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(54) HIGH-STRENGTH STEEL SHEET AND METHOD FOR PRODUCING SAME

(57) A high-strength steel sheet having a tensile strength of 1320 MPa or more and excellent in ductility, hole expandability, and delayed fracture resistance characteristics is provided. The above-described high-strength steel sheet includes a specific component composition including Ti and the like, wherein a diffusible hydrogen amount in steel is 0.50 ppm by mass or less, tempered martensite and bainite are 70.0 to 95.0%, fresh martensite is 15.0% or less, retained austenite is 5.0 to 15.0%, an average grain size of a precipitate A, which is a carbide, nitride, or carbonitride containing at least one selected from the group consisting of Ti, Nb, and V is 0.001 to 0.050 μm, a number density N_S of the precipitate A having a major axis of 0.050 um or less is 10/μm^2 or more, and a ratio of the number density N_S and a number density N_L of the precipitate A having a major axis of more than 0.050 um is 10.0 or more.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a high-strength steel sheet and a method for producing the same.

BACKGROUND ART

[0002] In recent years, from the viewpoint of global environmental conservation, there is an increasing need to reduce the weight of a vehicle body of an automobile in order to improve the fuel efficiency of the automobile.

[0003] At this time, the weight of the vehicle body is reduced while maintaining the strength of the vehicle body. For example, it is desired to use a high-strength steel sheet having a tensile strength (TS) of 1320 MPa or more as a frame component around a cabin of the vehicle body.

[0004] The ductility of the steel sheet tends to decrease as the strength of the steel sheet increases. In this case, the formability of the steel sheet becomes insufficient, and it is difficult to press the steel sheet into a complicated shape.

[0005] Therefore, for example, Patent Literatures 1 and 2 disclose a technique for achieving both strength and ductility of a steel sheet.

CITATION LIST

PATENT LITERATURES

[0006]

Patent Literature 1: JP 2019-2078 A
Patent Literature 2: JP 2011-184756 A

SUMMARY OF INVENTION

TECHNICAL PROBLEMS

[0007] Conventionally, hot pressing has been applied when a high-strength steel sheet is processed into a component or the like, but recently, application of cold pressing has been studied in consideration of productivity.

[0008] However, in a component obtained by cold pressing a high-strength steel sheet having a tensile strength of 1320 MPa or more, delayed fracture may occur.

[0009] The delayed fracture is a phenomenon in which, when a component to which stress is applied is placed in a hydrogen intrusion environment, hydrogen intrudes into the component to reduce an interatomic bonding force or to cause local deformation, so that a microcrack is generated, and the component is broken as the microcrack develops.

[0010] Therefore, the high-strength steel sheet is required to have not only sufficient formability (ductility and hole expandability) but also favorable delayed fracture resistance characteristics.

[0011] The present invention has been made in view of the above points, and an object thereof is to provide a high-strength steel sheet having a tensile strength of 1320 MPa or more and excellent in formability (ductility and hole expandability) and delayed fracture resistance characteristics.

SOLUTION TO PROBLEMS

[0012] The present inventors have conducted intensive studies, and as a result, have found that the above object is achieved by adopting the following configuration, thereby completing the present invention.

[0013] That is, the present invention provides the following [1] to [8].

[1] A high-strength steel sheet comprising:

a component composition including, by mass%:

C: 0.130 to 0.350%,
Si: 0.50 to 2.50%,
Mn: 2.00 to 4.00%,
P: 0.100% or less,

S: 0.0500% or less,
Al: 0.010 to 2.000%,
N: 0.0100% or less, and

at least one element selected from the group consisting of Ti: 0.001 to 0.100%, Nb: 0.001 to 0.100%, and V: 0.001 to 0.500%, and
a balance consisting of Fe and inevitable impurities; and a microstructure, wherein
a diffusible hydrogen amount in steel is 0.50 ppm by mass or less,
a total area fraction of tempered martensite and bainite in the microstructure is 70.0 to 95.0%,
an area fraction of fresh martensite is 15.0% or less,
an area fraction of retained austenite is 5.0 to 15.0%,
an average grain size of a precipitate A, which is a carbide, nitride, or carbonitride containing at least one selected from the group consisting of Ti, Nb, and V is 0.001 to 0.050 um,
a number density N_S of a precipitate A_S, which is the precipitate A having a major axis of 0.050 um or less, is $10/\mu m^2$ or more, and
a ratio N_S/N_L of the number density N_S of the precipitate A_S and a number density N_L of a precipitate A_L, which is the precipitate A having a major axis of more than 0.050 um, is 10.0 or more.

[2] The high-strength steel sheet according to [1], wherein
the component composition further includes, by mass%, at least one element selected from the group consisting of:

W: 0.500% or less,
B: 0.0100% or less,
Ni: 2.000% or less,
Co: 2.000% or less,
Cr: 1.000% or less,
Mo: 1.000% or less,
Cu: 1.000% or less,
Sn: 0.500% or less,
Sb: 0.500% or less,
Ta: 0.100% or less,
Zr: 0.200% or less,
Hf: 0.020% or less,
Ca: 0.0100% or less,
Mg: 0.0100% or less, and
REM: 0.0100% or less.

[3] The high-strength steel sheet according to [1] or [2], comprising a plating layer on a surface.
[4] The high-strength steel sheet according to [3], wherein the plating layer is an alloyed plating layer.
[5] A method for producing the high-strength steel sheet according to [1] or [2], the method comprising:

heating a steel slab having the component composition according to [1] or [2] to 1100°C or higher and hot rolling the steel slab at a finish rolling finishing temperature of 850 to 950°C to obtain a hot-rolled steel sheet;
coiling the hot-rolled steel sheet at a coiling temperature T of 400 to 700°C, retaining the coiled hot-rolled steel sheet, and then cold rolling the coiled hot-rolled steel sheet to obtain a cold-rolled steel sheet; and
subjecting the cold-rolled steel sheet to a heat treatment, wherein
in the retention, when a total time during which a temperature of the coiled hot-rolled steel sheet is the coiling temperature T - 50°C or more is taken as t as a unit s, the following Formula 1 is satisfied, and
in the heat treatment, the cold-rolled steel sheet is held in a temperature region T1 of 800 to 950°C for 30 seconds or more, then cooled to a cooling stop temperature T2 of 150 to 250°C, and then held in a temperature region T3 of 250 to 400°C for 30 seconds or more.

$$0.001 < [1.17 \times 10^{-6} \times \{t/(T + 273.15)\}]^{1/3} < 0.050 \qquad \text{Formula 1:}$$

[6] The method for producing the high-strength steel sheet according to [5], wherein

the steel slab is casted and then cooled before the hot rolling, and
in the cooling of the steel slab, an average cooling rate v1 at 700 to 600°C is 5.0°C/h or more, and an average cooling rate v2 at 600 to 500°C is 2.5°C/h or more.

[7] The method for producing the high-strength steel sheet according to [5] or [6], wherein the cold-rolled steel sheet is subjected to a plating treatment for forming a plating layer after the heat treatment.
[8] The method for producing the high-strength steel sheet according to [7], wherein the plating treatment includes an alloying plating treatment for alloying the plating layer.

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] According to the present invention, it is possible to provide a high-strength steel sheet having a tensile strength of 1320 MPa or more and excellent in formability (ductility and hole expandability) and delayed fracture resistance characteristics.

DESCRIPTION OF EMBODIMENTS

[High-strength steel sheet]

[0015] A high-strength steel sheet of the present invention has a component composition and a microstructure described below, and satisfies a diffusible hydrogen amount in steel described below.

[0016] Hereinafter, the "high-strength steel sheet" is also simply referred to as "steel sheet".

[0017] The sheet thickness of the steel sheet is not particularly limited, and is, for example, 0.3 to 3.0 mm and preferably 0.5 to 2.8 mm.

[0018] The high strength means that a tensile strength (TS) is 1320 MPa or more.

[0019] The high-strength steel sheet of the present invention has a tensile strength of 1320 MPa or more, and is also excellent in formability (ductility and hole expandability) and delayed fracture resistance characteristics. Therefore, the high-strength steel sheet of the present invention has a very high utility value in industrial fields such as automobiles and electric equipment, and is particularly extremely useful for weight reduction of a frame component of a vehicle body of an automobile.

<Component composition>

[0020] The component composition of the high-strength steel sheet of the present invention (hereinafter, also referred to as "component composition of the present invention" for convenience) will be described.

[0021] "%" in the component composition of the present invention means "mass%" unless otherwise specified.

<<C: 0.130 to 0.350%>>

[0022] C increases the strength of tempered martensite, bainite, and fresh martensite.

[0023] C also improves the stability of retained austenite and improves the ductility of the steel sheet.

[0024] C precipitates a fine precipitate (precipitate A_S described below) that becomes a trap site of hydrogen inside tempered martensite and bainite, and improves delayed fracture resistance characteristics.

[0025] In order to sufficiently obtain these effects, the amount of C is 0.130% or more, preferably 0.150% or more, more preferably 0.160% or more, and still more preferably 0.170% or more.

[0026] On the other hand, when the amount of C is too large, C is distributed into austenite during reheating in a heat treatment described below, martensite transformation and bainite transformation during cooling after the heat treatment are suppressed, and the area fraction of retained austenite becomes excessive. When the amount of C is too large, the strength of the steel sheet becomes excessively high, so that the hydrogen embrittlement susceptibility of the steel is increased, and sufficient delayed fracture resistance characteristics cannot be obtained. Weldability, which is important in joining automobile components, is deteriorated.

[0027] Therefore, the amount of C is 0.350% or less, preferably 0.330% or less, and more preferably 0.310% or less.

<<Si: 0.50 to 2.50%>>

[0028] Si suppresses the formation of a carbide, so that a decrease in hole expandability due to a difference in hardness between the carbide and each structure is suppressed. Si provides stable retained austenite and ensures favorable ductility.

[0029] From the viewpoint of obtaining these effects, the amount of Si is 0.50% or more, preferably 0.55% or more, and more preferably 0.60% or more.

