

(19)



(11)

EP 3 643 803 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

29.04.2020 Bulletin 2020/18

(51) Int Cl.:

C22C 38/00 ^(2006.01) **C21D 1/06** ^(2006.01)
C22C 38/38 ^(2006.01) **C22C 38/58** ^(2006.01)
C21D 8/06 ^(2006.01)

(21) Application number: **18820105.7**

(22) Date of filing: **22.06.2018**

(86) International application number:

PCT/JP2018/023905

(87) International publication number:

WO 2018/235962 (27.12.2018 Gazette 2018/52)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

(72) Inventors:

- **YAMASAKI, Shingo**
Tokyo 100-8071 (JP)
- **MANABE, Toshiyuki**
Tokyo 100-8071 (JP)

(74) Representative: **Vossius & Partner**

Patentanwälte Rechtsanwälte mbB
Siebertstrasse 3
81675 München (DE)

(30) Priority: **23.06.2017 JP 2017123347**

(71) Applicant: **Nippon Steel Corporation**
Tokyo 1008071 (JP)

(54) **HIGH-STRENGTH STEEL MEMBER**

(57) A high-strength steel member having a predetermined chemical composition, having a tensile strength of 1,000 MPa or higher, containing 0.10% or more of, in terms of percent (%) by area, at least one Ti precipitate that has an average size of from 30 to 200 nm in terms of an average equivalent circle diameter and is selected

from the group consisting of a Ti carbide, a Ti nitride, and a composite compound thereof, at a location of 1 mm in depth from a surface of the steel member, and containing 0.5 ppm by mass or more of non-diffusible hydrogen that is released in a temperature range of from 400 to 800°C in a thermal desorption hydrogen analysis.

EP 3 643 803 A1

Description

Technical Field

5 **[0001]** The present disclosure relates to a high-strength steel member.

Background Art

10 **[0002]** Among steel members used for machines, automobiles, bridges, or buildings, steel members that are required to have particularly high strength are, for example, those in which chromium steels or chromium-molybdenum steels defined in JIS G 4104 or JIS G 4105 have been subjected to a quenching/tempering treatment. Some steel members, such as gears, are carburized and then quenched to have high strength.

15 **[0003]** Quenching is made after heating steel members to high temperatures at which austenite phases are formed. However, absorption of hydrogen into steel members from atmosphere during heating may cause quenching crack after quenching. Further, for example, a low tempering temperature of from 150 to 200°C as in the case of high-strength steel members may cause deterioration in ductility or toughness after tempering, since hydrogen absorbed into the steel members during quenching is not sufficiently released by the tempering.

20 **[0004]** With regard to hydrogen embrittlement resistance of high-strength steel members (steel members having tensile strengths of 1,000 MPa or higher), for example, Patent Literature 1 describes that adding V, Nb and Ti to steel to refine a prior austenite grain is effective for improvement in delayed fracture resistance.

[0005] Patent Literatures 2 to 4 each describe a technique of dispersing, in steel, a fine precipitate that exhibits a hydrogen trapping ability by high-temperature tempering after quenching, to improve delayed fracture resistance.

[0006]

25 Patent Literature 1: Japanese Patent Application Laid-Open (JP-A) No. H03-243745

Patent Literature 2: JP-A No. 2000-26934

Patent Literature 3: JP-A No. 2006-45670

Patent Literature 4: JP-A No. 2001-288539

30 SUMMARY OF INVENTION

Technical Problem

35 **[0007]** However, the conventional techniques described in Patent Literatures 1 to 4 and the like have a limitation to fundamental improvement in delayed fracture resistance of, for example, high-strength steel members that are subjected to low-temperature tempering at from 150 to 200°C after quenching.

[0008] An object in one aspect of the present disclosure is to provide a high-strength steel member excellent in delayed fracture resistance, which is one kind of hydrogen embrittlement resistance.

40 Solution to Problem

[0009] Solutions for achieving the object in one aspect of the present disclosure include the following aspects.

<1> A high-strength steel member having a chemical composition of, in terms of percent (%) by mass:

45 C: from 0.10 to 0.50%,
Si: from 0.02 to 2.00%,
Mn: from 0.05 to 2.00%,
Cr: from 0.10 to 2.00%,
50 Ti: from 0.20 to 1.00%,
N: from 0.0020 to 0.0250%,
Al: from 0 to 0.100%,
V: from 0 to 0.50%,
Nb: from 0 to 0.50%,
55 Mo: from 0 to 1.00%,
B: from 0 to 0.0100%,
Cu: from 0 to 2.00%,
Ni: from 0 to 3.00%, and

a balance consisting of Fe and impurities,
 having a tensile strength of 1,000 MPa or higher,
 containing 0.10% or more of, in terms of percent (%) by area, at least one Ti precipitate that has an average
 size of from 30 to 200 nm in terms of an average equivalent circle diameter and is selected from the group
 consisting of a Ti carbide, a Ti nitride, and a composite compound thereof, at a location of 1 mm in depth from
 a surface of the steel member, and
 containing 0.5 ppm by mass or more of non-diffusible hydrogen that is released in a temperature range of from
 400 to 800°C in a thermal desorption hydrogen analysis.

<2> The high-strength steel member according to <1>, having a chemical composition including, in terms of percent
 (%) by mass, one or more of

Al: from 0.005 to 0.100%,

V: from 0.01 to 0.50%,

Nb: from 0.01 to 0.50%, or

Mo: from 0.01 to 1.00%.

<3> The high-strength steel member according to <1> or <2>, having a chemical composition including, in terms of
 percent (%) by mass,

B: from 0.0003 to 0.0100%.

<4> The high-strength steel member according to any one of <1> to <3>, having a chemical composition including,
 in terms of percent (%) by mass,

one or both of Cu: from 0.05 to 2.00% or Ni: from 0.05 to 3.00%.

<5> The high-strength steel member according to any one of <1> to <4>, wherein the Ti precipitate has an average
 aspect ratio of from 1.0 to 3.0.

Advantageous Effect of Invention

[0010] According to one aspect of the present disclosure, a high-strength steel member excellent in delayed fracture
 resistance, which is one kind of hydrogen embrittlement resistance, can be provided.

BRIEF DESCRIPTION OF DRAWING

[0011] Fig. 1 shows a schematic view for describing, in a case in which a measurement object is larger than a "round
 rod steel having a size of 10 mm in diameter $\phi \times 50$ mm in length L", an extraction location of a test piece when a test
 piece for measurement of a content of non-diffusible hydrogen is extracted from the measurement object.

DESCRIPTION OF EMBODIMENTS

[0012] Hereinafter, an embodiment that is an example of the present disclosure will be specifically described.

[0013] In the present description, a numerical value range represented by "(from)...to..." means a range that encom-
 passes respective numerical values indicated before and after "to" as a lower limit value and an upper limit value.

