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(54) **HIGH STRENGTH STEEL SHEET, HIGH STRENGTH PLATED STEEL SHEET, METHODS FOR PRODUCING THESE, AND MEMBER**

(57) To provide a high strength steel sheet with a tensile strength of 1180 MPa or higher, excellent bendability and toughness, and a high yield ratio, and a method of producing the same. The high strength steel sheet comprising a chemical composition containing C, Si, Mn, P, S, Al, N, Ti, Nb, and B, with the balance being Fe and inevitable impurities, and satisfying formula (1) below, in which the total area ratio of martensite and bainite is 95 % or more, the average grain size of prior austenite grains is 10 μ m or less, the B concentration at a prior austenite grain boundary is 0.10 % or more in mass%, a C-concentrated region is provided along a martensitic grain boundary, and the C-concentrated region has a C concentration of 4.0 times or more than the C content in the steel, and the C-concentrated region has a concentration width of 3 nm or more and 100 nm or less in a direction perpendicular to the martensitic grain boundary and a length of 100 nm or more in a direction parallel to the martensitic grain boundary:

$$([\%N]/14)/([\%Ti]/47.9) < 1.0 \dots (1),$$

in formula (1), [%N] and [%Ti] indicate the N content and the Ti content in the steel in mass%, respectively.

FIG. 1A

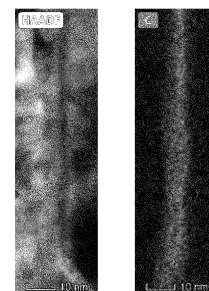
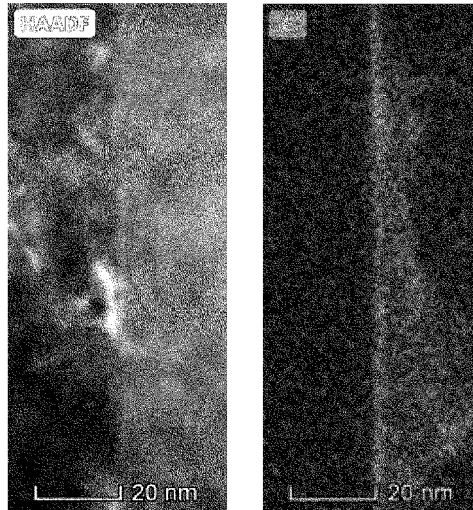


FIG. 1B



Description

TECHNICAL FIELD

5 **[0001]** The present disclosure relates to a high strength steel sheet, a method of producing the same, and a member.

BACKGROUND

10 **[0002]** Automotive steel sheets are required to have higher strength to improve fuel efficiency by reducing the weight of the automotive body. High strength steel sheets with a tensile strength of 1180 MPa or higher are required for frame parts. In addition, high bendability is required for steel sheets to be subjected to press working and formed into desired shapes. Furthermore, from the viewpoint of crashworthiness of automobiles, there are some automotive parts required not to easily deform to ensure driver's and passenger's living space during a collision, in addition to strength. The use of steel sheets with a high yield ratio is desirable for such automotive parts. In addition, high toughness is required to ensure that automotive parts do not fracture in a collision.

15 **[0003]** JP5728108B (PTL 1) discloses a high strength steel sheet with excellent formability and low-temperature toughness and a method of producing the same. JP6597939B (PTL 2) discloses a high strength steel sheet with excellent formability and anti-crash property, and a method of producing a high strength steel sheet with excellent formability and anti-crash property. JP6700398B (PTL 3) discloses a high yield ratio type high strength steel sheet and a method of producing the same.

CITATION LIST

Patent Literature

25 **[0004]**

PTL 1: JP5728108B

PTL 2: JP6597939B

30 PTL 3: JP6700398B

SUMMARY

(Technical Problem)

35 **[0005]** However, the yield ratio is not considered in PTLs 1 and 2. Toughness is not considered in PTL 3.

[0006] As described above, it is difficult to produce a high strength steel sheet with a tensile strength of 1180 MPa or higher, excellent bendability and toughness, and a high yield ratio using conventional techniques.

40 **[0007]** This disclosure has been made in view of these circumstances. It could be helpful to provide a high strength steel sheet with a tensile strength of 1180 MPa or higher, excellent bendability and toughness, and a high yield ratio, and a method of producing the same.