[0030] On the other hand, when Si is excessively contained, hole expandability is deteriorated due to embrittlement of the steel sheet, so that it is difficult to obtain desired formability.

[0031] Therefore, the amount of Si is 2.50% or less, preferably 2.30% or less, and more preferably 2.00% or less.

<<Mn: 2.00 to 4.00%>>

[0032] Mn forms a microstructure mainly including tempered martensite and bainite, thereby suppressing a difference in hardness between respective structures and improving the hole expandability.

[0033] Mn is an element contributing to the stabilization of retained austenite and is effective for ensuring favorable ductility.

[0034] From the viewpoint of obtaining these effects, the amount of Mn is 2.00% or more, preferably 2.20% or more, and more preferably 2.50% or more.

[0035] On the other hand, when the amount of Mn is too large, the steel sheet becomes brittle, the hole expandability is poor, and it is difficult to obtain desired formability.

[0036] Therefore, the amount of Mn is 4.00% or less, preferably 3.70% or less, and more preferably 3.50% or less.

<<P: 0.100% or less>>

[0037] P embrittles the steel sheet due to grain boundary segregation, and adversely affects delayed fracture resistance characteristics and weldability. Therefore, the amount of P is 0.100% or less, preferably 0.070% or less, more preferably 0.050% or less, still more preferably 0.030% or less, and particularly preferably 0.010% or less.

<<S: 0.0500% or less>>

[0038] S segregates at grain boundaries and embrittles the steel sheet during hot working. S forms a sulfide, thereby adversely affecting delayed fracture resistance characteristics. Therefore, the amount of S is 0.0500% or less, preferably 0.0100% or less, and more preferably 0.0050% or less.

<<Al: 0.010 to 2.000%>>

[0039] Al acts as a deoxidizer to reduce an inclusion in the steel sheet. Therefore, the amount of Al is 0.010% or more, preferably 0.015% or more, and more preferably 0.020% or more.

[0040] On the other hand, when the amount of Al is too large, the risk of cracking in the steel slab during casting the steel slab increases, and manufacturability is deteriorated. Therefore, the amount of Al is 2.000% or less, preferably 1.500% or less, more preferably 1.000% or less, still more preferably 0.500% or less, and particularly preferably 0.100% or less.

<<N: 0.0100% or less>>

[0041] When a coarse nitride is present in the steel sheet, voids are formed at the time of shearing the steel sheet, delayed fracture starting from the voids is likely to occur, and the delayed fracture resistance characteristics of the steel sheet are deteriorated. Therefore, the amount of N is preferably smaller. Specifically, the amount of N is 0.0100% or less, preferably 0.0090% or less, and more preferably 0.0080% or less.

<<At least one element selected from the group consisting of Ti: 0.001 to 0.100%, Nb: 0.001 to 0.100%, and V: 0.001 to 0.500%>>

[0042] Ti, Nb, and V contribute to precipitation strengthening, and are thus effective in increasing the strength of the steel sheet. Ti, Nb, and V make the delayed fracture resistance characteristics better by making the grain size of prior austenite grains finer, accordingly making tempered martensite and bainite finer, or forming a fine precipitate (precipitate A_S described below) that becomes a trap site of hydrogen.

[0043] From the viewpoint of obtaining these effects, the amount of Ti, the amount of Nb, and the amount of V are each 0.001% or more, preferably 0.003% or more, and more preferably 0.005% or more.

[0044] On the other hand, when the amounts of Ti, Nb, and V are too large, Ti, Nb, and V remain in an undissolved state when the steel slab is heated in hot rolling, and a coarse precipitate (precipitate A_L described below) increases, so that the delayed fracture characteristics may be deteriorated.

[0045] Therefore, the amount of Ti and the amount of Nb are each 0.100% or less, preferably 0.080% or less, and more preferably 0.050% or less.

[0046] The amount of V is 0.500% or less, preferably 0.450% or less, and more preferably 0.400% or less.

<<Other elements>>

[0047] The component composition of the present invention may further include, by mass%, at least one element selected from the group consisting of elements described below.

(W: 0.500% or less)

[0048] W improves the hardenability of the steel sheet. W makes the delayed fracture resistance characteristics better by generating a fine carbide containing W and becoming a trap site of hydrogen, or making tempered martensite and bainite finer.

[0049] However, when the amount of W is too large, coarse precipitates such as WN and WS remaining in an undissolved state increase when the steel slab is heated in hot rolling, and the delayed fracture resistance characteristics are deteriorated. Therefore, the amount of W is preferably 0.500% or less, more preferably 0.300% or less, and still more preferably 0.150% or less.

[0050] The lower limit of the amount of W is not particularly limited, but is, for example, 0.010% and preferably 0.050% from the viewpoint of obtaining the addition effect of W.

(B: 0.0100% or less)

[0051] B is effective for improving hardenability. B forms a microstructure mainly including tempered martensite and bainite and prevents deterioration of hole expandability.

[0052] However, when the amount of B is too large, formability may be deteriorated. Therefore, the amount of B is preferably 0.0100% or less, more preferably 0.0070% or less, and still more preferably 0.0050% or less.

[0053] The lower limit of the amount of B is not particularly limited, but is, for example, 0.0005% and preferably 0.0010% from the viewpoint of obtaining the addition effect of B.

(Ni: 2.000% or less)

[0054] Ni is an element stabilizing retained austenite and is effective for ensuring favorable ductility. Ni increases the strength of the steel by solid-solution strengthening.

[0055] However, when the amount of Ni is too large, the area fraction of fresh martensite becomes excessive, and the hole expandability is deteriorated. Therefore, the amount of Ni is preferably 2.000% or less, more preferably 1.000% or less, and still more preferably 0.500% or less.

[0056] The lower limit of the amount of Ni is not particularly limited, but is, for example, 0.010% and preferably 0.050% from the viewpoint of obtaining the addition effect of Ni.

(Co: 2.000% or less)

[0057] Co is an element effective for improving hardenability, and is effective for strengthening the steel sheet.

[0058] However, when the amount of Co is too large, deterioration of formability occurs. Therefore, the amount of Co is preferably 2.000% or less, more preferably 1.000% or less, and still more preferably 0.500% or less.

[0059] The lower limit of the amount of Co is not particularly limited, but is, for example, 0.010% and preferably 0.050% from the viewpoint of obtaining the addition effect of Co.

(Cr: 1.000% or less)

[0060] Cr improves the balance between strength and ductility.

[0061] However, when the amount of Cr is too large, the cementite solid solution rate is delayed during reheating in a heat treatment described below, and a relatively coarse carbide containing Fe such as cementite as a main component remains in an undissolved state, and the delayed fracture resistance characteristics are deteriorated. Therefore, the amount of Cr is preferably 1.000% or less, more preferably 0.800% or less, and still more preferably 0.500% or less.

[0062] The lower limit of the amount of Cr is not particularly limited, but is, for example, 0.030% and preferably 0.050% from the viewpoint of obtaining the addition effect of Cr.

(Mo: 1.000% or less)

[0063] Mo improves the balance between strength and ductility. Mo makes the delayed fracture resistance characteristics better by generating a fine carbide containing Mo and becoming a trap site of hydrogen, or making tempered martensite and bainite finer.

[0064] However, when the amount of Mo is too large, conversion treatability is significantly deteriorated. Therefore, the amount of Mo is preferably 1.000% or less, more preferably 0.800% or less, and still more preferably 0.500% or less.

[0065] The lower limit of the amount of Mo is not particularly limited, but is, for example, 0.010% and preferably 0.050% from the viewpoint of obtaining the addition effect of Mo.

(Cu: 1.000% or less)

[0066] Cu is an element effective for strengthening steel. Cu suppresses intrusion of hydrogen into the steel sheet, so that Cu is more excellent in delayed fracture resistance characteristics.

[0067] However, when the amount of Cu is too large, the area fraction of fresh martensite becomes excessive, and the hole expandability is deteriorated. Therefore, the amount of Cu is preferably 1.000% or less, more preferably 0.500% or less, and still more preferably 0.200% or less.

[0068] The lower limit of the amount of Cu is not particularly limited, but is, for example, 0.010% and preferably 0.050% from the viewpoint of obtaining the addition effect of Cu.

(Sn: 0.500% or less, Sb: 0.500% or less)

[0069] Sn and Sb suppress decarburization of a surface layer region of the steel sheet (a region having a depth of about several tens um from the surface of the steel sheet) caused by nitriding or oxidation of the surface of the steel sheet, and prevent a decrease in the area fraction of tempered martensite on the surface of the steel sheet.

[0070] However, when the amounts of these elements are too large, toughness is reduced. Therefore, the amount of Sn and the amount of Sb are each preferably 0.500% or less, more preferably 0.100% or less, and still more preferably 0.050% or less.

[0071] The lower limits of the amount of Sn and the amount of Sb are not particularly limited, but are each, for example, 0.001% and preferably 0.003% from the viewpoint of obtaining the addition effect of Sn and Sb.

(Ta: 0.100% or less)

[0072] Ta generates an alloy carbide or an alloy carbonitride and contributes to high strength. Ta is partially dissolved in Nb carbide or Nb carbonitride to form a composite precipitate such as (Nb, Ta) (C, N), thereby significantly suppressing coarsening of the precipitate and stabilizing contribution to strength due to precipitation strengthening.

[0073] However, even when Ta is excessively added, these effects are saturated, and the cost also increases. Therefore, the amount of Ta is preferably 0.100% or less, more preferably 0.080% or less, and still more preferably 0.070% or less.

[0074] The lower limit of the amount of Ta is not particularly limited, but is, for example, 0.005% and preferably 0.010% from the viewpoint of obtaining the addition effect of Ta.

(Zr: 0.200% or less)

[0075] Zr improves the hardenability of the steel sheet. Zr makes the delayed fracture resistance characteristics better by generating a fine carbide containing Zr and becoming a trap site of hydrogen, or making tempered martensite and bainite finer.