[0014] A content of each element in a chemical composition is expressed as an element amount (for example, a C
 amount, a Si amount).

[0015] The indication "%" with respect to the content of each element in a chemical composition means "percent (%)
 by mass".

[0016] A high-strength steel member according to the present embodiment (hereinafter, also simply referred to as
 "steel member") is a steel member having a predetermined chemical composition and having a tensile strength of 1,000
 MPa or higher. The tensile strength of the steel member is a value obtained by measurement according to JIS-Z 2241
 (2015).

[0017] The steel member according to the present embodiment contains 0.10% or more of, in terms of percent (%)
 by area, at least one Ti precipitate that has an average size of from 30 to 200 nm in terms of an average equivalent
 circle diameter and is selected from the group consisting of a Ti carbide, a Ti nitride, and a composite compound thereof,
 at a location of 1 mm in depth from a surface of the steel member, and contains 0.5 ppm by mass or more of non-
 diffusible hydrogen that is released in a range of from 400 to 800°C in a thermal desorption hydrogen analysis.

[0018] The steel member according to the present embodiment has the configuration described above and thus is a
 high-strength steel member excellent in delayed fracture resistance, which is one kind of hydrogen embrittlement re-
 sistance. The steel member according to the present embodiment has been found as follows.

[0019] The inventors have specifically analyzed a delayed fracture behavior, which is one kind of hydrogen embrittle-
 ment phenomenon, using various strength of steel members that are produced by quenching/tempering treatments.

[0020] It has been already found that, of hydrogen that has been absorbed from an external environment into a steel member, diffusible hydrogen that diffuses in the steel member at room temperature particularly causes delayed fracture. The diffusible hydrogen can be measured from a curve having a peak at a temperature of about 100°C in a "curve representing the relationship between the temperature and the rate of hydrogen release from a steel member" obtained

by heating the steel member at a rate of 100°C/hour.

[0021] Accordingly, if hydrogen that has been absorbed from an external environment is trapped at some portion in a steel member so as not to be diffused, it is possible to render hydrogen harmless and delayed fracture due to absorbed hydrogen is suppressed.

[0022] The presence of a trapping site of hydrogen (hereinafter, also referred to as "hydrogen-trapping site") can be confirmed by comparing peak temperatures and peak heights of hydrogen release curves obtained by heating, at 100°C/hour, a steel member before charging with hydrogen and a steel member after charging with hydrogen, respectively. The amount of hydrogen trapped in a certain hydrogen-trapping site (hereinafter, also referred to as "hydrogen trapping capacity") can be determined by an area integral value of the peak.

[0023] The inventors have performed the following evaluation with respect to delayed fracture resistance of a steel member that has been subjected to low-temperature tempering at from 150 to 200°C after quenching. A test piece of a circularly notched rod steel having a diameter of 10 mm is heated for 20 minutes in an atmosphere of 1 atm containing from 30 to 100% of hydrogen, quenched by cooling with water, and thereafter tempered at 150°C for 30 minutes. A constant load (90% relative to tensile strength) is applied to the test piece in the air and a time is measured until rupture is caused, thereby evaluating delayed fracture resistance. A longer rupture time means that the steel member is more favorable in delayed fracture resistance.

[0024] As a result, the inventors have found that a steel member having a steel structure containing 0.10% or more of, in terms of percent (%) by area, at least one Ti precipitate that has an average grain size of from 30 to 200 nm and is selected from the group consisting of a Ti carbide, a Ti nitride, and a composite compound thereof, at a location of 1 mm in depth from a surface of the steel member is excellent in delayed fracture resistance.

[0025] The steel member that has such a steel structure and is excellent in delayed fracture resistance exhibits, in a temperature range of from 400 to 800°C, a hydrogen release peak which indicates that hydrogen stably trapped in a hydrogen-trapping site consisting of the Ti precipitate described above has been released, in the case of performing a thermal desorption hydrogen analysis at a rate of 100°C/hour after the heat treatment under the conditions described above. The amount of hydrogen that is released (hydrogen trapping capacity) is 0.5 ppm by mass or more.

[0026] The inventors have made investigation by comparison with the "technique of dispersing, in steel, a fine precipitate that exhibits a hydrogen trapping ability by high-temperature tempering after quenching, to improve delayed fracture resistance" described in Patent Literature 2 (JP-A No. 2000-26934) and, as a result, have obtained the following finding. A fine Ti precipitate (at least one Ti precipitate selected from the group consisting of a Ti carbide, a Ti nitride, and a composite compound thereof) is precipitated at a higher temperature in the case of containing a large amount of 0.20% or more of Ti. Therefore, it is possible to cause precipitation during heating in quenching without tempering, and hydrogen that has been trapped is released at a higher temperature. As can be seen therefrom, hydrogen is stably trapped, and thus hydrogen that has been absorbed from a heating atmosphere during quenching can be trapped during cooling in quenching, thereby allowing for rendering hydrogen harmless even in subsequent low-temperature tempering. It has been thus found that delayed fracture resistance is excellent as compared with the technique of Patent Literature 2.

[0027] It is noted that inclusion of an excess C causes deterioration in delayed fracture resistance. It is also noted that no inclusion of a predetermined amount of N causes generation of a coarse grain during quenching and deterioration in delayed fracture resistance. Therefore, a C amount is set as from 0.10 to 0.50% and an N amount is set as from 0.0020 to 0.0250%, as described below.

[0028] It has been found, based on the finding above, that the steel member according to the present embodiment has the configuration described above and thus is a high-strength steel member excellent in delayed fracture resistance, which is one kind of hydrogen embrittlement resistance.

[0029] Further, a technique has been established which involves forming, in a steel member, a steel structure where "at least one Ti precipitate selected from the group consisting of a Ti carbide, a Ti nitride, and a composite compound thereof" serving as a hydrogen-trapping site is finely precipitated.

[0030] The reason why the steel structure at a location of 1 mm in depth from a surface of the steel member has been focused on is that delayed fracture due to hydrogen embrittlement occurs at an inner portion that is at a depth of several hundred micrometers or more from the surface of the steel member, originating at a site that is high in stress triaxiality.

[0031] Hereinafter, the steel member according to the present embodiment will be specifically described.

(Hydrogen Trapping Capacity)

[0032] First, the reason for limiting the hydrogen trapping capacity (namely, the content of non-diffusible hydrogen) that is the most important for improvement in delayed fracture characteristics of a high-strength steel member is described.

[0033] Diffusible hydrogen that causes delayed fracture of a steel member obtained by low-temperature tempering after quenching is absorbed into the steel member from a heating atmosphere during quenching. For example, several ppm by mass of hydrogen is absorbed during heating to an austenite region, in a case of carburization quenching or quenching with heat by RX gas (endothermic converted gas) firing. Hydrogen in a martensite structure obtained by quenching is low in diffusion coefficient, and thus hydrogen may be difficult to be completely released by low-temperature tempering after quenching, possibly resulting in hydrogen embrittlement.