[0008] In this disclosure, high strength means that a tensile strength TS measured in accordance with JIS Z2241 is 1180 MPa or higher.

45 **[0009]** Excellent bendability means that a bending test specimen does not crack at the ridge of a tip thereof in a bend test conducted in accordance with JIS Z2248.

[0010] Excellent toughness means that the brittle-ductile transition temperature is -40 °C or lower in a Charpy impact test conducted in accordance with JIS Z2242.

[0011] A high yield ratio means that a ratio YS/TS of yield stress to tensile strength measured in accordance with JIS Z2241 is 0.80 or more.

50 (Solution to Problem)

[0012] We conducted diligent studies to accomplish the above-mentioned tasks and discovered the following.

55 (1) Crack initiation and propagation during bending and a fracture path during brittle fracture are along the prior austenite grain boundary. Therefore, refining crystal grains to complicate the fracture path and increasing the strength of the grain boundary are effective in improving bendability. To refine prior austenite grains, it is effective to keep the annealing temperature as low as possible at a temperature equal to or higher than 850 °C, which is an austenite

single phase region. On the other hand, grain boundary segregation of B is effective in strengthening the grain boundary, but the grain boundary segregation amount of B increases as being annealed at higher temperature. Therefore, to increase the grain boundary segregation amount of B while maintaining fine crystal grain size, annealing is performed at around 850 °C to obtain fine austenite grains, followed by rapid heating and rapid cooling. This promotes grain boundary segregation of B by diffusion while inhibiting crystal grain growth, thereby simultaneously achieving austenite grain size refinement and grain boundary segregation of B.

(2) Dislocations present in quenched martensitic microstructure are mobile dislocations that easily generate sliding motion at low stresses, resulting in low yield stresses in the martensitic microstructure. However, when the steel sheet after quenching is slightly processed, these dislocations move close to the grain boundary, where they become entangled and form immobile dislocations. This can increase the yield ratio of the steel sheet.

(3) Tempering the steel sheet at low temperatures causes carbon segregation on dislocations or cluster precipitation. Tempering at low temperatures the steel sheet after processing, in which dislocations are accumulated near the crystal grain boundary, forms a region of high C concentration (C-concentrated region) on the network along the grain boundary, which significantly increases the strength near the grain boundary. Since C is concentrated not only in the grain boundary but also in the matrix phases sandwiching the grain boundary, its strength-increasing effect is extremely large. Since the grain boundary is not easily deformed, the yield ratio also increases significantly due to the formation of the C-concentrated region.

[0013] This disclosure is based on the aforementioned discoveries and primary features thereof are described below.

[1] A high strength steel sheet comprising a chemical composition containing (consisting of), in mass%:

C: 0.10 % or more and 0.30 % or less;
 Si: 0.20 % or more and 1.20 % or less;
 Mn: 2.5 % or more and 4.0 % or less;
 P: 0.050 % or less;
 S: 0.020 % or less;
 Al: 0.10 % or less;
 N: 0.01 % or less;
 Ti: 0.100 % or less;
 Nb: 0.002 % or more and 0.050 % or less; and
 B: 0.0005 % or more and 0.0050 % or less,

with the balance being Fe and inevitable impurities, and satisfying the following formula (1), wherein

the total area ratio of martensite and bainite is 95 % or more,
 the average grain size of prior austenite grains is 10 μm or less,
 the B concentration at a prior austenite grain boundary is 0.10 % or more in mass%,
 a C-concentrated region is provided along a martensitic grain boundary,
 the C concentration in the C-concentrated region is 4.0 times or more than the C content in the steel, and
 the C-concentrated region has a concentration width of 3 nm or more and 100 nm or less in a direction perpendicular to the martensitic grain boundary and a length of 100 nm or more in a direction parallel to the martensitic grain boundary:

$$([\%N]/14)/([\%Ti]/47.9) < 1.0 \dots (1),$$

in the formula (1), [%N] and [%Ti] indicate the N content and the Ti content in the steel in mass%, respectively.