[0076] However, when the amount of Zr is too large, an increase in inclusions and the like is caused, defects on the surface and the inside of the steel sheet are caused, and the delayed fracture resistance characteristics are deteriorated. Therefore, the amount of Zr is preferably 0.200% or less, more preferably 0.150% or less, and still more preferably 0.100% or less.

[0077] The lower limit of the amount of Zr is not particularly limited, but is, for example, 0.005% and preferably 0.010% from the viewpoint of obtaining the addition effect of Zr.

(Hf: 0.020% or less)

[0078] Hf affects the distribution state of an oxide and makes the delayed fracture resistance characteristics better.

[0079] However, when the amount of Hf is too large, the formability of the steel sheet is deteriorated. Therefore, the amount of Hf is preferably 0.020% or less, more preferably 0.015% or less, and still more preferably 0.010% or less.

[0080] The lower limit of the amount of Hf is not particularly limited, but is, for example, 0.001% and preferably 0.003% from the viewpoint of obtaining the addition effect of Hf.

(Ca: 0.0100% or less, Mg: 0.0100% or less, REM: 0.0100% or less)

[0081] Ca, Mg, and REM (rare earth metal) spheroidize the shape of sulfides and improve the negative impact of sulfides on hole expandability.

[0082] However, when the amounts of these elements are too large, an increase in inclusions and the like is caused, defects and the like on the surface and the inside of the steel sheet are caused, and the delayed fracture resistance characteristics are deteriorated. Therefore, the amount of Ca, the amount of Mg, and the amount of REM are each preferably 0.0090% or less, more preferably 0.0080% or less, and still more preferably 0.0070% or less.

[0083] The lower limits of the amount of Ca, the amount of Mg, and the amount of REM are not particularly limited, but are each, for example, 0.0005% and preferably 0.0010% from the viewpoint of obtaining the addition effect of Ca, Mg, and REM.

«Balance: Fe and inevitable impurities>>

[0084] The balance in the component composition of the present invention consists of Fe and inevitable impurities.

<Microstructure>

[0085] Next, the microstructure of the high-strength steel sheet of the present invention (hereinafter, also referred to as "microstructure of the present invention" for convenience) will be described.

[0086] In order to obtain the effect of the present invention, it is insufficient to satisfy only the component composition of the present invention described above, and it is necessary to satisfy the microstructure of the present invention described below.

[0087] Hereinafter, the area fraction is an area fraction with respect to the entire microstructure. The area fraction of each structure is determined by the method described in EXAMPLES described below.

<<Total area fraction of tempered martensite and bainite: 70.0 to 95.0%>>

[0088] Tempered martensite and bainite contribute to tensile strength.

[0089] By mainly including tempered martensite and bainite, it is effective for enhancing hole expandability while maintaining high strength.

[0090] In order to sufficiently obtain these effects, the total area fraction of bainite and tempered martensite is 70.0% or more, preferably 72.0% or more, and more preferably 74.0% or more.

[0091] On the other hand, too much tempered martensite and bainite results in too little retained austenite.

[0092] Therefore, the total area fraction of bainite and tempered martensite is 95.0% or less, preferably 93.0% or less, and more preferably 90.0% or less.

<<Area fraction of fresh martensite: 15.0% or less>>

[0093] Fresh martensite causes a large difference in hardness between tempered martensite and bainite, thus reducing the hole expandability during punching due to the difference in hardness. Therefore, it is necessary to avoid excessive presence of fresh martensite in the steel sheet.

[0094] Specifically, from the viewpoint of obtaining favorable hole expandability, the area fraction of fresh martensite is 15.0% or less, preferably 14.0% or less, and more preferably 13.0% or less.

[0095] On the other hand, the lower limit is not particularly limited, but from the viewpoint of tensile strength, the area fraction of fresh martensite is preferably 1.0% or more, more preferably 3.0% or more, and still more preferably 5.0% or more.

<<Area fraction of retained austenite: 5.0 to 15.0%>>

[0096] During working, retained austenite undergoes martensite transformation due to the TRIP (Transformation Induced plasticity) effect to increase the strength and, at the same time, to improve the ductility by increasing the strain dispersion ability.

[0097] Therefore, the area fraction of retained austenite is 5.0% or more, preferably 6.0% or more, and more preferably

7.0% or more.

[0098] On the other hand, when the amount of retained austenite is too large, voids are likely to be generated at an interface between retained austenite and tempered martensite during working, and hydrogen embrittlement occurs from the voids, so that the delayed fracture resistance characteristics of the steel sheet are deteriorated.

[0099] Since retained austenite undergoes stress-induced martensite transformation during press molding, the hole expandability is reduced.

[0100] Therefore, the area fraction of retained austenite is 15.0% or less, preferably 14.0% or less, more preferably 13.0% or less, and still more preferably 12.0% or less.

«Balance structure»

[0101] Examples of the structure (balance structure) excluding tempered martensite, bainite, fresh martensite, and retained austenite include ferrite and pearlite. For the reason that the effect of the present invention is not inhibited, the area fraction of the balance structure in the microstructure of the present invention is preferably 5.0% or less.

<<Precipitate A»

[0102] Next, the precipitate A will be described.

[0103] The precipitate A is a carbide, nitride, or carbonitride containing at least one element selected from the group consisting of Ti, Nb, and V.

(Average grain size of precipitate A: 0.001 to 0.050 um)

[0104] When the precipitate A is too small, the effect of precipitation strengthening cannot be obtained, and the strength is insufficient.

[0105] Therefore, the average grain size of the precipitate A is 0.001 um or more, preferably 0.005 μm or more, and more preferably 0.010 um or more.

[0106] On the other hand, when the precipitate A is too large, the delayed fracture resistance characteristics of a sheared end face are adversely affected.

[0107] Therefore, the average grain size of the precipitate A is 0.050 μm or less, preferably 0.040 μm or less, more preferably less than 0.040 μm, still more preferably 0.035 μm or less, particularly preferably 0.030 μm or less, and most preferably 0.020 μm or less.

[0108] The average grain size of the precipitate A is determined by the method described in EXAMPLES described below.

(N_S: 10/μm^2 or more)

[0109] The precipitate A_S is the precipitate A having a major axis of 0.050 um or less.

[0110] A number density (number per unit area) N_S of the precipitate A_S is 10/μm^2 or more.

[0111] This increases the strength of the steel sheet by precipitation strengthening. The fine precipitate A_S act as a trap site of hydrogen, thereby improving the delayed fracture resistance characteristics.

[0112] For the reason that the delayed fracture resistance characteristics are more excellent, N_S is preferably more than 125/μm^2, more preferably 200/μm^2 or more, and still more preferably 310/μm^2 or more.

[0113] The upper limit of N_S is not particularly limited. However, when the absolute amount of the fine precipitate A_S increases, the rolling force increases, and it may be difficult to produce the steel sheet. Therefore, N_S is preferably 1,000/μm^2 or less and more preferably 800/μm^2 or less.

(N_S/N_L: 10.0 or more)

[0114] The precipitate A_L is the precipitate A having a major axis of more than 0.050 um.

[0115] A ratio (N_S/N_L) of the number density N_S (unit: number/μm^2) of the precipitate A_S and a number density N_L (unit: number/μm^2) of the precipitate A_L is 10.0 or more. As a result, favorable delayed fracture resistance characteristics can be obtained. The reason for this is presumed as follows.

[0116] Since the fine precipitate A_S has a small grain size, it is considered that it is difficult to accumulate strain and stress. Since the fine precipitate A_S has a circular shape, the surface thereof is understood to be a curved surface, and it is considered that strain and stress easily escape along the curved surface.

[0117] On the other hand, since the coarse precipitate A_L has a larger movement distance of strain and stress than the fine precipitate A_S, it is considered that strain and stress are likely to be accumulated.

[0118] In particular, the coarse precipitate A_L includes the precipitate A having a quadrangular shape, and the surface thereof is considered to be flat, and it is considered that strain and stress are more likely to be accumulated. In this case, it is presumed that local strain or residual stress inside the sheared end face increases. When the local strain or residual stress in the sheared end face increases, an initial crack is likely to occur in the sheared end face, and the delayed fracture resistance characteristics of the sheared end face are deteriorated.

[0119] Therefore, the delayed fracture resistance characteristics of the steel sheet can be improved by reducing the abundance ratio of the coarse precipitate A_L.

[0120] For the reason that the delayed fracture resistance characteristics are more excellent, N_S/N_L is preferably 11.0 or more, more preferably 12.0 or more, still more preferably more than 12.1, particularly preferably 12.2 or more, and most preferably 13.0 or more.

[0121] The upper limit of N_S/N_L is not particularly limited, but is preferably 100.0 or less, more preferably 80.0 or less, still more preferably 50.0 or less, and particularly preferably 30.0 or less.

[0122] The upper limit of N_L is not particularly limited. However, when the absolute amount of the coarse precipitate A_L increases, it is considered that the local strain or residual stress in the sheared end face increases, and an initial crack is likely to occur in the sheared end face. Therefore, N_L is preferably $50/\mu m^2$ or less and more preferably $35/\mu m^2$ or less.

[0123] N_S and N_L are determined by the method described in EXAMPLES described below.

<Diffusible hydrogen amount in steel: 0.50 ppm by mass or less>

[0124] From the viewpoint of securing favorable delayed fracture resistance characteristics, the diffusible hydrogen amount in steel is 0.50 ppm by mass or less, preferably 0.40 ppm by mass or less, more preferably 0.30 ppm by mass or less, and still more preferably 0.25 ppm by mass or less.

[0125] The lower limit of the diffusible hydrogen amount in steel is not particularly limited, but is, for example, 0.01 ppm by mass due to restrictions on production technology.

[0126] The diffusible hydrogen amount in steel is determined by the method described in EXAMPLES described below.

<Plating layer>

[0127] The high-strength steel sheet of the present invention may include a plating layer on a surface thereof. The plating layer is formed by a plating treatment described below.

[0128] Examples of the plating layer include a zinc plating layer (Zn plating layer) and an Al plating layer, and among them, a zinc plating layer is preferable. The zinc plating layer may contain elements such as Al and Mg. The plating layer may be a plating layer subjected to alloying (alloyed plating layer).