[0034] When hydrogen is stably trapped in a hydrogen-trapping site during heating in such an atmosphere and quenching, the content of non-diffusible hydrogen after quenching is increased, thereby allowing for suppression of hydrogen embrittlement. In other words, hydrogen that is released during re-heating to a temperature range of from 400 to 800°C after quenching is in a form of hydrogen stably trapped in a hydrogen-trapping site, and is rendered harmless and does not contribute to hydrogen embrittlement.

[0035] Therefore, the steel member according to the present embodiment is a steel member containing 0.5 ppm by mass or more of non-diffusible hydrogen that is released in a temperature range of from 400 to 800°C in a thermal desorption hydrogen analysis. In other words, the hydrogen trapping capacity (content of non-diffusible hydrogen) is 0.5 ppm by mass or more.

[0036] The hydrogen trapping capacity is preferably 0.8 ppm by mass or more, and more preferably 1.0 ppm by mass or more, from the viewpoint of improvement in delayed fracture resistance. The content of non-diffusible hydrogen is preferably 3.0 ppm by mass or less, from the viewpoint of suppression of deterioration in forgeability due to increase of a precipitate.

[0037] The steel member is controlled so as to have a steel structure in which the amount of non-diffusible hydrogen that is released in a temperature range of from 400 to 800°C in a thermal desorption hydrogen analysis is 0.5 ppm by mass or more, thereby allowing delayed fracture characteristics to be improved.

[0038] The thermal desorption hydrogen analysis is performed as follows. First, a test piece of a round rod steel having a size of 10 mm in diameter $\phi \times 50$ mm in length L is taken from a steel member as a measurement object. Next, the test piece is heated at 100°C/hour using a "gas chromatography type temperature rising hydrogen analysis apparatus" and the amount (mass) of hydrogen that is released at each temperature is analyzed.

[0039] A hydrogen release curve is thus obtained which exhibits the relationship between the temperature and the amount of hydrogen that is released. The amount of non-diffusible hydrogen that is released in a temperature range of from 400 to 800°C, namely, the hydrogen trapping capacity (the content of non-diffusible hydrogen) is determined by an area integral value of the peak in the hydrogen release curve.

[0040] In a case in which the measurement object is larger than the "round rod steel having a size of 10 mm in diameter $\phi \times 50$ mm in length L", a test piece obtained by scraping, from the measurement object, a "round rod steel having a size of 10 mm in diameter $\phi \times 50$ mm in length L", whose outer peripheral surface corresponds to a location at a depth of 1 mm from a surface of the measurement object, is used as the test piece (see Figure 1). In Figure 1, OM represents the steel member as the measurement object and SP represents the test piece.

[0041] In contrast, in a case in which the measurement object is smaller than the "round rod steel having a size of 10 mm in diameter $\phi \times 50$ mm in length L", the measurement object is directly used as the test piece. This is because the content value of non-diffusible hydrogen that is measured does not vary even in a case in which the test piece is smaller than the "round rod steel having a size of 10 mm in diameter $\phi \times 50$ mm in length L".

[0042] It is noted that, even in a case in which the test piece is provided with a circular notch, the content of non-diffusible hydrogen that is measured does not vary depending on presence or absence of the circular notch.

(Steel Structure)

[0043] The steel member according to the present embodiment contains 0.10% or more of, in terms of percent (%) by area, at least one Ti precipitate that has an average size of from 30 to 200 nm in terms of an average equivalent circle diameter and is selected from the group consisting of a Ti carbide, a Ti nitride, and a composite compound thereof, at a location of 1 mm in depth from a surface of the steel member. In other words, a volume (area) fraction of the Ti precipitate is 0.10% or more in terms of percent (%) by area.

[0044] The Ti precipitate has hydrogen trapping ability and serves as a hydrogen-trapping site that releases hydrogen at a relatively high temperature of from 400 to 800°C. The presence of the Ti precipitate having hydrogen trapping ability enables non-diffusible hydrogen to be stably trapped during quenching of the steel member. In other words, the hydrogen trapping capacity (the content of non-diffusible hydrogen) of 0.5 ppm by mass or more can be achieved. Thus, the steel member can be improved in delayed fracture characteristics.

[0045] Ti oxides also have hydrogen trapping ability. However, it is preferable that Ti oxides are not included in the steel member from the viewpoint of securement of forgeability.

[0046] The Ti carbide, the Ti nitride, or the composite compound thereof (namely, Ti carbonitride) in the Ti precipitate is a compound that mainly contains Ti as a metal component (Ti occupies 50% by atom or more of a metal site) and

has an FCC (face-centered cubic) structure.

[0047] From the viewpoint of increase in hydrogen trapping capacity and improvement in delayed fracture characteristics, the volume (area) fraction of the Ti precipitate is preferably 0.10% or more, and more preferably 0.20% or more, in terms of percent (%) by area. From the viewpoint of securement of toughness, the volume (area) fraction of the Ti precipitate is preferably 1.00% or less, and more preferably 0.50% or less, in terms of percent (%) by area.

[0048] The volume (area) fraction of the Ti precipitate means a volume (area) fraction of the entire Ti precipitate contained in the steel member.

[0049] From the viewpoint of increase in hydrogen trapping capacity and improvement in delayed fracture characteristics with securement of tensile strength, the average size of the Ti precipitate is preferably 100 nm or less, and more preferably 80 nm or less, in terms of the average equivalent circle diameter. From the same viewpoint, the average size of the Ti precipitate is preferably 60 nm or more.

[0050] From the viewpoint of increase in hydrogen trapping capacity and improvement in delayed fracture characteristics with securement of tensile strength, an average aspect ratio of the Ti precipitate is preferably from 1.0 to 3.0. An upper limit of the average aspect ratio of the Ti precipitate is more preferably 2.0, and still more preferably 1.5.

[0051] The volume (area) fraction of the Ti precipitate, the average size of the Ti precipitate (average equivalent circle diameter), and the average aspect ratio of the Ti precipitate are each measured using a test piece prepared by an extraction replica method, by means of a transmission electron microscope (TEM) equipped with an energy dispersive X-ray analyzer (EDS). Specifically, the measurement is performed as follows.

[0052] A portion that is located 1 mm in depth from a surface of the steel member (hereinafter, also referred to as a "measurement surface") is taken from an arbitrary site of the steel member serving as the measurement object, and a test piece is prepared by an extraction replica method.

[0053] Next, an arbitrary region of the measurement surface of the test piece (region having a size of $5\ \mu\text{m} \times 5\ \mu\text{m}$) is observed using TEM-EDS at a magnification of 30,000.

[0054] Next, a component of the precipitate present in the field of view for observation is subjected to analysis of an electron beam diffraction pattern with TEM and analysis with EDS, thereby identifying the Ti precipitate.