[2] The high strength steel sheet according to [1] above, wherein the chemical composition further contains at least one element selected from, in mass%:

V: 0.100 % or less;
 Mo: 0.500 % or less;
 Cr: 1.00 % or less;
 Cu: 1.00 % or less;
 Ni: 0.50 % or less;
 Sb: 0.200 % or less;

Sn: 0.200 % or less;
Ta: 0.200 % or less;
W: 0.400 % or less;
Zr: 0.0200 % or less;
Ca: 0.0200 % or less;
Mg: 0.0200 % or less;
Co: 0.020 % or less;
REM: 0.0200 % or less;
Te: 0.020 % or less;
Hf: 0.10 % or less; or
Bi: 0.200 % or less.

[3] A high strength coated or plated steel sheet having a coated or plated layer on at least one surface of the high strength steel sheet according to [1] or [2] above.

[4] A method of producing a high strength steel sheet, comprising:

hot rolling a steel slab having the chemical composition according to [1] or [2] above to form a hot-rolled sheet;
cold rolling the hot-rolled sheet to form a cold-rolled sheet;
performing an annealing process in which the cold-rolled sheet is heated to a first heating temperature of 850 °C or higher and 920 °C or lower and held for 10 seconds or longer, the temperature is then raised to a second heating temperature of 1000 °C or higher and 1200 °C or lower at an average heating rate of 50 °C/s or more, and the sheet is cooled to 500 °C or lower at an average cooling rate of 50 °C/s or more within 5 seconds after reaching the second heating temperature,
after the annealing process, performing a rolling process in which the cold-rolled sheet is rolled at an elongation rate of 0.5 % or more to obtain a second cold-rolled sheet, and
after the rolling process, performing a reheating process in which the second cold-rolled sheet is held at a reheating temperature of 70 °C or higher and 200 °C or lower for 600 seconds or longer to obtain a high strength steel sheet.

[5] A method of producing a high strength coated or plated steel sheet, comprising a coating or plating process in which, after the annealing process according to [4] above and before the reheating process, at least one surface of the high strength steel sheet is subjected to coating or plating treatment to obtain a high strength coated or plated steel sheet.

[6] A member formed using the high strength steel sheet according to [1] or [2] above for at least a portion thereof.

[7] A member formed using the high strength coated or plated steel sheet according to [3] above for at least a portion thereof.

(Advantageous Effect)

[0014] According to this disclosure, it is possible to provide a high strength steel sheet with a tensile strength of 1180 MPa or higher, excellent bendability and toughness, and a high yield ratio, and a method of producing the same.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] In the accompanying drawings:
FIG. 1A and FIG. 1B are drawings illustrating an example of C-concentrated regions.

DETAILED DESCRIPTION

[0016] The following describes embodiments of the present disclosure. However, this disclosure is not limited to the following embodiments. First, description will be made on the appropriate range of the chemical composition of steel sheets and the reasons for its limitation. The "%" representations below indicating the chemical composition of the steel sheet are in "mass%" unless stated otherwise. In the present specification, a numerical range expressed by using "to" means a range including numerical values described before and after "to", as the lower limit value and the upper limit value.

C: 0.10 % or more and 0.30 % or less

[0017] In addition to strengthening the martensitic microstructure and bainitic microstructure, C has the effect of

strengthening the grain boundary by segregating at dislocations accumulated near the prior austenite grain boundary, thereby increasing bendability, toughness, and yield ratio. When the C content is less than 0.10 %, the area ratios of martensite and bainite decrease, and a TS of 1180 MPa or higher cannot be obtained. When the C content exceeds 0.30 %, carbon borides with B and iron are formed during annealing, and a sufficient amount of B cannot be segregated at the prior austenite grain boundary. The C content is preferably 0.11 % or more. The C content is preferably 0.28 % or less.

Si: 0.20 % or more and 1.20 % or less

[0018] Si is an element effective for solid solution strengthening and requires an addition of 0.20 % or more. On the other hand, Si is an element that stabilizes ferrite and raises the transformation temperature. Therefore, when the Si content exceeds 1.20 %, it is difficult to make the prior austenite grain size 10 μm or less. The Si content is preferably 0.50 % or more. The Si content is preferably 1.10 % or less.

Mn: 2.5 % or more and 4.0 % or less

[0019] Mn is effective in improving hardenability. When the Mn content is less than 2.5 %, the area ratios of martensite and bainite decrease, resulting in lower strength. On the other hand, when the Mn content exceeds 4.0 %, the segregated portions are excessively hardened, resulting in lower bendability. The Mn content is preferably 2.8 % or more. The Mn content is preferably 3.5 % or less.

