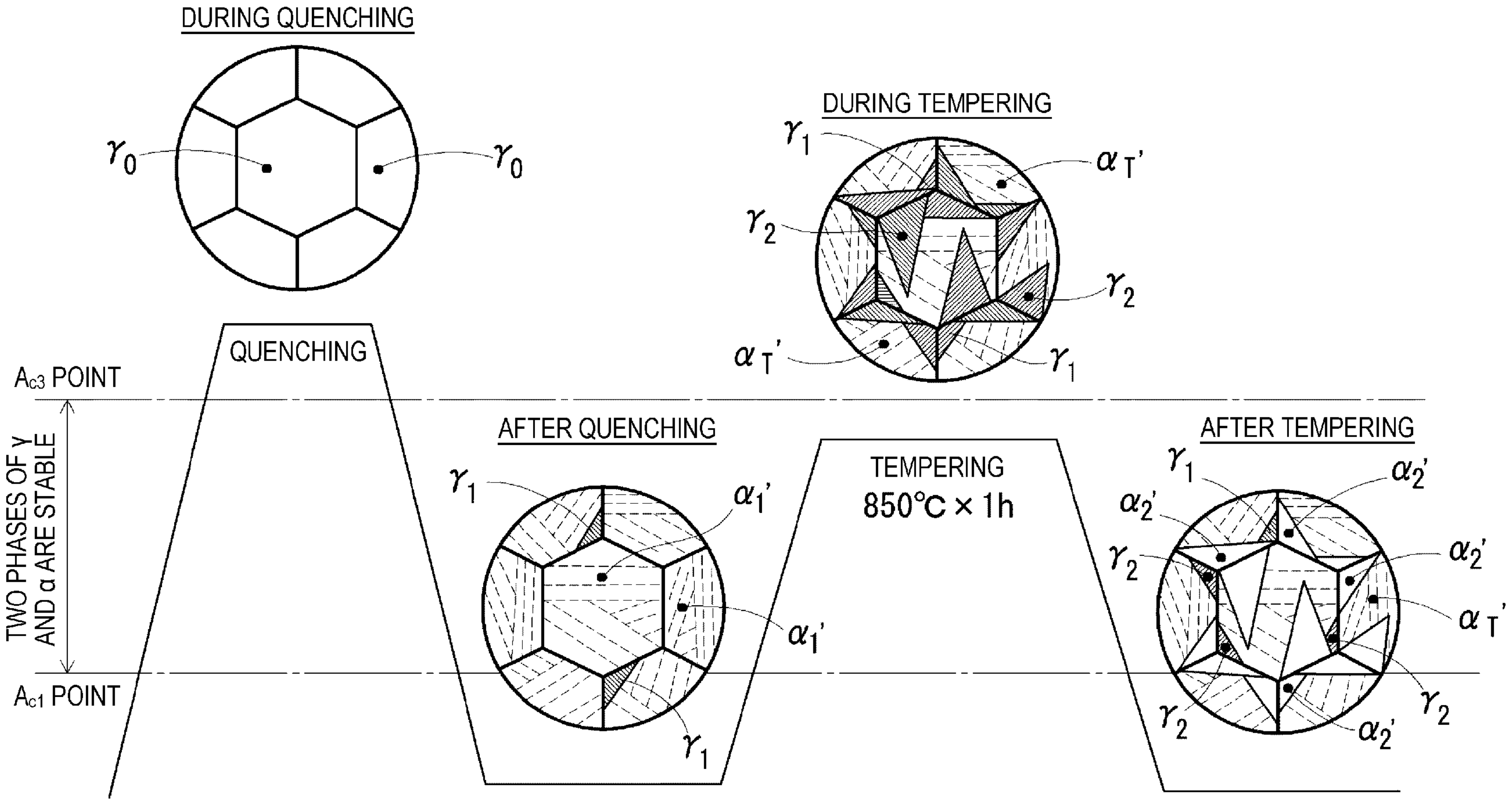


FIG. 3

COMPARATIVE EXAMPLE 3

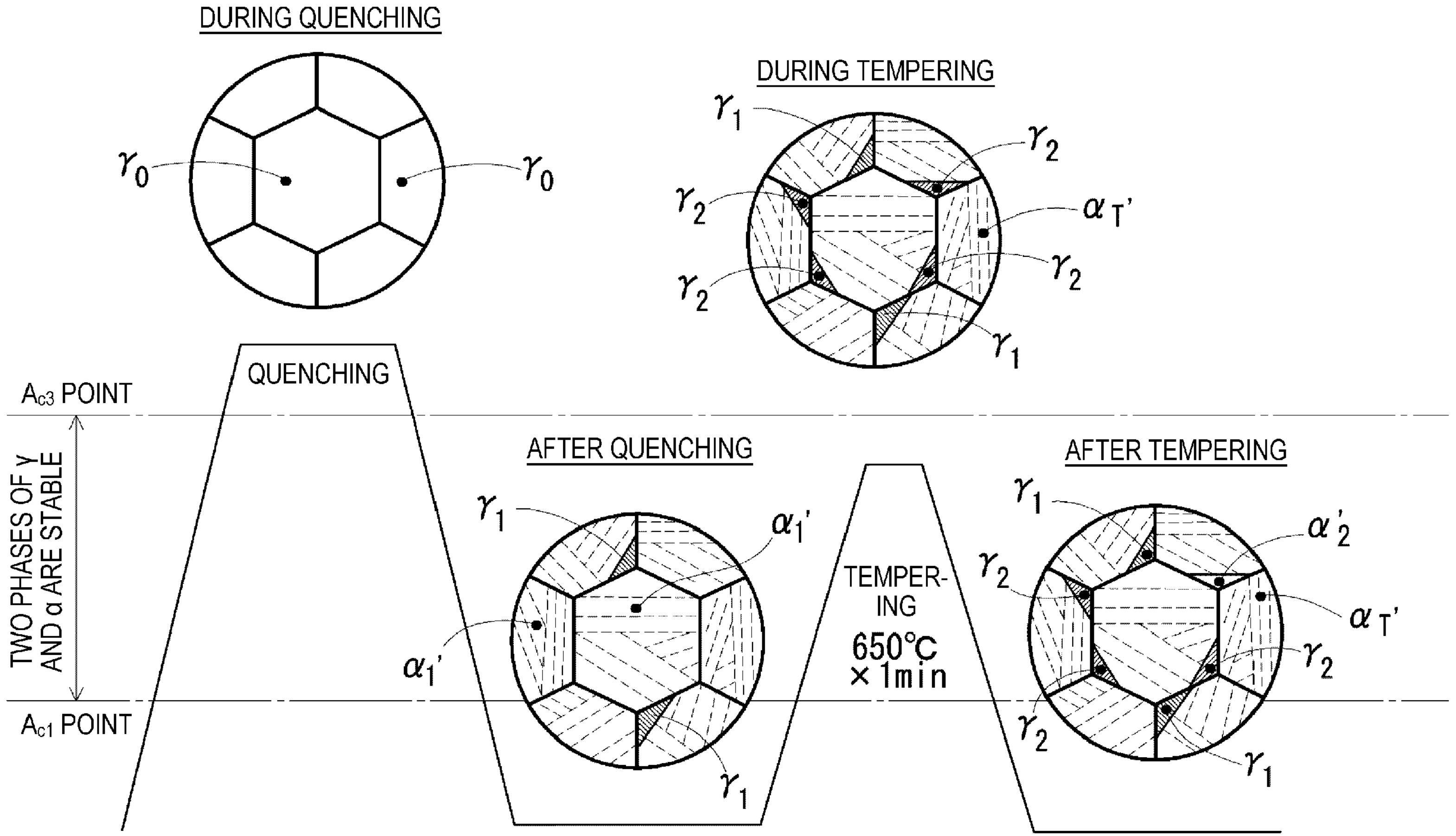


FIG. 4

COMPARATIVE EXAMPLE 1

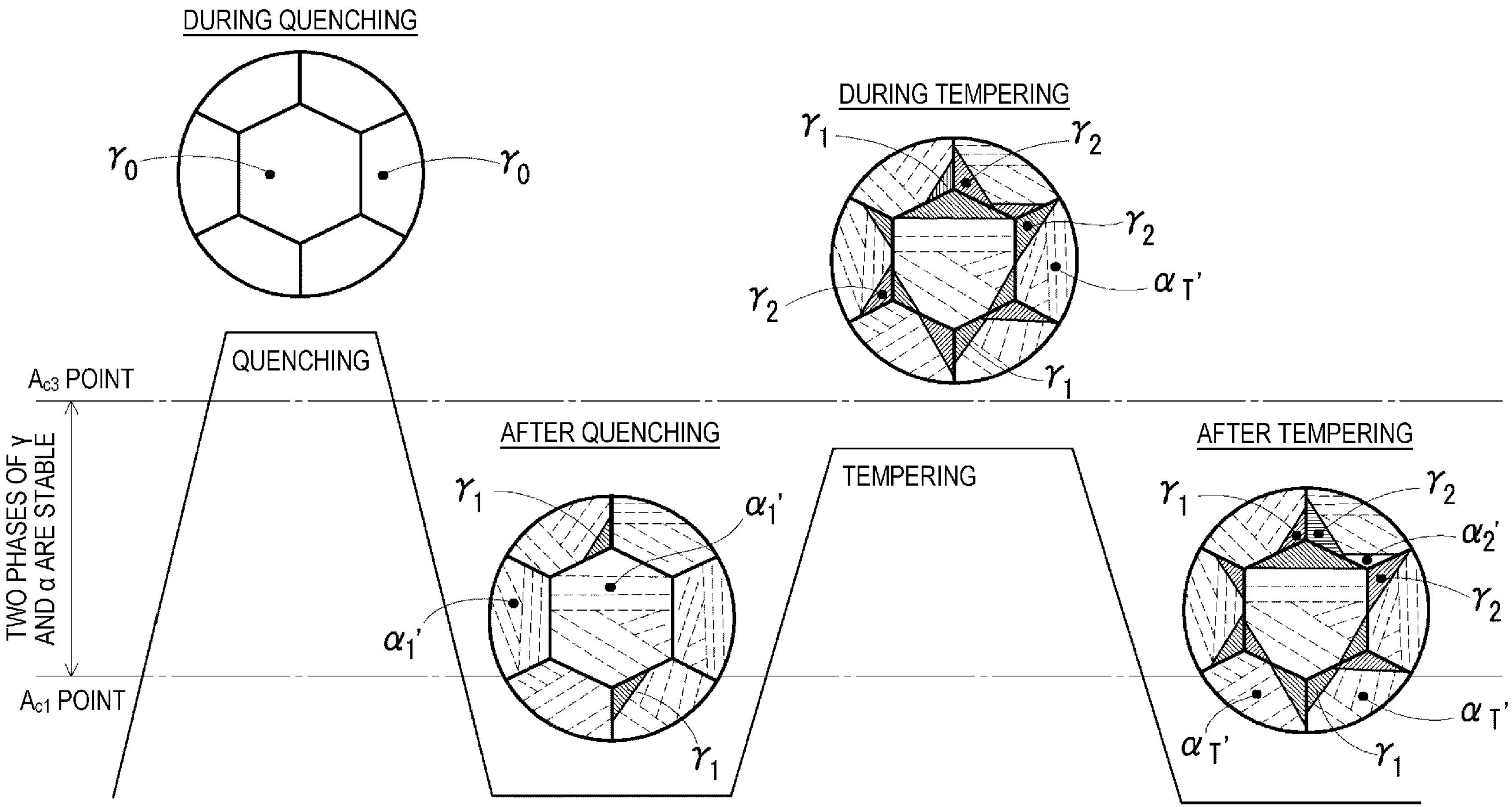


FIG. 5