[0055] Next, an area ratio of the entire Ti precipitate present in the field of view for observation is calculated.

[0056] The foregoing operation is performed five times, and the average value of the resulting area ratio of the Ti precipitate is defined as the volume (area) fraction of the Ti precipitate.

[0057] An equivalent circle diameter of the entire Ti precipitate present in the field of view for observation is determined.

[0058] The foregoing operation is performed five times, and the average value of the resulting "equivalent circle diameter" is defined as the average size (average equivalent circle diameter) of the Ti precipitate.

[0059] A long axis length and a short axis length of the entire Ti precipitate present in the field of view for observation are determined. The long axis length of the Ti precipitate is defined as the maximum diameter of the Ti precipitate. The short axis length of the Ti precipitate is defined as the maximum length of the Ti precipitate along with a direction perpendicular to the long axis.

[0060] The foregoing operation is performed five times, and the average value of the resulting "aspect ratio (= ratio of long axis length and short axis length (long axis length/short axis length))" is defined as the average aspect ratio of the Ti precipitate.

[0061] The steel member according to the present embodiment preferably includes a refined prior austenite grain, from the viewpoint of improvement in delayed fracture characteristics.

[0062] A grain size of the prior austenite grain (hereinafter, also referred to as "prior γ grain size") is preferably from 5 to 50 μm , more preferably from 10 to 40 μm , and still more preferably from 15 to 30 μm , in terms of an equivalent circle diameter at a location of 1 mm in depth from a surface of the steel member.

[0063] The prior γ grain size is measured by the following method.

[0064] A portion that is located 1 mm in depth from a surface of the steel member (hereinafter, also referred to as a "measurement surface") is taken from an arbitrary site of the steel member serving as the measurement object, and the measurement surface of the sample that has been taken is subjected to embedded polishing, and thereafter etched with a picral solution (mixed solution of hydrochloric acid, picric acid, and alcohol) as a corrosive liquid. The measurement surface of the sample is imaged using an optical microscope (at a magnification of 250), a γ grain boundary that has been imaged is subjected to digitization and binarization, a grain size of the prior γ grain is measured, and the average value thereof is determined.

(Chemical Composition)

[0065] The steel member according to the present embodiment preferably has a chemical composition of, in terms of percent (%) by mass: C: from 0.10 to 0.50%, Si: from 0.02 to 2.00%, Mn: from 0.05 to 2.00%, Cr: from 0.10 to 2.00%, Ti: from 0.20 to 1.00%, N: from 0.0020 to 0.0250%, Al: from 0 to 0.100%, V: from 0 to 0.50%, Nb: from 0 to 0.50%, Mo: from 0 to 1.00%, B: from 0 to 0.0100%, Cu: from 0 to 2.00%, Ni: from 0 to 3.00%, and a balance consisting of Fe and

impurities, from the viewpoint of improvement in delayed fracture characteristics.

[0066] Al, V, Nb, Mo, B, Cu, and Ni in the chemical composition of the steel member according to the present embodiment are optional components, namely, components that do not have to be included in the steel member. In cases in which these components are contained, each component is preferably contained in an amount equal to or greater than the lower limit of the respective content amount of the component, which will be described below.

- C: from 0.10 to 0.50%

[0067] C is an element essential to secure the tensile strength of the steel member (hereinafter, also referred to as "strength"). When the amount of C is less than 0.10%, required strength cannot be obtained. In this regard, when the amount of C is more than 0.50%, deterioration in delayed fracture resistance is caused as well as deterioration in toughness. Thus, the amount of C is from 0.10 to 0.50%. The amount of C is preferably from 0.20 to 0.40% from the viewpoint of strength and toughness.

- Si: from 0.02 to 2.00%

[0068] Si has an effect of increasing the strength of the steel member by a solid-solution hardening action. When the amount of Si is less than 0.02%, the action cannot be exerted. In this regard, when the amount of Si is more than 2.00%, the action is saturated and it is not possible to expect any effect commensurate with the amount. Thus, the amount of Si is 0.02 to 2.00%. The amount of Si is preferably from 0.20 to 2.00% from the viewpoint of exertion of the solid-solution hardening action.

- Mn: from 0.05 to 2.00%

[0069] Mn is an element not only necessary for deoxidation and desulfuration, but also effective for improvement in hardenability for providing a martensite structure. When the amount of Mn is less than 0.05%, the effect cannot be obtained. In this regard, when the amount of Mn is more than 2.00%, a Mn precipitate is segregated in a grain boundary during heating to an austenite region, thereby resulting in not only embrittlement of the grain boundary but also deterioration in delayed fracture resistance. Thus, the amount of Mn is from 0.05 to 2.00%. The amount of Mn is preferably from 0.50 to 1.50% from the viewpoint of improvement in hardenability and delayed fracture resistance.

- Cr: from 0.10 to 2.00%

[0070] Cr is an element effective for improvement in hardenability and increase in softening resistance during a tempering treatment. When the amount of Cr is less than 0.10%, the effect cannot be sufficiently exerted. In this regard, when the amount of Cr is more than 2.00%, deterioration in toughness and deterioration in cold workability are caused. Thus, the amount of Cr is from 0.10 to 2.00%. The amount of Cr is preferably from 0.50 to 1.50% from the viewpoint of improvement in hardenability, and suppression of deterioration in toughness and deterioration in cold workability.

- Ti: from 0.20 to 1.00%

[0071] Ti is an element that forms a fine Ti precipitate (at least one Ti precipitate selected from the group consisting of a Ti carbide, a Ti nitride, and a composite compound thereof) having hydrogen trapping ability at a relatively high temperature of from 400 to 800°C, and that contributes to improvement in delayed fracture resistance. Further, Ti has not only an effect of forming TiN during deoxidation and heat treatment, thereby preventing coarsening of an austenite grain, but also an effect of fixing N. When the amount of Ti is less than 0.20%, these effects cannot be exerted. In this regard, when the amount of Ti is more than 1.00%, Ti cannot be melted even with heat during rolling and a coarse Ti precipitate remains, thereby resulting in adverse effect on machinability or toughness. Thus, the amount of Ti is from 0.20 to 1.00%. The amount of Ti is preferably from 0.30 to 0.80%, and more preferably from 0.40 to 0.60%, from the viewpoint of formation of a fine Ti precipitate, machinability, toughness, or the like.

- N: from 0.0020 to 0.0250%

[0072] N is an element that forms a Ti nitride and contributes to improvement in delayed fracture resistance. N has an effect of forming nitrides of Al, V, and Nb, thereby allowing refinement of a prior austenite grain and increase in yield strength. When the amount of N is less than 0.0020%, these effects are less exerted. In this regard, when the amount of N is more than 0.0250%, these effect are saturated. Thus, the amount of N is from 0.0020 to 0.0250%. The amount of N is preferably from 0.0030 to 0.0150%, from the viewpoint of improvement in delayed fracture resistance, refinement

of a prior austenite grain, and increase in yield strength.