P: 0.050 % or less

[0020] The P content is 0.050 % or less because P segregates at the prior austenite grain boundary and reduces toughness. No particular lower limit is placed on the P content, which may be 0 %. However, the P content is preferably 0.001 % or more because a P content of less than 0.001 % increases the production cost. The P content is preferably 0.025 % or less.

S: 0.020 % or less

[0021] The S content is 0.020 % or less because S segregates at the prior austenite grain boundary and reduces toughness. No particular lower limit is placed on the S content. However, the S content is preferably 0.0001 % or more because a S content of less than 0.0001 % increases the production cost. The S content is preferably 0.018 % or less.

Al: 0.10 % or less

[0022] Al is an element that acts as a deoxidizing material. To obtain such an effect, the Al content is preferably 0.005 % or more. On the other hand, when the Al content exceeds 0.10 %, ferrite is easily generated, and strength is reduced. The Al content is preferably 0.05 % or less.

N: 0.01 % or less

[0023] N forms nitrides with Nb and B, reducing the effect of Nb and B addition. Therefore, the N content is 0.01 % or less. No particular lower limit is placed on the N content. However, from the viewpoint of production cost, the N content is preferably 0.0001 % or more.

Ti: 0.100 % or less

[0024] Ti has the effect of fixing N in steel as TiN and inhibiting the generation of BN and NbN. To achieve these effects, the Ti content is preferably 0.005 % or more. On the other hand, when the Ti content exceeds 0.100 %, coarse Ti carbides are formed on the grain boundary, and toughness is reduced. The Ti content is preferably 0.05 % or less.

Nb: 0.002 % or more and 0.050 % or less

[0025] Nb precipitates as a solute or fine carbides and inhibits the growth of austenite grains during annealing. To achieve such an effect, the Nb content is 0.002 % or more. On the other hand, when the Nb content exceeds 0.050 %, not only does the effect saturate, but coarse Nb carbides precipitate and the toughness is reduced. The Nb content is preferably 0.005 % or more. The Nb content is preferably 0.040 % or less.

B: 0.0005 % or more and 0.0050 % or less

[0026] B segregates at the prior austenite grain boundary and has the effect of increasing grain boundary strength. To achieve such an effect, the B content is 0.0005 % or more. On the other hand, when the B content exceeds 0.0050 %, carbon borides are formed, and toughness is reduced. The B content is preferably 0.0010 % or more. The B content is preferably 0.0030 % or less.

$$([\%N]/14)/([\%Ti]/47.9) < 1.0 \dots (1)$$

[0027] To achieve the above-described effect of B and Nb addition, N, which readily combines with these elements, needs to be fixed by Ti. Therefore, the mole fraction of N is set to be smaller than the mole fraction of Ti. In other words, the N content and the Ti content in the steel are adjusted to satisfy the above formula (1). In the formula (1), [%N] and [%Ti] indicate the N content and the Ti content in the steel (mass%), respectively.

[Optional component]

[0028] The high strength cold-rolled steel sheet according to the embodiment may further contain at least one element selected from, in mass%: V: 0.100 % or less; Mo: 0.500 % or less; Cr: 1.00 % or less; Cu: 1.00 % or less; Ni: 0.50 % or less; Sb: 0.200 % or less; Sn: 0.200 % or less; Ta: 0.200 % or less; W: 0.400 % or less; Zr: 0.0200 % or less; Ca: 0.0200 % or less; Mg: 0.0200 % or less; Co: 0.020 % or less; REM: 0.0200 % or less; Te: 0.020 % or less; Hf: 0.10 % or less; or Bi: 0.200 % or less, in addition to the above-described chemical composition.

V: 0.100 % or less

[0029] V has the effect of forming fine carbides and increasing strength. When the V content exceeds 0.100 %, coarse V carbides precipitate, and toughness is reduced. No particular lower limit is placed on the V content, which may be 0.000 %. However, the V content is preferably 0.001 % or more because V has the effect of forming fine carbides and increasing strength.

Mo: 0.500 % or less

[0030] Mo has the effect of improving hardenability and increasing the fractions of bainite and martensite. When the Mo content exceeds 0.500 %, the effect is saturated. No particular lower limit is placed on the Mo content, which may be 0.000 %. However, the Mo content is preferably 0.010 % or more because Mo has the effect of improving hardenability and increasing the fractions of bainite and martensite.