EXAMPLE 1

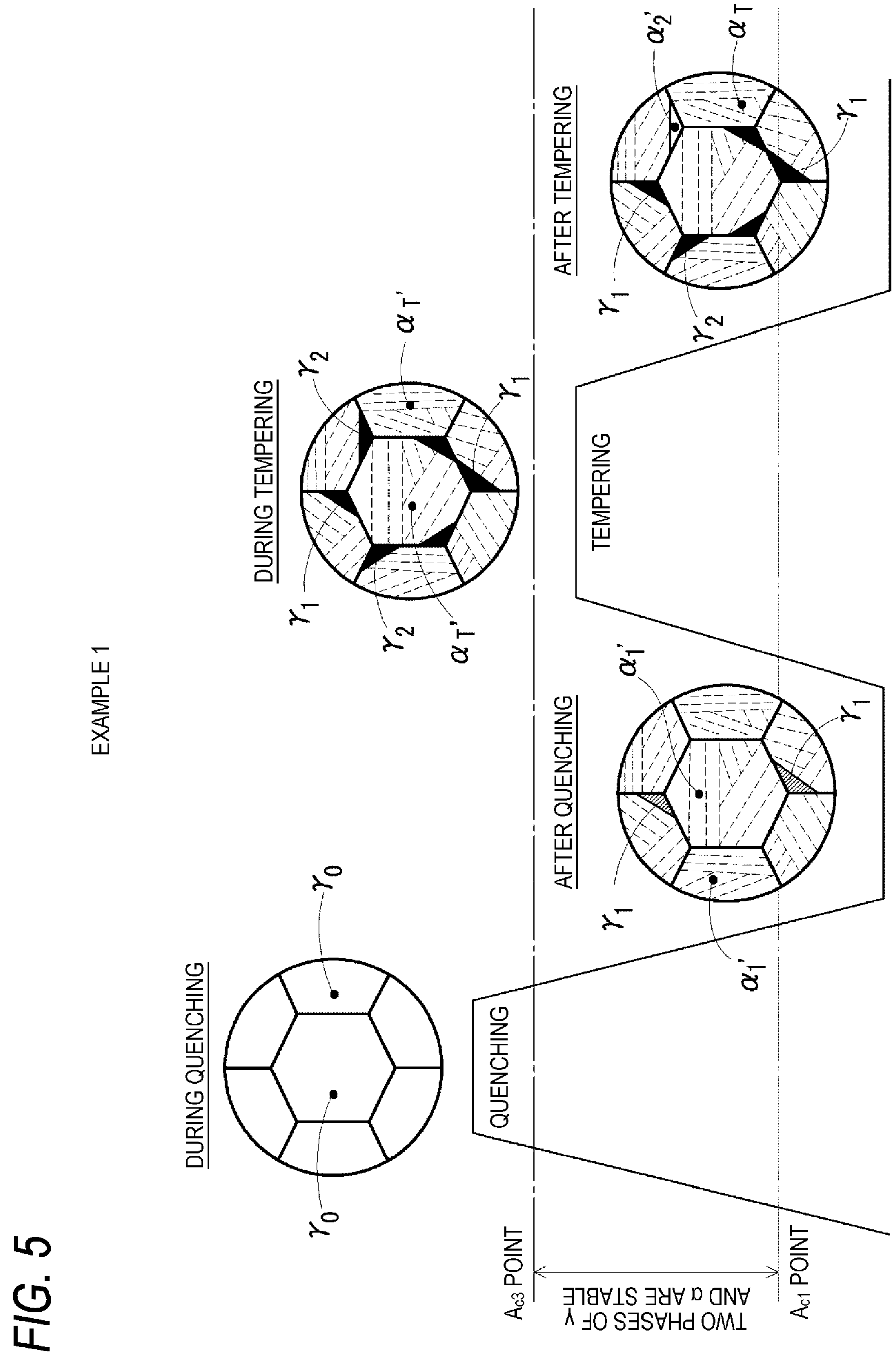


FIG. 6A

EXAMPLE 1

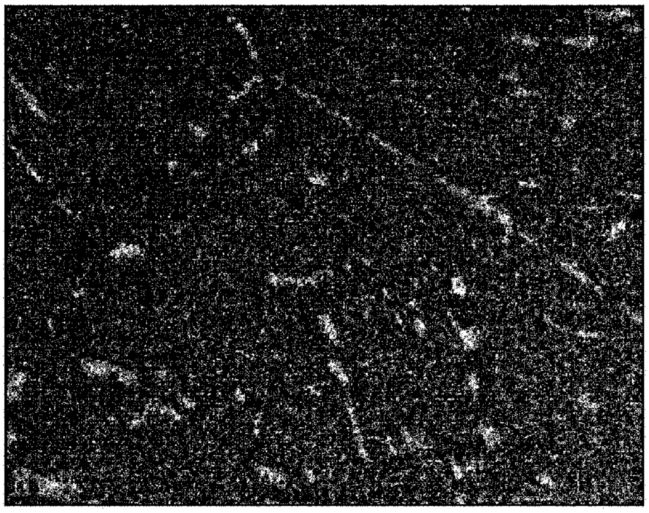


FIG. 6B

COMPARATIVE EXAMPLE 5

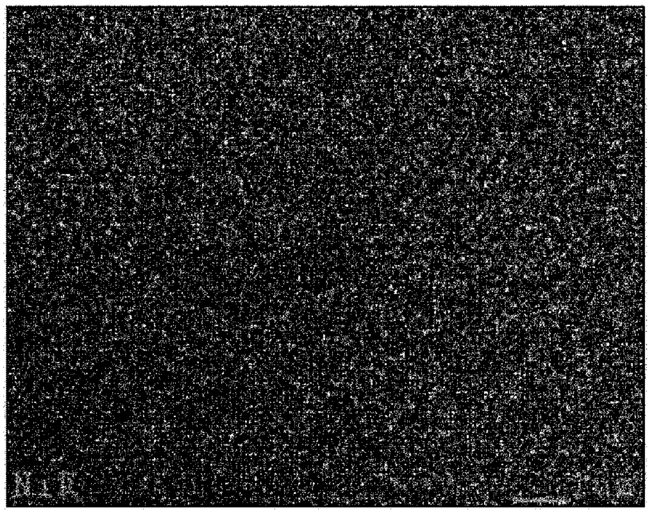