[0129] A coating weight (coating weight per one surface) of the plating layer is preferably 20 g/m^2 or more, more preferably 25 g/m^2 or more, and still more preferably 30 g/m^2 or more, from the viewpoint of controlling the coating weight of the plating layer and the viewpoint of corrosion resistance.

[0130] On the other hand, from the viewpoint of adhesion, the coating weight of the plating layer is preferably 120 g/m^2 or less, more preferably 100 g/m^2 or less, and still more preferably 70 g/m^2 or less.

[Method for producing high-strength steel sheet]

[0131] Next, the method for producing the high-strength steel sheet of the present invention (hereinafter, also referred to as "production method of the present invention" for convenience) will be described.

<Steel slab>

[0132] In the production method of the present invention, first, a steel slab (steel material) having the above-described component composition of the present invention is prepared.

[0133] The steel slab is cast from molten steel, for example, by a known method such as a continuous casting method.

[0134] The method for producing molten steel is not particularly limited, and a known method using a converter furnace, an electric furnace, or the like can be adopted.

<<Average cooling rate v1: 5.0°C/h or more and average cooling rate v2: 2.5°C/h or more>>

[0135] The steel slab may be cooled, for example, by being placed after casting and before being subjected to hot rolling described below.

[0136] In this cooling, an average cooling rate v1 at 700 to 600°C is preferably 5.0°C/h or more, more preferably

10.0°C/h or more, and still more preferably 15.0°C/h or more.

[0137] An average cooling rate v2 at 600 to 500°C is preferably 2.5°C/h or more, more preferably 5.0°C/h or more, and still more preferably 10.0°C/h or more.

[0138] In the steel slab, the coarse precipitate A_L may be precipitated during casting. When the average cooling rate v1 and the average cooling rate v2 satisfy the above ranges, the distribution state of the precipitate in the steel slab becomes uniform, and the coarse precipitate A_L precipitated during casting is easily redissolved when the steel slab is heated in hot rolling described below. That is, the value of N_S/N_L tends to be large.

[0139] The upper limit of the average cooling rate v1 is not particularly limited, but is, for example, 150.0°C/h and preferably 100.0°C/h.

[0140] The upper limit of the average cooling rate v2 is not particularly limited, but is, for example, 200.0°C/h or less and preferably 150.0°C/h.

<Hot rolling>

[0141] In the production method of the present invention, the prepared steel slab is subjected to hot rolling under the conditions (heating temperature and finish rolling finishing temperature) described below to obtain a hot-rolled steel sheet.

<<Heating temperature: 1100°C or higher>>

[0142] During hot rolling, the steel slab is heated.

[0143] When the heating temperature of the steel slab is too low, it is difficult to sufficiently form a solid solution of at least one element selected from the group consisting of Ti, Nb, and V. Furthermore, since excessive growth of the precipitate A occurs, the number density N_S of the fine precipitate A_S becomes too small, or the number density N_L of the coarse precipitate A_L becomes too large. That is, the value of N_S/N_L tends to be too small. Therefore, the heating temperature of the steel slab is 1100°C or higher, and preferably 1150°C or higher.

[0144] From the viewpoint of reducing the rolling force and the viewpoint of scaling off surface layer defects (bubbles, segregation, and the like) of the steel slab to smooth the surface of the steel sheet to be obtained, the heating temperature of the steel slab is preferably within the above range.

[0145] The upper limit of the heating temperature of the steel slab is not particularly limited, but when the heating temperature is too high, scale loss increases as the oxidation amount increases. Therefore, the heating temperature of the steel slab is preferably 1400°C or lower and more preferably 1350°C or lower.

<<Finish rolling finishing temperature: 850 to 950°C>>

[0146] The steel slab heated to the heating temperature described above is subjected to hot rolling including finish rolling to form a hot-rolled steel sheet.

[0147] When the finish rolling finishing temperature is too low, the rolling force increases and the rolling load increases. The average grain size of the precipitate A becomes excessively large, or the value of N_S/N_L becomes excessively small. Each structure of the hot-rolled steel sheet to be obtained may become coarse, and each structure during the subsequent heat treatment may also become coarse. In this case, for example, when cooling is stopped, it becomes difficult to stably obtain fine retained austenite that is mechanically stable and is less likely to undergo martensite transformation, and sufficient retained austenite cannot be obtained, and ductility is reduced.

[0148] Therefore, the finish rolling finishing temperature is 850°C or higher, preferably 855°C or higher, and more preferably 860°C or higher.

[0149] On the other hand, when the finish rolling finishing temperature is too high, austenite of the hot-rolled steel sheet becomes coarse, and as a result, austenite grains of the cold-rolled steel sheet become coarse. In this case, since the diffusion distance of C is increased, sufficient C enrichment for obtaining stable austenite is not caused in the heat treatment described below. As a result, sufficient retained austenite is not obtained in the final microstructure, and ductility is reduced.

[0150] Furthermore, the amount of oxide (scale) produced rapidly increases, and the surface quality tends to deteriorate after pickling and cold rolling described below.

[0151] When scale cannot be sufficiently removed by pickling, the ductility and the hole expandability are adversely affected.

[0152] The crystal grain size becomes excessively coarse, and surface roughness may occur during press working.

[0153] Therefore, the finish rolling finishing temperature is 950°C or lower, preferably 940°C or lower, and more preferably 930°C or lower.

<Coiling>

[0154] The hot-rolled steel sheet obtained by hot rolling is coiled under the conditions (coiling temperature T) described below.

<<Coiling temperature T: 400 to 700°C>>

[0155] When the coiling temperature T is too low, the precipitate A is not sufficiently formed, and the number density N_S of the fine precipitate A_S becomes too small or the value of N_S/N_L becomes too small.

[0156] Furthermore, since the strength of the hot-rolled steel sheet increases, the rolling load in the cold rolling increases, or the shape defect of the cold-rolled steel sheet obtained by cold rolling occurs, the productivity decreases.

[0157] Therefore, the coiling temperature T is 400°C or higher, preferably 420°C or higher, and more preferably 430°C or higher.

[0158] On the other hand, when the coiling temperature T is too high, the growth of the precipitate A proceeds, and the average grain size of the precipitate A becomes excessively large or the value of N_S/N_L becomes excessively small.

[0159] Therefore, the coiling temperature T is 700°C or lower, preferably 680°C or lower, and more preferably 670°C or lower.

[0160] The coiling temperature T is an end face temperature of the coiled hot-rolled steel sheet (that is, coil).

<Retention>

[0161] The coiled hot-rolled steel sheet (coil) is retained until cold rolling described below is performed.

[0162] In the retention, when a total time (unit: s) during which a temperature of the coiled hot-rolled steel sheet is the coiling temperature T - 50°C or more is taken as t (also referred to as "retention time t"), the following Formula 1 is satisfied.

$$0.001 < [1.17 \times 10^{-6} \times \{t/(T + 273.15)\}]^{1/3} < 0.050 \qquad \text{Formula 1:}$$

[0163] Hereinafter, for convenience, "$[1.17 \times 10^{-6} \times \{t/(T + 273.15)\}]^{1/3}$" in the above Formula 1 is described as "X".

[0164] When X in the above Formula 1 is less than the lower limit value, the retention of the coil is stopped in a state where sufficient nucleation does not occur or a state where nucleus growth is insufficient, the average grain size of the precipitate A becomes too small or the value of N_S/N_L becomes too small.

[0165] On the other hand, when X in the above Formula 1 exceeds the upper limit value, the precipitate A undergoes excessively Ostwald growth due to the diffusion of Ti, Nb, or V, and C or N, and the average grain size of the precipitate A becomes too large or the value of N_S/N_L becomes too small.

[0166] The method of controlling the thermal history of the coiled hot-rolled steel sheet (coil) is not particularly limited, and examples thereof include a method of covering the coil, and a method of applying hot air and/or cold air to the coil.

[0167] The temperature of the coiled hot-rolled steel sheet (coil) is the temperature of the surface of the coil measured using a radiation thermometer when there is no cover, and is the temperature inside the cover measured using a thermocouple when there is a cover.

[0168] The coil retained under the condition satisfying the above Formula 1 may be subjected to pickling as necessary before cold rolling described below. The pickling method may be performed according to a conventional method. In order to correct the shape and improve pickling properties, skin pass rolling may be performed.

<Cold rolling>

[0169] The coiled hot-rolled steel sheet is retained under the condition satisfying the above Formula 1, subjected to pickling as necessary, and then subjected to cold rolling to obtain a cold-rolled steel sheet.

[0170] A reduction ratio in the cold rolling is preferably 25% or more and more preferably 30% or more.

[0171] On the other hand, excessive reduction makes the rolling load excessive and causes an increase in the load of a mill used for cold rolling. Therefore, the reduction ratio is preferably 75% or less and more preferably 70% or less.

<Heat treatment>

[0172] The cold-rolled steel sheet obtained by cold rolling is subjected to the heat treatment under the conditions described below.

[0173] Schematically, the cold-rolled steel sheet is held (heated) in a temperature region T1, then cooled to a cooling stop temperature T2, and then held (reheated) in a temperature region T3.

<<Temperature region T1: 800 to 950°C>>

[0174] When the temperature in the temperature region T1 is too low, the cold-rolled steel sheet is held in a two-phase region, and thus the total area fraction of tempered martensite and bainite in the finally obtained microstructure becomes too small.

[0175] Therefore, the temperature in the temperature region T1 is 800°C or higher, preferably 830°C or higher, and more preferably 850°C or higher.

[0176] On the other hand, when the temperature in the temperature region T1 is too high, the precipitate A formed during hot rolling becomes coarse, and the average grain size of the precipitate A becomes excessively large or the value of N_S/N_L becomes excessively small.

[0177] Therefore, the temperature in the temperature region T1 is 950°C or lower, preferably 940°C or lower, and more preferably 930°C or lower.