Cr: 1.00 % or less

[0031] Cr has the effect of improving hardenability and increasing the fractions of bainite and martensite. When the Cr content exceeds 1.00 %, the effect is saturated. No particular lower limit is placed on the Cr content, which may be 0.000 %. However, the Cr content is preferably 0.01 % or more because Cr has the effect of improving hardenability and increasing the fractions of bainite and martensite.

Cu: 1.00 % or less

[0032] Cu has the effect of increasing strength by the formation of a solute. When the Cu content exceeds 1.00 %, intergranular cracking tends to be generated. No particular lower limit is placed on the Cu content, which may be 0.000 %. However, the Cu content is preferably 0.01 % or more because Cu has the effect of increasing strength by the formation of a solute.

Ni: 0.50 % or less

[0033] Ni has the effect of improving hardenability. However, when the Ni content exceeds 0.50 %, the effect is saturated. No particular lower limit is placed on the Ni content, which may be 0.000 %. However, the Ni content is preferably 0.01 % or more because Ni has the effect of improving hardenability.

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Sb: 0.200 % or less

5 **[0034]** Sb has the effect of suppressing surface oxidation, nitriding, and decarburization of steel sheets. However, when the Sb content exceeds 0.200 %, the effect is saturated. No particular lower limit is placed on the Sb content, which may be 0.000 %. However, the Sb content is preferably 0.001 % or more because Sb has the effect of suppressing surface oxidation, nitriding, and decarburization of steel sheets.

Sn: 0.200 % or less

10 **[0035]** Sn, like Sb, has the effect of suppressing surface oxidation, nitriding, and decarburization of steel sheets. When the Sn content exceeds 0.200 %, the effect is saturated. No particular lower limit is placed on the Sn content, which may be 0.000 %. However, the Sn content is preferably 0.001 % or more because Sn has the effect of suppressing surface oxidation, nitriding, and decarburization of steel sheets.

15 Ta: 0.200 % or less

20 **[0036]** Ta has the effect of forming fine carbides and increasing strength. When the Ta content exceeds 0.200 %, coarse Ta carbides precipitate, and toughness is reduced. No particular lower limit is placed on the Ta content, which may be 0.000 %. However, the Ta content is preferably 0.001 % or more because Ta has the effect of forming fine carbides and increasing strength.

W: 0.400 % or less

25 **[0037]** W has the effect of forming fine carbides and increasing strength. When the W content exceeds 0.400 %, coarse W carbides precipitate, and toughness is reduced. No particular lower limit is placed on the W content, which may be 0.000 %. However, the W content is preferably 0.001 % or more because W has the effect of forming fine carbides and increasing strength.

Zr: 0.0200 % or less

30 **[0038]** Zr has the effect of spheronizing the shape of inclusions, suppressing stress concentration, and improving toughness. When the Zr content exceeds 0.0200 %, a large amount of inclusions are formed, and toughness is reduced. No particular lower limit is placed on the Zr content, which may be 0.000 %. However, the Zr content is preferably 0.0001 % or more because Zr has the effect of spheronizing the shape of inclusions, suppressing stress concentration, and improving toughness.

Ca: 0.0200 % or less

40 **[0039]** Ca can be used as a deoxidizing material. When the Ca content exceeds 0.0200 %, a large amount of Ca-based inclusions are formed, and toughness is reduced. No particular lower limit is placed on the Ca content, which may be 0.000 %. However, the Ca content is preferably 0.0001 % or more because Ca can be used as a deoxidizing material.

Mg: 0.0200 % or less

45 **[0040]** Mg can be used as a deoxidizing material. When the Mg content exceeds 0.0200 %, a large amount of Mg-based inclusions are formed, and toughness is reduced. No particular lower limit is placed on the Mg content, which may be 0.000 %. However, the Mg content is preferably 0.0001 % or more because Mg can be used as a deoxidizing material.

50 Co: 0.020 % or less

55 **[0041]** Co has the effect of increasing strength by solid solution strengthening. When the Co content exceeds 0.020 %, the effect is saturated. No particular lower limit is placed on the Co content, which may be 0.000 %. However, the Co content is preferably 0.001 % or more because Co has the effect of increasing strength by solid solution strengthening.