FIG. 7A

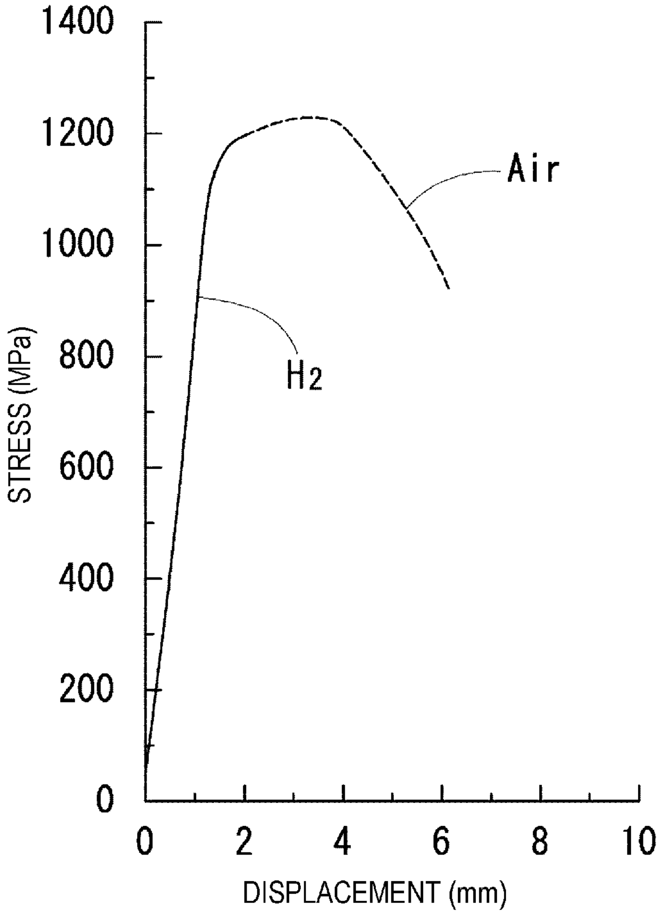
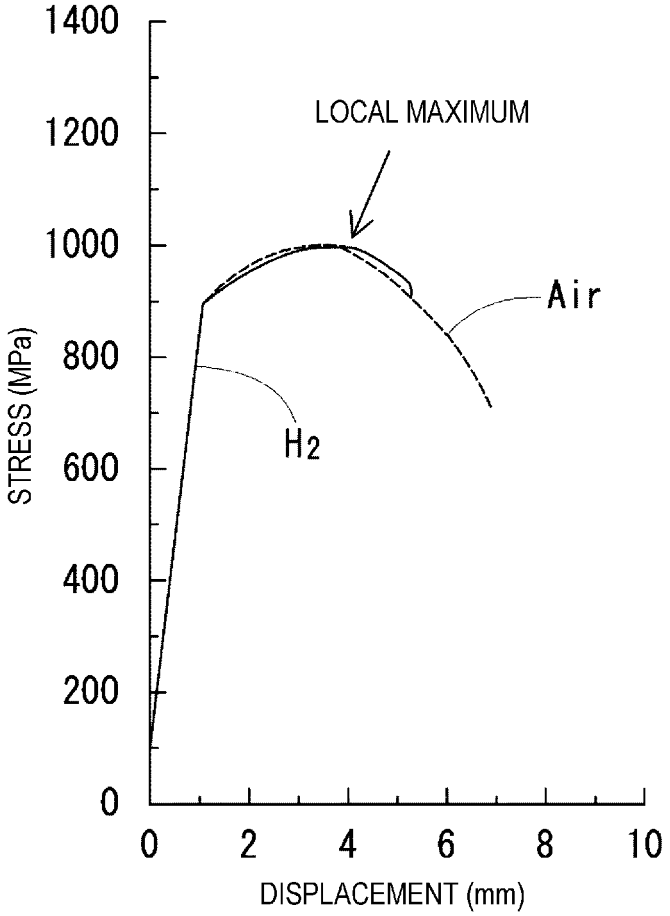

1400
1200
1000
800
600
400
200
0
STRESS (MPa)
0
2
4
6
8
10
DISPLACEMENT (mm)
Air
H2

FIG. 7B


LOCAL MAXIMUM
Air
H₂
STRESS (MPa)
1400
1200
1000
800
600
400
200
0
0
2
4
6
8
10
DISPLACEMENT (mm)

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EUROPEAN SEARCH REPORT

Application Number
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1

Place of search	Date of completion of the search	Examiner
The Hague	2 July 2024	Vlassi, Eleni

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