<<Retention time in temperature region T1: 30 seconds or more»

[0178] When the retention time in the temperature region T1 is too short, sufficient recrystallization is not performed. The generation of austenite becomes insufficient, and the area fraction of retained austenite becomes too small.

[0179] Therefore, the retention time in the temperature region T1 is 30 seconds or more, preferably 65 seconds or more, and more preferably 100 seconds or more.

[0180] The upper limit of the retention time in the temperature region T1 is not particularly limited, but is, for example, 800 seconds, preferably 500 seconds, and more preferably 200 seconds.

<<Cooling stop temperature T2: 150 to 250°C>>

[0181] When the cooling stop temperature T2 is too low, a small amount of untransformed austenite remains when cooling is stopped, and finally the area fraction of retained austenite becomes too small.

[0182] Therefore, the cooling stop temperature T2 is 150°C or higher, preferably 160°C or higher, and more preferably 170°C or higher.

[0183] On the other hand, when the cooling stop temperature T2 is too high, a large amount of austenite remains when cooling is stopped, and finally the area fraction of retained austenite becomes too large.

[0184] Therefore, the cooling stop temperature T2 is 250°C or lower, preferably 240°C or lower, and more preferably 230°C or lower.

<<Temperature region T3: 250 to 400°C>>

[0185] When the temperature in the temperature region T3 is too low, C is not sufficiently enriched in the untransformed austenite, and the area fraction of retained austenite becomes too small.

[0186] Therefore, the temperature in the temperature region T3 is 250°C or higher, preferably 260°C or higher, and more preferably 270°C or higher.

[0187] On the other hand, when the temperature in the temperature region T3 is too high, the decomposition of the untransformed austenite excessively proceeds, and the area fraction of retained austenite becomes too small, so that the ductility is deteriorated.

[0188] Therefore, the temperature in the temperature region T3 is 400°C or lower, preferably 380°C or lower, and more preferably 360°C or lower.

<<Retention time in temperature region T3: 30 seconds or more>>

[0189] When the retention time in the temperature region T3 is too short, the area fraction of fresh martensite becomes too large in the finally obtained microstructure, or the area fraction of retained austenite becomes too small due to insufficient C enrichment in retained austenite.

[0190] Therefore, the retention time in the temperature region T3 is 30 seconds or more, preferably 100 seconds or more, and more preferably 180 seconds or more.

[0191] The upper limit of the retention time in the temperature region T3 is not particularly limited, but is, for example, 800 seconds, preferably 500 seconds, and more preferably 300 seconds.

<Plating treatment>

[0192] The cold-rolled steel sheet subjected to the heat treatment described above may be subjected to a plating treatment for forming a plating layer. Examples of the plating treatment include a hot-dip galvanizing treatment. In this case, a zinc plating layer is formed as the plating layer.

[0193] When the hot-dip galvanizing treatment is performed, for example, the cold-rolled steel sheet subjected to the heat treatment described above is immersed in a hot-dip galvanizing bath at 440 to 500°C. After the immersion, the coating weight of the plating layer is adjusted by gas wiping or the like.

[0194] In the hot-dip galvanizing bath, elements such as Al, Mg, and Si may be mixed, and further elements such as Pb, Sb, Fe, Mg, Mn, Ni, Ca, Ti, V, Cr, Co, and Sn may be mixed. The amount of Al in the hot-dip galvanizing bath is preferably 0.08 to 0.30%.

[0195] The plating treatment may include an alloying treatment for alloying the formed plating layer.

[0196] When the alloying treatment is performed after the hot-dip galvanizing treatment, the zinc plating layer is alloyed at a temperature (alloying temperature) of 450 to 600°C. When the alloying temperature is too high, untransformed austenite transforms into pearlite, and the area fraction of retained austenite becomes too small.

[0197] The concentration of Fe in the alloyed zinc plating layer is preferably 8 to 17 mass%.

[0198] In the case of performing the plating treatment, the cold-rolled steel sheet subjected to the heat treatment and the plating treatment corresponds to the high-strength steel sheet of the present invention.

[0199] On the other hand, in the case of not performing the plating treatment, the cold-rolled steel sheet subjected to the heat treatment corresponds to the high-strength steel sheet of the present invention.

EXAMPLES

[0200] Hereinafter, the present invention will be specifically described with reference to Examples. However, the present invention is not limited to Examples described below.

<Production of steel sheet>

[0201] Molten steel having the component composition shown in Table 1 below and the balance consisting of Fe and inevitable impurities was produced by a converter furnace and a steel slab was obtained by a continuous casting method.

[0202] The obtained steel slab was cooled under the conditions shown in Table 2 below.

[0203] Then, the cooled steel slab was subjected to hot rolling, coiling, retention, cold rolling, and the heat treatment under the conditions shown in Table 2 below to obtain a cold-rolled steel sheet (CR) having a sheet thickness of 1.4 mm. The reduction ratio of the cold rolling was set to 50%.

[0204] Some cold-rolled steel sheets were subjected to a hot-dip galvanizing treatment to form zinc plating layers on both surfaces, thereby obtaining hot-dip galvanized steel sheets (GI). The coating weight (coating weight per one surface) of the zinc plating layer was set to 45 g/m^2.

[0205] Some hot-dip galvanized steel sheets (GI) were subjected to an alloying treatment to alloy the formed zinc plating layer, thereby obtaining a galvannealed steel sheet (GA). In the alloying treatment, the concentration of Fe in the alloyed zinc plating layer was adjusted to fall within a range of 9 to 12 mass%.

[0206] For the hot-dip galvanized steel sheet (GI), a hot-dip galvanizing bath having an amount of Al of 0.19 mass% was used. For the galvannealed steel sheet (GA), a hot-dip galvanizing bath having an amount of Al of 0.14 mass% was used. The bath temperature was set to 465°C in both cases.

[0207] Hereinafter, for convenience, all of the cold-rolled steel sheet (CR), the hot-dip galvanized steel sheet (GI), and the galvannealed steel sheet (GA) are simply referred to as "steel sheet".

[0208] In the column of "Type" in Table 2 below, any one of "CR", "GI", and "GA" was described according to the obtained steel sheet.

<Observation of microstructure>

[0209] The obtained steel sheet was polished such that a cross section (L cross section) at a position of 1/4 of the sheet thickness parallel to the rolling direction (a position corresponding to 1/4 of the sheet thickness in the depth direction from the surface of the steel sheet) was an observation surface, and an observation sample was prepared.

[0210] Using the prepared observation sample, the microstructure was observed as follows, and the area fraction of each structure and the like were determined. The results are shown in Table 3 below.

[0211] In Table 3 below, tempered martensite is denoted as "TM", bainite is denoted as "B", fresh martensite is denoted as "FM", and retained austenite is denoted as "γR".

<<Area fraction of tempered martensite, bainite, and fresh martensite>>

[0212] The observation surface of the observation sample was corroded using nital, and then an SEM image was obtained by observing 10 fields of view at a magnification of 2000 times using a scanning electron microscope (SEM).

[0213] For the obtained SEM image, the area fraction (unit: %) of each structure was determined. The average area fraction of the 10 fields of view was taken as the area fraction of each structure.

[0214] In the SEM image, the light gray region was determined as fresh martensite, and the dark gray region where a carbide was precipitated was determined as tempered martensite and bainite.

[0215] Since fresh martensite and retained austenite cannot be clearly distinguished in the SEM image, the area fraction of fresh martensite was set to a value obtained by subtracting the area fraction of retained austenite obtained by the method described below from the area fraction of the light gray region.

<<Area fraction of retained austenite>>

[0216] The area fraction (unit: %) of retained austenite was determined by an X-ray diffraction method.

[0217] Specifically, first, the observation surface of the observation sample was polished by 0.1 mm in the sheet thickness direction and further polished by 0.1 mm by chemical polishing to obtain a polished surface.

[0218] For this polished surface, the integrated intensity of diffraction peaks of each of planes of {200}, {220}, and {311} of fcc iron and each of planes of {200}, {211}, and {220} of bcc iron was measured using CoKα ray.

[0219] In addition, a ratio (integrated intensity) of the integrated intensity of each of planes of {200}, {220}, and {311} of fcc iron to the integrated intensity of each of planes of {200}, {211}, and {220} of bcc iron was determined.

[0220] An average value of the nine obtained integrated intensity ratios was taken as a volume fraction of retained austenite, and this volume fraction was regarded as an area fraction (unit: %) of retained austenite.

<<Average grain size, N_S, and N_L of precipitate A>>

[0221] A replica sample was collected from the observation surface of the observation sample by a replica method.

[0222] For the collected replica sample, 10 fields of view were observed at a magnification of 20,000 times at an acceleration voltage of 200 kV using a transmission electron microscope (TEM) to obtain a TEM image. The size of one field of view was 0.5 μm × 0.5 um.

[0223] The presence of the precipitate was confirmed by viewing the obtained TEM image.

[0224] Energy dispersive X-ray spectroscopy (EDS) in the same field of view as the TEM image was performed to confirm elements contained in the precipitate.

[0225] Among the precipitates confirmed in the TEM image, a precipitate containing at least one selected from the group consisting of Ti, Nb, and V was identified as the precipitate A.

[0226] The circle equivalent diameter of each precipitate identified as the precipitate A was determined, and the average value for 10 fields of view was taken as the average grain size (unit: um) of the precipitate A.

[0227] The major axis of the precipitate A was measured.

[0228] Specifically, for the particles of each precipitate identified as the precipitate A, the longest length through the particles was measured, and this was taken as the major axis of the precipitate A.

[0229] In addition, the number of precipitates A (that is, the precipitates A_S) having a major axis of 0.050 um or less was measured, and the measured number was divided by the area of 10 fields of view to obtain the number density N_S (unit: number/μm^2) of the precipitate A_S.

[0230] Similarly, the number of precipitates A (that is, the precipitates A_L) having a major axis of more than 0.050 um was measured, and the measured number was divided by the area of 10 fields of view to obtain the number density N_L (unit: number/μm^2) of the precipitate A_L.