REM: 0.0200 % or less

[0042] REM has the effect of spheronizing the shape of inclusions, suppressing stress concentration, and improving toughness. When the REM content exceeds 0.0200 %, a large amount of inclusions are formed, and toughness is reduced. No particular lower limit is placed on the REM content, which may be 0.000 %. However, the REM content is preferably 0.0001 % or more because REM has the effect of spheronizing the shape of inclusions, suppressing stress concentration, and improving toughness.

Te: 0.020 % or less

[0043] Te has the effect of spheronizing the shape of inclusions, suppressing stress concentration, and improving toughness. When the Te content exceeds 0.020 %, a large amount of inclusions are formed, and toughness is reduced. No particular lower limit is placed on the Te content, which may be 0.000 %. However, the Te content is preferably 0.001 % or more because Te has the effect of spheronizing the shape of inclusions, suppressing stress concentration, and improving toughness.

Hf: 0.10 % or less

[0044] Hf has the effect of spheronizing the shape of inclusions, suppressing stress concentration, and improving toughness. When the Hf content exceeds 0.10 %, a large amount of inclusions are formed, and toughness is reduced. No particular lower limit is placed on the Hf content, which may be 0.000 %. However, the Hf content is preferably 0.01 % or more because Hf has the effect of spheronizing the shape of inclusions, suppressing stress concentration, and improving toughness.

Bi: 0.200 % or less

[0045] Bi has the effect of reducing segregation and improving bendability. When the Bi content exceeds 0.200 %, a large amount of inclusions are formed, and bendability is reduced. No particular lower limit is placed on the Bi content, which may be 0.000 %. However, the Bi content is preferably 0.001 % or more because Bi has the effect of reducing segregation and improving bendability.

[0046] The balance other than the above-described components is Fe and inevitable impurities. The effect of this disclosure is not impaired when each of the contents of the above optional components is less than the lower limit. Thus, these optional components are treated as inevitable impurities when they are contained with a content that is less than the lower limit.

[Steel microstructure]

[0047] Next, a steel microstructure of the high strength steel sheet will be described.

Martensite and bainite: total area ratio of 95 % or more

[0048] Both martensite and bainite are hard phases and are necessary to achieve a TS of 1180 MPa or higher. Therefore, the total area ratio of martensite and bainite is 95 % or more. The total area ratio of martensite and bainite is preferably 96 % or more. No particular upper limit is placed on the total area ratio of martensite and bainite, which may be 100 %.

[0049] The steel microstructure may contain residual microstructures other than martensite and bainite. The residual microstructures include ferrite, residual austenite, and cementite. The residual microstructures are 5 % or less of the total area ratio.

[0050] The area ratio of each microstructure is measured as follows. The area ratio of residual austenite is obtained by chemically polishing the rolled surface of a test specimen taken from each steel sheet up to 1/4t of the sheet thickness, measuring the X-ray diffraction intensity and diffraction peak positions of the polished surface using an X-ray diffraction (XRD) device, calculating the volume fraction, and considering the volume fraction as the area ratio of residual austenite. Next, a cross section of each steel sheet taken in the sheet thickness direction parallel to the rolling direction is polished and then etched with 3 % nital, and the 1/4t position of the sheet thickness is used as the observation plane. SEM images in three fields of view are taken of the observation plane at a magnification of 2000x. The total area ratio of martensite, bainite, and residual austenite and the area ratio of microstructures (ferrite and cementite) other than martensite, bainite, and residual austenite are determined by image analysis of the obtained SEM images. The area ratio of martensite and bainite is determined by subtracting the area ratio of residual austenite obtained by XRD from the area ratio of martensite,

bainite, and residual austenite obtained by image analysis. The average value of the three fields of view is taken as the area ratio of the microstructure.

Average grain size of prior austenite grains: 10 μm or less

[0051] Toughness and bendability can be improved by refining crystal grains and complicating a crack propagation path. Further refining crystal grains and strengthening has the effect of increasing yield stress. To obtain these effects, the average grain size of prior austenite grains needs to be 10 μm or less. The average grain size of prior austenite grains is preferably 9 μm or less. No particular lower limit is placed on the average grain size of prior austenite grains. However, from the viewpoint of production technology, the average grain size of prior austenite grains is preferably 1 μm or more.