[0073] The chemical composition of the steel member according to the present embodiment may include, in terms of percent (%) by mass, one or more of Al: from 0 to 0.100%, V: from 0 to 0.50%, Nb: from 0 to 0.50%, or Mo: from 0 to 1.00%, and preferably includes, in terms of percent (%) by mass, one or more of Al: from 0.005 to 0.100%, V: from 0.01 to 0.50%, Nb: from 0.01 to 0.50%, or Mo: from 0.01 to 1.00%.

- Al: from 0.005 to 0.100%

[0074] Al is an element that has not only an effect of forming AlN during deoxidation and heat treatment, thereby preventing coarsening of an austenite grain, but also an effect of fixing N. When the amount of Al is less than 0.005%, these effects are difficult to be exerted. In this regard, when the amount of Al is more than 0.100%, these effects are easily saturated. Thus, Al is preferably from 0.005 to 0.100%.

- V: from 0.01 to 0.50%

[0075] V is an element that is precipitated in combination with TiC and that contributes to fine dispersion of a precipitate. Further, V is an element effective for forming a carbonitride, thereby refining an austenite grain. It is noted that the effect is less exerted when the amount of V is not 0.01% or more, and is easily saturated when the amount of V is more than 0.50%. When the amount of V is more than 0.50%, workability is easily impaired due to increase in deformation resistance. Thus, the amount of V is preferably from 0.01 to 0.50%.

- Nb: from 0.01 to 0.50%

[0076] Nb is an element that is precipitated in combination with TiC and that contributes to fine dispersion of a precipitate, as is the case with V. Further, Nb is an element effective for forming a carbonitride, thereby refining an austenite grain. It is noted that the effect is insufficient when the amount of Nb is less than 0.01%, and is easily saturated when the amount of Nb is more than 0.50%. Thus, the amount of Nb is preferably from 0.01 to 0.50%.

- Mo: from 0.01 to 1.00%

[0077] Mo is an element that is precipitated in combination with TiC and that contributes to fine dispersion of a precipitate, as is the case with V. It is noted that the effect is insufficient when the amount of Mo is less than 0.01%, and is easily saturated when the amount of Mo is more than 1.00%. Furthermore, when the amount of Mo is more than 1.00%, workability is easily impaired due to increase in deformation resistance. Thus, the amount of Mo is preferably from 0.01 to 1.00%.

[0078] The chemical composition of the steel member according to the present embodiment may include B: from 0 to 0.0100% in terms of percent (%) by mass, and preferably includes B: from 0.0003 to 0.0100% in terms of percent (%) by mass.

- B: from 0.0003 to 0.0100%

[0079] B is an element that suppresses grain boundary breakage and that improves delayed fracture resistance. Further, B is an element that is segregated in an austenite grain boundary, thereby resulting in a remarkable improvement in hardenability. It is noted that the effects are difficult to be exerted when the amount of B is less than 0.0003%, and are easily saturated when the amount of B is more than 0.0100%. Thus, the amount of B is preferably from 0.0003 to 0.0100%. The amount of B is more preferably from 0.0003 to 0.0050%, from the viewpoint of improvement in hardenability and delayed fracture resistance.

[0080] The chemical composition of the steel member according to the present embodiment may include one or both of Cu: from 0 to 2.00% or Ni: from 0 to 3.00% in terms of percent (%) by mass, and preferably includes one or both of Cu: from 0.05 to 2.00% or Ni: from 0.05 to 3.00% in terms of percent (%) by mass.

- Cu: from 0.05 to 2.00%

[0081] Cu is an element effective for improvement in softening resistance during a tempering treatment. When the amount of Cu is less than 0.05%, the effect is difficult to be exerted. Further, when the amount of Cu is more than 2.00%, hot workability is easily deteriorated. Thus, the amount of Cu is preferably from 0.05 to 2.00%. The amount of Cu is more preferably from 0.05 to 1.00% from the viewpoint of suppression of deterioration in hot workability.

- Ni: from 0.05 to 3.00%

[0082] Ni is an element for improvement in ductility that is deteriorated with increase in strength. Further, Ni is an element for improvement in hardenability during a heat treatment to increase in tensile strength. When the amount of Ni is less than 0.05%, these effects are less exerted. Further, when the amount of Ni is more than 3.00%, these effects are saturated and effects commensurate with the amount are difficult to be exerted. Thus, the amount of Ni is preferably from 0.05 to 3.00%.

[0083] The balance of the chemical composition of the steel member according to the present embodiment consists of Fe and impurities.

[0084] The impurities refer to any components that are contained in a raw material, or any components that are incorporated in the course of production and are not intentionally contained. Further, the impurities also encompass any components that are contained in amounts in ranges not having any effect on properties of the steel member, even if the components are intentionally contained.

[0085] Examples of the impurities include P and S. An amount of P and an amount of S are each preferably from 0 to 0.015%, for example, from the viewpoint of no effect on delayed fracture resistance. It is noted that the respective lower limits of the amount of P and the amount of S may be more than 0% from the viewpoint of reduction in cost of removal of P and cost of removal of S.

(Method of Producing Steel Member)

[0086] It is important for a method of producing the steel member according to the present embodiment to include previously precipitating a Ti precipitate that exhibits trapping ability in a rolling step during production of a rolling steel member serving as a material of the steel member, in order to address a variety of heat treatment conditions during production of the steel member.

[0087] For example, in a case in which a rolled bar steel member is used as the steel member, a steel piece (billet) having the chemical composition described above is heated to a temperature of 1,250°C or higher during rod steel rolling to cause the Ti compound to become a solid solution, thereafter hot-rolled at a finish rolling temperature of from 900 to 1,000°C, followed by being cooled to from 700 to 750°C at an average cooling rate of 40°C/s or less. Thus, an objective Ti precipitate can be precipitated. In this case, the Ti precipitate is isotropically precipitated.

[0088] The heating temperature of the steel piece (billet) refers to a surface temperature of the steel piece. The finish rolling temperature refers to a surface temperature of the rolled bar steel member immediately after finish rolling. The average cooling rate after finish rolling refers to a surface-cooling rate of the rolled bar steel member after finish rolling.

[0089] The rolled bar steel member in which the objective Ti precipitate has been precipitated is heated to an austenite region (for example, 850 to 1,050°C), cooled to from 20 to 100°C at a cooling rate of 40°C/s or less to be quenched, and subjected to low-temperature tempering at a temperature of from 150 to 200°C for a duration of from 15 to 60 minutes, thereby obtaining the steel member according to the present embodiment.

[0090] Even in a case of employing a method of producing the steel member without any rolling, such an objective Ti precipitate can be formed in the steel member by appropriately controlling solid-solution and precipitation of compounds.