[0231] The ratio (N_S/N_L) of N_S and N_L was determined.

<Measurement of diffusible hydrogen amount in steel>

[0232] A test piece having a size of 5 mm × 30 mm was cut out from the obtained steel sheet. When a plating layer (zinc plating layer or alloyed zinc plating layer) was formed, the plating layer was removed using a router (precision grinder).

[0233] The test piece was placed in a quartz tube, and the inside of the quartz tube was replaced with argon gas (Ar). Thereafter, the temperature in the quartz tube was raised to 400°C at a rate of 200°C/hr, and the amount of hydrogen generated from the inside of the quartz tube during the temperature rise was measured by a temperature rising analysis method using a gas chromatograph.

[0234] The cumulative value of the amount of hydrogen detected in a temperature region of room temperature (25°C) or higher and lower than 250°C was determined as the diffusible hydrogen amount in steel (unit: mass%). The results are shown in Table 3 below.

<Evaluation>

[0235] The obtained steel sheet was evaluated by the following test. The results are shown in Table 3 below.

<<Tensile test>>

[0236] From the obtained steel sheet, a JIS No. 5 test piece in which a direction perpendicular to the rolling direction was a tensile direction was collected. Using the collected test piece, a tensile test was performed in accordance with JIS Z 2241 (2011) to measure the tensile strength (TS) and the total elongation (EL).

[0237] When TS was 1320 MPa or more, it was evaluated as high strength.

[0238] When EL was 10.0% or more, it was evaluated that ductility was excellent.

<<Hole expansion test>>

[0239] The obtained steel sheet was subjected to a hole expansion test in accordance with JIS Z 2256 (2010).

[0240] Specifically, the obtained steel sheet was cut to collect a test piece having a size of 100 mm × 100 mm. A hole having a diameter of 10 mm was punched into the collected test piece with a clearance of 12 ± 1%. Thereafter, using a die having an inner diameter of 75 mm, a conical punch having an apex angle of 60° was pushed into the hole in a state of being pressed at a wrinkle pressing force of 9 ton, and a hole diameter D_f (unit: mm) at a crack generation limit was measured. With the initial hole diameter as D_0 (unit: mm), the hole expansion ratio λ (unit: %) was determined from the following formula. When λ was 25% or more, it was evaluated that the hole expandability was excellent.

$$\lambda = \{(D_f - D_0)/D_0\} \times 100$$

<<Evaluation test of delayed fracture resistance characteristics>>

[0241] A test piece was collected from the obtained steel sheet. When a plating layer was formed, the plating layer was dissolved and removed using diluted hydrochloric acid, stored (dehydrogenated) at room temperature for 1 day, and then a test piece was collected.

[0242] As for the size of the test piece, the length of the long side (the length in a direction perpendicular to the rolling direction) was set to 100 mm, and the length of the short side (the length in the rolling direction) was set to 30 mm.

[0243] In the test piece, the end face on the long side was defined as an evaluation end face, and the end face on the short side was defined as a non-evaluation end face.

[0244] Cutting of the evaluation end face was performed by shearing. The clearance for shearing was 10%, and the rake angle was 0.5 degrees. The evaluation end face was in a state of being subjected to shearing. That is, machining for removing burrs was not performed. On the other hand, machining for removing burrs was performed on the non-evaluation end face.

[0245] Such a test piece was subjected to bending. The bending was performed under the condition that a ratio (R/t) of a bending radius R and a sheet thickness t of the test piece was 4.0, and a bending angle was 90 degrees (V-shaped bending).

[0246] For example, when the sheet thickness t was 2.0 mm, a punch having a tip radius of 8.0 mm was used. More specifically, a punch having the above-described tip radius and having a U-shape (the tip portion has a semicircular shape, and the thickness of the body portion is 2R) was used.

[0247] A die having a corner bending radius of 30 mm was used for the bending.

[0248] In the bending, a bent portion having a bending angle of 90 degrees was formed on the test piece by adjusting a depth at which the punch pushes the test piece.

[0249] The test piece on which the bent portion was formed was sandwiched and clamped using a hydraulic jack, and bolted in a state where the following residual stress S1, S2, or S3 was loaded on the outermost layer of the bent portion.

- Residual stress S1: residual stress of 1300 MPa or more and 1500 MPa or less
- Residual stress S2: residual stress of more than 1500 MPa and 1700 MPa or less
- Residual stress S3: residual stress of more than 1700 MPa and 1900 MPa or less

[0250] The number of test pieces was two for each of the loaded residual stresses S1, S2, and S3.

[0251] The necessary clamping degree was calculated by CAE (Computer Aided Engineering) analysis.

[0252] Bolting was performed in advance by passing a bolt through an elliptical (minor axis: 10 mm, major axis: 15 mm) hole provided 10 mm inside from the non-evaluation end face of the test piece.

[0253] The test piece after bolting was immersed in hydrochloric acid (aqueous hydrogen chloride solution) having a pH of 4, and the pH was controlled to be constant under the condition of 25°C. The amount of hydrochloric acid was 1 L or more per test piece.

[0254] After a lapse of 48 hours from the immersion, the presence or absence of visible (having a length of about 1 mm) microcracks was confirmed for the test piece in hydrochloric acid. This microcrack indicates the initial state of the delayed fracture.

[0255] The results depending on the presence or absence of microcracks ("Poor", "Fair", "Good", or "Excellent" shown below) are described in Table 3 below.

[0256] Poor: One or more microcracks were observed in the test piece loaded with the residual stress S1.

[0257] Fair: No microcracks were observed in the test piece loaded with the residual stress S1, but one or more microcracks were observed in the test piece loaded with the residual stress S2.

[0258] Good: No microcracks were observed in the test piece loaded with the residual stress S1 and the residual stress S2, but one or more microcracks were observed in the test piece loaded with the residual stress S3.

[0259] Excellent: No microcracks were observed in any of the test pieces.

[0260] "Fair", "Good", or "Excellent" was evaluated to be excellent in delayed fracture resistance characteristics.

[0261] For the reason that the delayed fracture resistance characteristics are more excellent, "Good" or "Excellent" is preferable, and for the reason that the delayed fracture resistance characteristics are further excellent, "Excellent" is more preferable.

[0262] Underlined in Tables 1 to 3 below means outside the scope of the present invention.

[Table 1]

[0263]

Table 1

Steel symbol	Component composition [mass%]											Remarks
	C	Si	Mn	P	S	Al	N	Ti	Nb	V	Others	
A	0.234	0.31	3.03	0.005	0.0012	0.031	0.0045	0.023	-	-		Comparative steel
B	0.234	0.58	3.03	0.005	0.0012	0.031	0.0041	0.023	-	-	Ni: 0.100, Cr: 0.200	Suitable steel
C	0.123	0.88	2.99	0.005	0.0011	0.025	0.0046	0.021	0.008	-	B: 0.0020	Comparative steel
E	0.187	0.89	2.97	0.005	0.0011	0.024	0.0052	0.021	0.008	-	B: 0.0020, Cr :0.300	Suitable steel
F	0.259	0.88	2.96	0.005	0.0011	0.026	0.0055	0.021	0.008	-	B: 0.0020, Cu: 0.140	Suitable steel
G	0.227	0.94	1.97	0.005	0.0011	0.028	0.0035	0.023	0.021	-		Comparative steel
H	0.227	1.17	2.85	0.006	0.0009	0.028	0.0027	0.020	0.020	-	B: 0.0020, Cu: 0.130, Sb: 0.008	Suitable steel
I	0.232	1.17	2.72	0.005	0.0011	0.028	0.0035	0.020	-	0.100	Co: 0.100, Ca: 0.0050, Mg: 0.0050	Suitable steel
J	0.228	1.17	3.02	0.008	0.0011	0.028	0.0040	-	0.021	0.100		Suitable steel
K	0.234	1.19	2.97	0.005	0.0010	0.027	0.0042	0.023	-	-	Co: 0.100, Hi: 0.008	Suitable steel
L	0.233	1.19	2.89	0.008	0.0006	0.032	0.0032	0.040	-	-	Zr: 0.050, W: 0.130	Suitable steel
M	0.227	1.17	2.70	0.006	0.0009	0.028	0.0027	-	0.040	-	Ta: 0.050, Zr: 0.050, Mo: 0.200	Suitable steel
N	0.231	1.20	2.67	0.006	0.0009	0.028	0.0027	-	-	0.400	Sn: 0.010, REM: 0.0030	Suitable steel
O	0.238	0.91	2.71	0.004	0.0006	0.037	0.0018	-	-	-	Mo: 0.100	Comparative steel
P	0.153	2.49	3.01	0.005	0.0012	0.034	0.0027	-	0.039	-		Suitable steel
Q	0.233	1.52	3.04	0.006	0.0010	0.031	0.0034	0.002	0.012	-	Mo: 0.200	Suitable steel
R	0.233	1.53	3.05	0.006	0.0010	0.031	0.0032	-	0.002	-	Cr: 0.200	Suitable steel
S	0.226	2.01	2.03	0.005	0.0011	0.028	0.0041	0.022	-	0.005	Sb: 0.008	Suitable steel
T	0.143	1.48	3.98	0.007	0.0009	0.029	0.0036	-	0.041	0.005		Suitable steel
U	0.342	0.87	2.50	0.005	0.0009	0.026	0.0043	0.021	0.007	-	B: 0.0070, Cu: 0.130	Suitable steel

[Table 2]

Table 2 (1/3)

Sample No.	Steelsymbol	Cooling of steel slab		Hot rolling		Coiling	Retention		Heat treatment					Plating treatment	Type
		Average cooling rate v 1 at 700 to 600°C [°C/h]	Average cooling rate v2 at 600 to 500°C [°C/h]	Heating temperature [°C]	Finish rolling finishing temperature	Coiling temperature T [°C]	Retention time t [s]	X value in Formula 1	Temperature region T1 [°C]	Retention time in T1 [s]	Cooling stop temperature T2 [°C]	Temperature region T3 [°C]	Retention time in T3 [s]	Alloying temperature [°C]	
1	A	9.0	7.0	1260	900	650	14400	0.026	860	120	200	320	230	-	CR
2	B	9.0	6.0	1270	900	650	14400	0.026	870	120	200	280	230	-	CR
3	B	9.0	6.0	1240	900	650	54000	0.041	870	120	100	300	230	-	CR
4	B	9.0	6.0	1250	900	650	54000	0.041	870	120	200	450	230	-	CR
5	C	10.0	7.0	1250	900	650	14400	0.026	870	120	200	320	230	-	CR
6	E	9.0	6.0	1250	900	650	14400	0.026	860	120	200	320	230	-	CR
7	F	25.0	27.0	1240	880	500	54000	0.043	860	120	200	350	230	-	CR
8	F	25.0	27.0	1270	880	500	54000	0.043	870	120	320	350	230	-	CR
9	F	25.0	27.0	1210	870	500	86400	0.051	870	120	200	320	230	-	CR
10	F	25.0	27.0	1260	880	400	68400	0.049	870	120	200	320	230	-	CR
11	F	25.0	27.0	1250	880	350	72000	0.051	870	120	200	320	230	-	CR
12	F	25.0	27.0	1270	870	500	54000	0.043	880	20	170	280	230	-	CR
13	F	25.0	27.0	1240	880	500	54000	0.043	870	120	170	280	20	-	CR
14	F	25.0	27.0	1260	870	650	14400	0.026	860	120	200	330	230	-	CR
15	F	25.0	27.0	1290	980	500	54000	0.043	880	120	200	350	230	-	CR

(continued)

Sample No.	Steel symbol	Cooling of steel slab		Hot rolling		Coiling	Retention		Heat treatment					Plating treatment	Type
		Average cooling rate v 1 at 700 to 600°C [°C/h]	Average cooling rate v 2 at 600 to 500°C [°C/h]	Heating temperature [°C]	Finish rolling finishing temperature [°C]	Coiling temperature T [°C]	Retention time t [s]	X value in Formula 1	Temperature region T1 [°C]	Retention time in T1 [s]	Cooling stop temperature T2 [°C]	Temperature region T3 [°C]	Retention time in T3 [s]	Alloy ing temperature [°C]	
16	F	25.0	27.0	1280	820	450	61200	0.046	870	120	200	350	230	-	CR
17	G	25.0	30.0	1260	900	650	14400	0.026	870	120	200	320	230	-	CR
18	H	26.0	31.0	1260	900	500	54000	0.043	860	120	170	320	230	-	CR
19	H	9.0	6.0	1260	900	500	54000	0.043	860	120	170	320	230	-	CR
20	H	4.0	1.0	1260	900	500	54000	0.043	860	120	170	320	230	-	CR
21	H	26.0	31.0	1240	900	650	14400	0.026	860	120	150	200	230	-	CR
22	H	26.0	31.0	1240	900	650	14400	0.026	750	120	150	300	230	-	CR
23	H	26.0	31.0	1190	900	650	14400	0.026	900	120	150	300	230	-	CR
24	H	26.0	31.0	1220	900	500	54000	0.043	890	120	200	350	230	-	CR
25	H	26.0	31.0	1240	900	650	14400	0.026	880	120	170	280	230	-	CR
26	H	26.0	31.0	1230	870	650	10800	0.024	960	120	230	350	230	-	CR
27	H	26.0	31.0	1210	890	650	14400	0.026	890	120	200	300	230	-	CR
28	H	26.0	31.0	1250	900	650	14400	0.026	870	120	230	320	230	-	CR
29	I	84.0	115.0	1320	890	650	14400	0.026	870	120	200	320	230	-	CR
30	I	84.0	115.0	1170	880	800	3600	0.016	870	120	230	320	230	-	CR

(continued)

Average cooling rate v1 at 700 to 600° C [°C/h]	Average cooling rate v2 at 600 to 500° C [°C/h]	Heating temperature [°C]	Finish rolling finishing temperature [°C]	Coiling temperature T [°C]	Retention time t [s]	X value in Formula 1	Temperature region T1 [°C]	Retention time in T1 [s]	Cooling stop temperature T2 [°C]	Temperature region T3 [°C]	Retention time in T3 [s]	Alloying temperature [°C]			
31	I	84.0	115.0	1040	880	650	14400	0.026	880	120	230	320	230	-	CR
32	J	25.0	30.0	1250	880	500	54000	0.043	890	120	230	320	230	-	GI
33	K	25.0	30.0	1260	890	500	54000	0.043	870	120	150	280	230	490	GA
34	K	25.0	30.0	1260	890	500	54000	0.043	870	120	250	300	230	520	GA
35	L	25.0	30.0	1250	870	650	14400	0.026	920	120	200	320	230	-	CR
36	M	25.0	30.0	1270	900	650	14400	0.026	870	120	220	320	230	-	CR
37	M	25.0	30.0	1270	870	650	14400	0.026	870	120	200	250	230	-	CR
38	N	25.0	30.0	1270	900	650	14400	0.026	870	120	200	320	230	-	CR
39	O	25.0	30.0	1240	900	650	14400	0.026	870	120	200	300	230	-	CR
40	P	83.0	117.0	1270	900	500	54000	0.043	870	120	200	300	230	-	CR
41	Q	83.0	119.0	1230	900	500	54000	0.043	870	120	200	300	230	-	CR
42	R	86.0	116.0	1250	900	500	54000	0.043	870	120	200	300	230	-	CR
43	S	86.0	119.0	1260	900	500	54000	0.043	870	120	200	300	230	-	CR
44	T	83.0	122.0	1260	900	500	54000	0.043	870	120	200	300	230	-	CR
45	U	87.0	121.0	1240	900	650	14400	0.026	870	120	200	280	230	-	CR

[Table 3]

Table 3 (1/3)

Sample No.	Steel symbol	Microstructure							TS [MPa]	EL [%]	A [%]	Diffusible hydrogen amount in steel [ppm by mass]	Delayed fracture resistance characteristics	Remarks
		TM + B [%]	FM [%]	yR [%]	Average grain size of precipitate A [μm]	N_S [number μm^2]	N_L [number μm^2]	N_S/N_L						
1	A	91.0	9.0	0.0	0.020	365	32	11.4	1401	9.4	20	0.04	Fair	Comparative Example
2	B	83.5	11.0	5.5	0.020	324	20	16.2	1538	10.1	25	0.03	Excellent	Inventive Example
3	B	85.3	10.0	4.7	0.030	302	20	15.1	1453	9.0	48	0.09	Good	Comparative Example
4	B	88.4	7.0	4.6	0.040	282	19	14.8	1475	8.8	39	0.03	Fair	Comparative Example
5	C	94.4	1.0	4.6	0.020	342	31	11.0	1203	9.6	38	0.05	Fair	Comparative Example
6	E	89.6	5.0	5.4	0.020	384	33	11.6	1326	10.2	37	0.08	Fair	Inventive Example
7	F	77.6	13.0	9.4	0.030	398	26	15.3	1440	11.3	41	0.06	Good	Inventive Example
8	F	77.8	7.0	15.2	0.030	359	23	15.6	1401	13.1	21	0.03	Poor	Comparative Example
9	F	78.5	12.0	9.5	0.060	382	34	11.2	1515	10.5	26	0.18	Poor	Comparative Example
10	F	78.4	12.0	9.6	0.020	381	24	15.9	1543	10.7	40	0.05	Excellent	Inventive Example
11	F	77.8	13.0	9.2	0.030	183	34	5.4	1518	10.2	45	0.06	Poor	Comparative Example
12	F	70.9	13.0	4.1	0.020	388	33	11.8	1321	9.2	26	0.09	Fair	Comparative Example
13	F	77.2	18.0	4.8	0.020	321	29	11.1	1502	8.5	21	0.04	Fair	Comparative Example
14	F	75.0	15.0	10.0	0.020	385	24	16.0	1489	11.6	28	0.03	Excellent	Inventive Example

(continued)

Table 3 (1/3)

Sample No.	Steel symbol	Microstructure							TS [MPa]	EL [%]	A [%]	Diffusible hydrogen amount in steel [ppm by mass]	Delayed fracture resistance characteristics	Remarks
		TM + B [%]	FM [%]	yR [%]	Average grain size of precipitate A [μm]	N_S [number [μm^2]	N_L [number [μm^2]	N_S/N_L						
15	F	81.2	14.0	4.8	0.030	454	31	14.6	1422	8.4	22	0.11	Good	Comparative Example
16	F	80.3	10.0	4.8	0.020	401	33	12.2	1387	8.7	39	0.08	Good	Comparative Example
17	G	90.2	5.0	4.8	0.030	456	29	15.7	1454	8.4	32	0.06	Good	Comparative Example
18	H	81.0	9.0	10.0	0.020	393	28	14.0	1502	10.7	37	0.04	Excellent	Inventive Example
19	H	80.2	10.0	9.8	0.030	371	31	12.0	1495	10.6	39	0.03	Fair	Inventive Example
20	H	80.7	9.0	10.3	0.030	353	34	10.4	1497	10.4	31	0.24	Fair	Inventive Example
21	H	89.4	6.0	4.6	0.020	415	37	11.2	1654	9.3	33	0.05	Fair	Comparative Example
22	H	48.6	14.0	8.4	0.020	372	33	11.3	1216	13.0	4	0.04	Fair	Comparative Example
23	H	85.7	7.0	7.3	0.020	341	28	12.2	1567	11.1	34	0.09	Good	Inventive Example
24	H	79.0	11.0	10.0	0.020	400	26	15.4	1430	12.2	43	0.08	Excellent	Inventive Example
25	H	81.6	10.0	8.4	0.030	294	26	11.3	1576	10.6	28	0.06	Fair	Inventive Example
26	H	80.3	10.0	9.7	0.050	272	28	9.7	1442	10.0	25	0.04	Poor	Comparative Example
27	H	77.3	13.0	9.7	0.020	446	30	14.9	1488	10.6	40	0.07	Excellent	Inventive Example
28	H	74.2	14.0	11.8	0.020	483	31	15.6	1488	12.0	28	0.08	Excellent	Inventive Example
29	I	80.5	10.0	9.5	0.020	350	26	13.5	1474	11.8	45	0.06	Excellent	Inventive Example
30	I	79.6	11.0	9.4	0.060	305	26	11.7	1472	10.7	27	0.04	Poor	Comparative Example