EXAMPLES

[0091] Hereinafter, the present disclosure will be more specifically described with reference to Examples. It is noted that the respective Examples are not intended to limit the scope of the present disclosure.

[0092] A test material having a chemical composition shown in Table 1 was heated to a temperature shown in Table 2, thereafter hot-rolled at a finish rolling temperature shown in Table 2, and cooled to 700°C at an average cooling rate shown in Table 2 for rolling to a diameter ϕ of 20 mm, thereby producing a circularly notched test piece (notch depth of 2 mm, notch bottom radius of 0.25 mm, and notch angle of 60 degrees) made of a round rod steel having a size of 10 mm in diameter $\phi \times 50$ mm in length L.

[0093] The test piece was heated in a carburizing heating atmosphere or in a condition simulating RX gas heating (1 atm, mixed atmosphere of 50% of hydrogen and Ar, heating temperature of 1,000°C, and heating duration of 30 minutes), cooled to 20°C with water at a cooling rate of 40°C/s or less to be quenched, and thereafter tempered at 150°C for 20 minutes.

[0094] Note that No. 28 as a comparative steel was tempered at 520°C for 30 minutes and No. 29 as a comparative steel was tempered at 400°C for 40 minutes.

[0095] The resulting test piece was subjected to measurement of the rupture time with a constant load test at 3,000 kgf up to 100 hours. The tensile strength was also measured.

[0096] Separately, the test piece immediately after tempered was subjected to thermal desorption hydrogen analysis and the hydrogen trapping capacity released at a temperature range of from 400 to 800°C was measured, in accordance

EP 3 643 803 A1

with the method described above. The prior γ grain size, the volume (area) fraction of the Ti precipitate, the average size of the Ti precipitate (average equivalent circle diameter), and the average aspect ratio of the Ti precipitate were also measured in accordance with the methods described above.

5

10

15

20

25

30

35

40

45

50

55

[Table 1]

No	Chemical composition (% by mass), balance = Fe + impurities											Note
	C	Si	Mn	P	S	Cr	Ti	N	Al	B	Others	
1	0.41	0.20	0.80	0.010	0.005	1.21	0.55	0.0051	0.005	-	1.00Mo	Example steel
2	0.20	0.19	0.76	0.008	0.006	1.20	0.61	0.0152	-	-	-	Example steel
3	0.18	0.15	0.75	0.006	0.006	1.50	0.21	0.0121	0.007	0.0012	-	Example steel
4	0.10	0.02	1.05	0.006	0.005	1.90	1.00	0.0123	0.005	-	-	Example steel
5	0.20	2.00	2.00	0.008	0.004	1.17	0.62	0.0103	-	-	-	Example steel
6	0.48	0.20	0.80	0.008	0.006	0.10	0.51	0.0084	-	-	-	Example steel
7	0.22	0.15	0.77	0.007	0.004	1.00	0.62	0.0233	-	-	0.3V	Example steel
8	0.20	0.18	0.80	0.007	0.006	1.04	0.59	0.0152	-	-	0.01Nb	Example steel
9	0.18	0.20	0.76	0.007	0.004	1.20	0.20	0.0124	0.005	0.0003	0.10Cu	Example steel
10	0.22	0.20	0.05	0.008	0.004	1.38	0.51	0.0105	0.100	-	-	Example steel
11	0.20	0.19	0.75	0.008	0.007	1.20	0.55	0.0151	-	-	3.00Ni	Example steel
12	0.10	0.10	1.00	0.006	0.005	2.00	1.00	0.0103	0.005	-	-	Example steel
13	0.22	0.15	0.77	0.007	0.004	1.01	0.62	0.0020	-	-	0.01V	Example steel
14	0.20	0.20	0.75	0.008	0.004	1.19	0.61	0.0148	-	0.0100	-	Example steel
15	0.11	0.19	0.72	0.007	0.008	1.20	0.21	0.0119	0.006	0.0051	0.05Cu	Example steel
16	0.40	0.20	0.80	0.010	0.005	1.20	0.50	0.0050	0.007	-	0.01Mo, 0.50V	Example steel
17	0.19	0.22	0.75	0.008	0.004	1.18	0.55	0.0150	-	-	2.0Cu	Example steel
18	0.20	0.20	0.73	0.008	0.004	1.20	0.61	0.0155	-	-	0.05Ni	Example steel
19	0.20	0.18	0.80	0.007	0.004	1.05	0.60	0.0150	-	-	0.5Nb	Example steel
20	0.20	0.25	0.75	0.006	0.004	1.20	0.05	0.0150	-	-	-	Comparative steel
21	0.41	0.20	0.82	0.010	0.005	1.17	0.00	0.0050	0.005	-	0.20Mo	Comparative steel
22	0.40	0.18	0.81	0.010	0.005	1.19	0.05	0.0052	0.008	-	0.20Mo	Comparative steel
23	0.18	0.22	0.80	0.007	0.007	1.21	1.09	0.0050	-	-	-	Comparative steel
24	0.60	0.21	0.83	0.008	0.004	0.03	0.50	0.0120	-	-	-	Comparative steel

(continued)

No	Chemical composition (% by mass), balance = Fe + impurities											Note
	C	Si	Mn	P	S	Cr	Ti	N	Al	B	Others	
25	0.11	0.05	0.10	0.008	0.008	0.05	0.57	0.0152	-	-	-	Comparative steel
26	0.20	0.20	0.75	0.008	0.004	1.20	0.55	0.0015	-	-	-	Comparative steel
27	0.20	0.19	0.76	0.008	0.006	1.20	0.61	0.0152	-	-	-	Comparative steel
28	0.36	0.16	0.97	0.008	0.008	-	0.29	0.0049	0.071	-	0.05V, 2.93Mo	Comparative steel
29	0.10	0.10	1.00	0.006	0.005	2.00	1.00	0.0103	0.005	-	-	Comparative steel

[Table 2]

No	Production conditions			Hydrogen trapping capacity released at from 400 to 800°C (ppm by mass)	Prior γ grain size	Ti precipitate			Characteristics		Note
	Heating temperature (°C)	Finish rolling temperature (°C)	Average cooling rate (°C/s)			Volume (area) fraction (%)	Average size (average equivalent circle diameter)	Aspect ratio	Rupture time in constant load test (hr)	Tensile strength (Mpa)	
1	1280	950	20	0.83	20 μm	0.32	60 nm	1.6	No rupture	1560	Example steel
2	1300	900	15	0.90	28 μm	0.25	160 nm	1.3	No rupture	1350	Example steel
3	1265	925	20	0.53	31 μm	0.18	90 nm	1.1	No rupture	1340	Example steel
4	1310	930	15	2.10	21 μm	0.36	190 nm	1.4	No rupture	1235	Example steel
5	1290	900	25	1.05	33 μm	0.28	100 nm	1.5	No rupture	1360	Example steel
6	1280	1000	40	0.88	30 μm	0.31	90 nm	1.3	No rupture	1570	Example steel
7	1280	950	20	0.82	22 μm	0.21	60 nm	1.6	No rupture	1370	Example steel
8	1280	950	30	0.95	18 μm	0.28	70 nm	1.4	No rupture	1360	Example steel
9	1250	950	25	0.51	32 μm	0.12	60 nm	1.2	No rupture	1330	Example steel
10	1270	950	25	0.95	22 μm	0.28	100 nm	1.1	No rupture	1340	Example steel
11	1260	950	25	0.87	28 μm	0.30	90 nm	1.6	No rupture	1350	Example steel
12	1290	950	25	2.05	22 μm	0.26	190 nm	1.8	No rupture	1110	Example steel