(continued)

Table 3 (1/3)

Sample No.	Steel symbol	Microstructure							TS [MPa]	EL [%]	A [%]	Diffusible hydrogen amount in steel [ppm by mass]	Delayed fracture resistance characteristics	Remarks
		TM + B [%]	FM [%]	yR [%]	Average grain size of precipitate A [μm]	N_S [number [μm^2]	N_L [number [μm^2]	N_S/N_L						
31	I	80.3	10.0	9.7	0.030	225	24	9.4	1475	11.7	32	0.23	Poor	Comparative Example
32	J	78.3	12.0	9.7	0.020	121	8	15.1	1502	11.2	31	0.28	Good	Inventive Example
33	K	80.9	12.0	7.1	0.020	278	22	12.6	1575	10.9	32	0.24	Good	Inventive Example
34	K	78.5	14.0	7.5	0.010	258	21	12.3	1561	10.4	25	0.27	Good	Inventive Example
35	L	82.4	8.0	9.6	0.020	316	26	12.2	1449	11.1	35	0.07	Good	Inventive Example
36	M	78.7	12.0	9.3	0.020	142	8	17.8	1480	11.3	42	0.04	Good	Inventive Example
37	M	78.1	15.0	6.9	0.030	205	17	12.1	1641	10.0	30	0.06	Fair	Inventive Example
38	N	79.9	11.0	9.1	0.030	125	11	11.4	1493	11.2	41	0.08	Fair	Inventive Example
39	O	83.6	9.0	7.4	-	-	-	-	1499	10.3	42	0.03	Poor	Comparative Example
40	P	83.1	8.0	8.9	0.040	185	10	18.5	1512	11.8	37	0.03	Fair	Inventive Example
41	Q	77.1	11.0	9.9	0.020	127	9	14.1	1501	11.5	33	0.18	Good	Inventive Example
42	R	75.9	12.0	12.1	0.020	157	13	12.1	1520	12.1	35	0.04	Fair	Inventive Example
43	S	85.3	5.0	9.7	0.020	122	7	17.4	1422	12.4	32	0.25	Good	Inventive Example
44	T	81.7	7.0	11.3	0.020	377	25	15.1	1368	12.8	37	0.02	Good	Inventive Example
45	U	77.6	14.0	8.4	0.030	111	7	15.9	1894	11.2	26	0.03	Good	Inventive Example

<Summary of evaluation results

[0264] As shown in Table 3 above, in the steel sheets of Nos. 1, 3 to 5, 8 to 9, 11 to 13, 15 to 17, 21 to 22, 26, 30 to 31, and 39, at least any one of the tensile strength, the ductility, the hole expandability, and the delayed fracture resistance characteristics was insufficient.

[0265] On the other hand, it was found that all of the steel sheets of Nos. 2, 6 to 7, 10, 14, 18 to 20, 23 to 25, 27 to 29, 32 to 38, and 40 to 45 have a tensile strength of 1320 MPa or more, and are excellent in ductility, hole expandability, and delayed fracture resistance characteristics.

[0266] Among these steel sheets, a steel sheet satisfying all of the following (i) to (v) had an evaluation result of delayed fracture resistance characteristics of "Excellent".

(i) Area fraction of retained austenite: 12.0% or less
(ii) Average grain size of the precipitate A: 0.020 um or less
(iii) N_S: 310/μm^2 or more
(iv)N_S/N_L: 13.0 or more
(v) Diffusible hydrogen amount in steel: 0.25 ppm by mass or less

[0267] A steel sheet not satisfying at least one of the above (i) to (v) had an evaluation result of delayed fracture resistance characteristics of "Good".

[0268] The steel sheet of No. 44 (steel symbol: T) satisfies all of the above (i) to (v), but the amount of C is slightly small, so that the evaluation result of delayed fracture resistance characteristics is estimated to be "Good".

[0269] A steel sheet in which N_S/N_L was 12.1 or less or the average grain size of the precipitate A is 0.040 μm or more had an evaluation result of delayed fracture resistance characteristics of "Fair".

Claims

1. A high-strength steel sheet comprising:

a component composition including, by mass%:

C: 0.130 to 0.350%,
Si: 0.50 to 2.50%,
Mn: 2.00 to 4.00%,
P: 0.100% or less,
S: 0.0500% or less,
Al: 0.010 to 2.000%,
N: 0.0100% or less, and

at least one element selected from the group consisting of Ti: 0.001 to 0.100%, Nb: 0.001 to 0.100%, and V: 0.001 to 0.500%, and
a balance consisting of Fe and inevitable impurities; and a microstructure, wherein
a diffusible hydrogen amount in steel is 0.50 ppm by mass or less,
a total area fraction of tempered martensite and bainite in the microstructure is 70.0 to 95.0%,
an area fraction of fresh martensite is 15.0% or less,
an area fraction of retained austenite is 5.0 to 15.0%,
an average grain size of a precipitate A, which is a carbide, nitride, or carbonitride containing at least one selected from the group consisting of Ti, Nb, and V is 0.001 to 0.050 μm,
a number density N_S of a precipitate A_S, which is the precipitate A having a major axis of 0.050 um or less, is 10/μm^2 or more, and
a ratio N_S/N_L of the number density N_S of the precipitate A_S and a number density N_L of a precipitate A_L, which is the precipitate A having a major axis of more than 0.050 μm, is 10.0 or more.

2. The high-strength steel sheet according to claim 1, wherein
the component composition further includes, by mass%, at least one element selected from the group consisting of:

W: 0.500% or less,
B: 0.0100% or less,

Ni: 2.000% or less,
Co: 2.000% or less,
Cr: 1.000% or less,
Mo: 1.000% or less,
Cu: 1.000% or less,
Sn: 0.500% or less,
Sb: 0.500% or less,
Ta: 0.100% or less,
Zr: 0.200% or less,
Hf: 0.020% or less,
Ca: 0.0100% or less,
Mg: 0.0100% or less, and
REM: 0.0100% or less.

3. The high-strength steel sheet according to claim 1 or 2, comprising a plating layer on a surface.

4. The high-strength steel sheet according to claim 3, wherein the plating layer is an alloyed plating layer.

5. A method for producing the high-strength steel sheet according to claim 1 or 2, the method comprising:

heating a steel slab having the component composition according to claim 1 or 2 to 1100°C or higher and hot rolling the steel slab at a finish rolling finishing temperature of 850 to 950°C to obtain a hot-rolled steel sheet;
coiling the hot-rolled steel sheet at a coiling temperature T of 400 to 700°C, retaining the coiled hot-rolled steel sheet, and then cold rolling the coiled hot-rolled steel sheet to obtain a cold-rolled steel sheet; and
subjecting the cold-rolled steel sheet to a heat treatment, wherein
in the retention, when a total time during which a temperature of the coiled hot-rolled steel sheet is the coiling temperature T - 50°C or more is taken as t as a unit s, the following Formula 1 is satisfied, and
in the heat treatment, the cold-rolled steel sheet is held in a temperature region T1 of 800 to 950°C for 30 seconds or more, then cooled to a cooling stop temperature T2 of 150 to 250°C, and then held in a temperature region T3 of 250 to 400°C for 30 seconds or more.

$$0.001 < [1.17 \times 10^{-6} \times \{t/(T + 273.15)\}]^{1/3} < 0.050 \qquad \text{Formula 1:}$$

6. The method for producing the high-strength steel sheet according to claim 5, wherein

the steel slab is casted and then cooled before the hot rolling, and
in the cooling of the steel slab, an average cooling rate v1 at 700 to 600°C is 5.0°C/h or more, and an average cooling rate v2 at 600 to 500°C is 2.5°C/h or more.

7. The method for producing the high-strength steel sheet according to claim 5 or 6, wherein the cold-rolled steel sheet is subjected to a plating treatment for forming a plating layer after the heat treatment.

8. The method for producing the high-strength steel sheet according to claim 7, wherein the plating treatment includes an alloying plating treatment for alloying the plating layer.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/044900

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; ***C21D 9/46***(2006.01)i; ***C22C 38/60***(2006.01)i; *C22C 18/00*(2006.01)n
FI: C22C38/00 301U; C21D9/46 F; C21D9/46 J; C22C38/00 301T; C22C38/60; C22C18/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00-38/60; C21D9/46; C22C18/00

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2021/019947 A1 (JFE STEEL CORP) 04 February 2021 (2021-02-04)	1-8
A	JP 2021-25094 A (JFE STEEL CORP) 22 February 2021 (2021-02-22)	1-8
A	WO 2018/055695 A1 (NIPPON STEEL & SUMITOMO METAL CORP) 29 March 2018 (2018-03-29)	1-8
A	WO 2014/156187 A1 (JFE STEEL CORP) 02 October 2014 (2014-10-02)	1-8

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 February 2023	**28 February 2023**

Name and mailing address of the ISA/JP	Authorized officer
Japan Patent Office (ISA/JP) **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/044900

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2021/019947 A1	04 February 2021	US 2022/0251676 A1	
		EP 4006190 A1	
		CN 114008234 A	
		KR 10-2022-0013405 A	
JP 2021-25094 A	22 February 2021	(Family: none)	
WO 2018/055695 A1	29 March 2018	US 2019/0330721 A1	
		EP 3517644 A1	
		CN 109312433 A	
		KR 10-2019-0007055 A	
		MX 2018016000 A	
WO 2014/156187 A1	02 October 2014	US 2016/0053355 A1	
		EP 2980246 A1	
		CA 2907507 C	
		KR 10-2015-0119952 A	
		CN 105102657 A	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2019002078 A **[0006]**
- JP 2011184756 A **[0006]**