(continued)

No	Production conditions			Hydrogen trapping capacity released at from 400 to 800°C (ppm by mass)	Prior γ grain size	Ti precipitate			Characteristics		Note
	Heating temperature (°C)	Finish rolling temperature (°C)	Average cooling rate (°C/s)			Volume (area) fraction (%)	Average size (average equivalent circle diameter)	Aspect ratio	Rupture time in constant load test (hr)	Tensile strength (Mpa)	
13	1270	950	30	0.82	25 μm	0.25	60 nm	1.5	No rupture	1320	Example steel
14	1270	950	12	0.90	33 μm	0.26	160 nm	1.7	No rupture	1330	Example steel
15	1250	900	15	0.51	20 μm	0.18	60 nm	1.3	No rupture	1310	Example steel
16	1265	920	30	0.80	18 μm	0.41	60 nm	1.8	No rupture	1520	Example steel
17	1270	980	25	0.87	35 μm	0.32	90 nm	1.3	No rupture	1360	Example steel
18	1280	950	30	0.90	36 μm	0.33	160 nm	1.4	No rupture	1340	Example steel
19	1275	900	30	0.95	16 μm	0.31	70 nm	1.3	No rupture	1330	Example steel
20	1260	930	25	0.03	35 μm	0.05	10 nm	1.2	25	1330	Comparative steel
21	1260	920	25	0.00	22 μm	0.00	-	1.3	4	1510	Comparative steel
22	1260	950	25	0.05	21 μm	0.04	20 nm	1.2	6	1520	Comparative steel
23	1250	970	25	0.18	35 μm	0.68	310 nm	1.1	76	1350	Comparative steel
24	1260	920	30	0.81	37 μm	0.35	-	1.6	32	1620	Comparative steel

(continued)

No	Production conditions			Hydrogen trapping capacity released at from 400 to 800 °C (ppm by mass)	Prior γ grain size	Ti precipitate			Characteristics		Note
	Heating temperature (°C)	Finish rolling temperature (°C)	Average cooling rate (°C/s)			Volume (area) fraction (%)	Average size (average equivalent circle diameter)	Aspect ratio	Rupture time in constant load test (hr)	Tensile strength (Mpa)	
25	1260	900	35	0.91	38 μm	0.38	100 nm	1.3	0	980	Comparative steel
26	1260	900	20	0.86	65 μm	0.25	120 nm	1.2	52	1350	Comparative steel
27	1115	920	16	<u>0.21</u>	26 μm	0.24	<u>350 nm</u>	1.6	83	1340	Comparative steel
28	1260	920	25	<u>0.13</u>	36 μm	1.40	<u>10 nm</u>	5.4	32	1737	Comparative steel
29	1250	945	24	1.84	21 μm	0.25	180 nm	1.9	0	<u>960</u>	Comparative steel

[0097] In Tables 1 and 2, Nos. 1 to 19 correspond to Example steels and the others correspond to Comparative steels. All of the Example steels exhibited 0.5 ppm by mass or more of hydrogen trapping ability as shown in the Tables, and thus were found to be excellent in delayed fracture resistance.

[0098] On the contrary, Nos. 20, 21 and 22 corresponding to Comparative steels were each an example where the Ti content was so low that the size of the Ti precipitate was small or no Ti precipitate was present, thereby resulting in a small amount of hydrogen trapping.

[0099] No. 23 corresponding to Comparative steel was an example where the amount of Ti was excess, by which a solid solution of TiC was not sufficiently formed and a coarse carbide was generated during heating in rolling, thereby resulting in a small amount of hydrogen trapping.

[0100] No. 24 corresponding to Comparative steel was an example where the amount of C was excess, thereby resulting in deterioration in delayed fracture resistance.

[0101] No. 25 corresponding to Comparative steel was an example where the amount of Cr was small and hardenability was insufficient, as a result of which the steel was low in tensile strength after quenching and thus could not withstand any load in the constant load test.

[0102] No. 26 corresponding to Comparative steel was an example where the steel was small in amount of N, thereby resulting in generation of a coarse grain during heating in quenching and deterioration in delayed fracture resistance.

[0103] No. 27 corresponding to Comparative steel was an example where the heating temperature during rolling was low, by which a solid-solution of the Ti compound was not sufficiently formed and a coarse Ti precipitate was generated, thereby resulting in deterioration in delayed fracture resistance.

[0104] No. 28 corresponding to Comparative steel was an example where the tempering temperature was high, by which most of the Ti precipitate was precipitated during tempering and thus the size of the Ti precipitate was small, thereby resulting in deterioration in delayed fracture resistance.

[0105] No. 29 corresponding to Comparative steel was an example where the tempering temperature was high, as a result of which the tensile strength after tempering was low and thus the steel could not withstand any load in the constant load test.

[0106] It was thus found that the Comparative steels were low in delayed fracture resistance.

[0107] The disclosure of Japanese Patent Application No. 2017-123347 is incorporated herein by reference in its entirety.

[0108] All documents, patent applications, and technical standards described herein are incorporated herein by reference to the same extent as if each individual document, patent application, or technical standard was specifically and individually indicated to be incorporated herein by reference.

Claims

1. A high-strength steel member having a chemical composition of, in terms of percent (%) by mass:

C: from 0.10 to 0.50%,

Si: from 0.02 to 2.00%,

Mn: from 0.05 to 2.00%,

Cr: from 0.10 to 2.00%,

Ti: from 0.20 to 1.00%,

N: from 0.0020 to 0.0250%,

Al: from 0 to 0.100%,

V: from 0 to 0.50%,

Nb: from 0 to 0.50%,

Mo: from 0 to 1.00%,

B: from 0 to 0.0100%,

Cu: from 0 to 2.00%,

Ni: from 0 to 3.00%, and

a balance consisting of Fe and impurities,

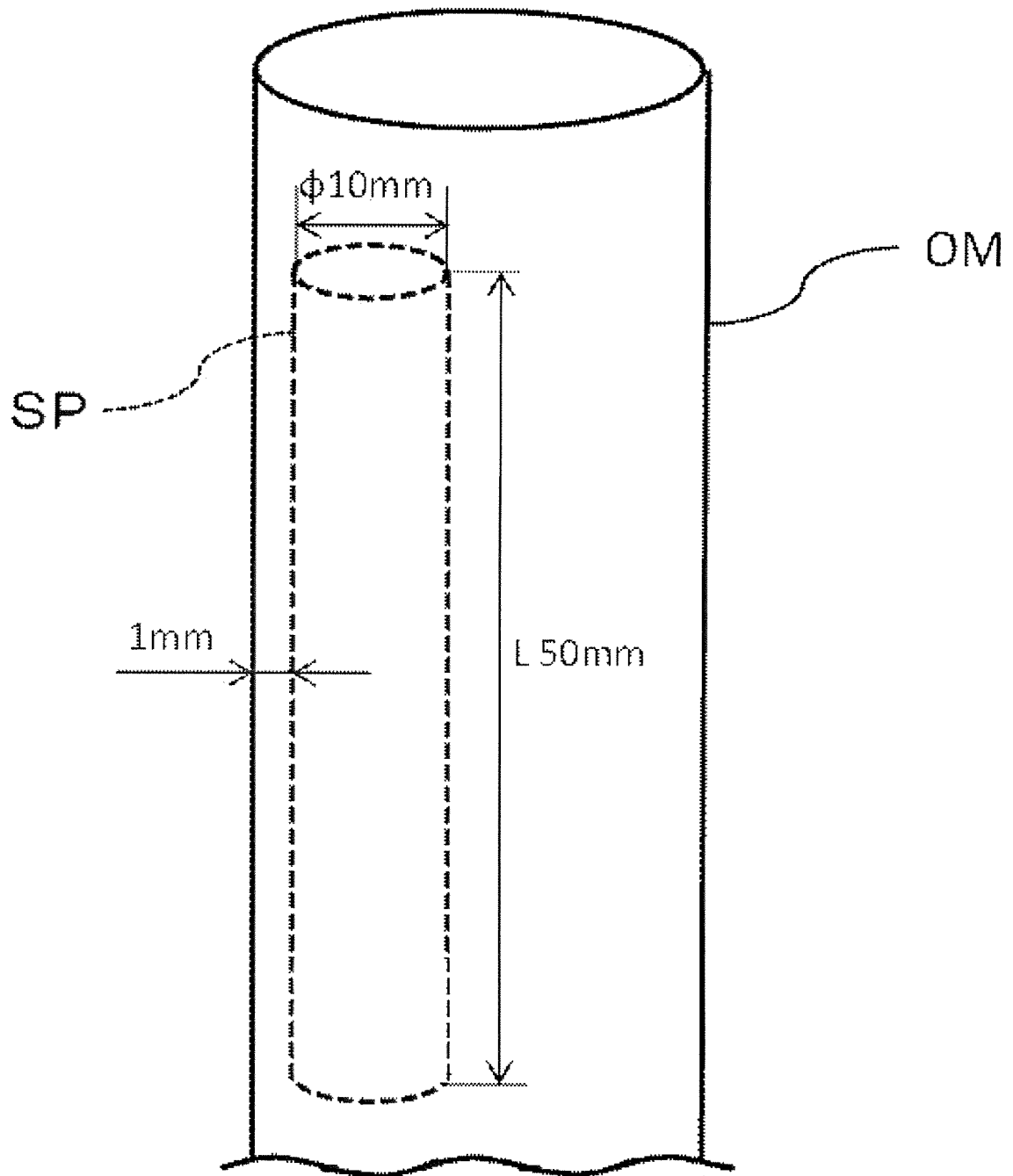
having a tensile strength of 1,000 MPa or higher,

containing 0.10% or more of, in terms of percent (%) by area, at least one Ti precipitate that has an average size of from 30 to 200 nm in terms of an average equivalent circle diameter and is selected from the group consisting of a Ti carbide, a Ti nitride, and a composite compound thereof, at a location of 1 mm in depth from a surface of the steel member, and

containing 0.5 ppm by mass or more of non-diffusible hydrogen that is released in a temperature range of from 400 to 800°C in a thermal desorption hydrogen analysis.

2. The high-strength steel member according to claim 1, having a chemical composition including, in terms of percent (%) by mass, one or more of
Al: from 0.005 to 0.100%,
V: from 0.01 to 0.50%,
Nb: from 0.01 to 0.50%, or
Mo: from 0.01 to 1.00%.
3. The high-strength steel member according to claim 1 or 2, having a chemical composition including, in terms of percent (%) by mass,
B: from 0.0003 to 0.0100%.
4. The high-strength steel member according to any one of claims 1 to 3, having a chemical composition including, in terms of percent (%) by mass,
one or both of Cu: from 0.05 to 2.00% or Ni: from 0.05 to 3.00%.
5. The high-strength steel member according to any one of claims 1 to 4, wherein the Ti precipitate has an average aspect ratio of from 1.0 to 3.0.

FIG.1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/023905

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C38/00(2006.01)i, C21D1/06(2006.01)i, C22C38/38(2006.01)i,
C22C38/58(2006.01)i, C21D8/06(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C22C38/00, C21D1/06, C22C38/38, C22C38/58, C21D8/06

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 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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	WO 2011/077904 A1 (YAMAHA MOTOR CO., LTD.) 30 June 2011, claims 1, 6, paragraphs [0004], [0062], [0068], [0069], [0095]-[0097], table 2 (Family: none)	1-5
A	JP 2015-178673 A (KOBE STEEL, LTD.) 08 October 2015, claims 1, 3, paragraphs [0019], [0020], [0022], [0033], table 4 & EP 3112491 A1, claims 1, 2, paragraphs [0019], [0020], [0022], [0033], table 4 & US 2017/0058376 A1 & CN 106062229 A & KR 10-2016-0119216 A & TW 201540845 A & MX 2016011156 A	1-5

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
05 September 2018 (05.09.2018)

Date of mailing of the international search report
18 September 2018 (18.09.2018)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/023905

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-201168 A (NSK LTD.) 27 July 1999, claim 1, paragraphs [0022], [0032]-[0036], [0051]-[0054], tables 1, 3, fig. 1 & US 6095692 A, claim 1, column 5, lines 25-42, column 7, line 1 to column 8, line 61, column 12, line 32 to column 13, line 38, tables 1, 3, fig. 1 & GB 2333106 A	1-5
A	JP 2014-101565 A (JFE BARS & SHAPES CORPORATION) 05 June 2014, claim 1, paragraphs [0024], [0045], [0051] (Family: none)	1-5
A	JP 2002-069572 A (NIPPON STEEL CORP.) 08 March 2002, claim 1, paragraphs [0014], [0015], [0027]-[0030], table 1 (Family: none)	1-5

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

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP H03243745 A [0006]
- JP 2000026934 A [0006] [0026]
- JP 2006045670 A [0006]
- JP 2001288539 A [0006]
- JP 2017123347 A [0107]