[0052] The average grain size of prior austenite grains is measured as follows. A cross section of each steel sheet taken in the sheet thickness direction parallel to the rolling direction is polished and then etched with picral, and three-fields-of-view SEM images are taken of the microstructure at the 1/4t position of the sheet thickness with a magnification of 2000x in three fields of view. The grain size of each prior austenite grain is determined from the obtained microstructure image by image analysis, and the average value of the three fields of view is considered as the average grain size of prior austenite grains.

B concentration at prior austenite grain boundary: 0.10 % or more in mass%

[0053] B can strengthen the grain boundary by segregating at the prior austenite grain boundary and improve toughness and bendability. This effect can be achieved when the B concentration at the prior austenite grain boundary is 0.10 % or more in mass%. The B concentration at the prior austenite grain boundary is preferably 0.15 % or more, and more preferably 0.20 % or more in mass%. No upper limit is placed on the B concentration at the prior austenite grain boundary. However, the B concentration at the prior austenite grain boundary is preferably less than 20 % to suitably prevent precipitation of hard carbon borides on the grain boundary and to further improve toughness.

[0054] The B concentration at the prior austenite grain boundary is measured as follows. A needle sample is prepared from the region containing the prior austenite grain boundary by the SEM-Focused Ion Beam (FIB) method. The obtained needle sample is subjected to 3DAP analysis using a 3Dimensional Atom Probe (3DAP) instrument (LEAP 4000X Si, made by AMETEK). The measurement is performed in laser mode. The B concentration at the prior austenite grain boundary is determined from the number of B ions and the number of other ions, which are detected from the prior austenite grain boundary.

C-concentrated region

[0055] Bendability and yield ratio can be improved by strengthening the martensitic grain boundary and the matrix phases sandwiching the martensitic grain boundary by C concentration. In this specification, "martensitic grain boundary" includes all of the prior austenite grain boundary, the block grain boundary, and the packet grain boundary that exist in martensite and bainite. FIG. 1A and FIG. 1B each illustrate an example of the C-concentrated region. FIG. 1A illustrates an observation result of a C-concentrated region that exists in the block grain boundary and the packet grain boundary. FIG. 1B illustrate an observation result of a C-concentrated region that exists in the prior austenite grain boundary. In FIG. 1A and FIG. 1B, the drawing on the left is an example of the observation result using a scanning transmission electron microscope (STEM), indicating the presence of a martensitic grain boundary in the center of the drawing. The drawing on the right is an example of the observation result of the C concentration amount using the STEM. From these drawings, it can be seen that there is a C-concentrated region along the martensitic grain boundary and across the base metals sandwiching the martensitic grain boundary.

C concentration in C-concentrated region: 4.0 times or more than C content in steel

[0056] Sufficient grain boundary strength can be achieved when C is concentrated to 4.0 times or more than the C content in the steel, in the C-concentrated region. That is, the C concentration in the C-concentrated region satisfies the following formula (2).

$$\text{C concentration in C-concentrated region (mass\%)/C content in steel (mass\%)} \geq 4.0 \quad (2)$$

[0057] The C concentration in the C-concentrated region is preferably 4.5 times or more than the C content in the steel. No particular upper limit is placed on the C concentration in the C-concentrated region. However, the C concentration

is preferably 6 % or less to suitably prevent cementite precipitation and suitably prevent decrease in solute C concentration.

C-concentrated region: Concentration width of 3 nm or more and 100 nm or less in direction perpendicular to martensitic grain boundary

[0058] As illustrated in FIG. 1A and FIG. 1B, bendability and yield ratio can be improved by strengthening not only the martensitic grain boundary but also the matrix phases sandwiching the martensite grain boundary by C concentration. Therefore, the C-concentrated region is formed in a direction perpendicular to the martensitic grain boundary with a concentration width of 3 nm or more and 100 nm or less. When the concentration width of the C-concentrated region is less than 3 nm, the above effect is small. On the other hand, when the width of the C-concentrated region exceeds 100 nm, C cannot be sufficiently concentrated at the grain boundary and near the grain boundary. The width of the C-concentrated region is preferably 3.5 nm or more. The width of the C-concentrated region is preferably 80 nm or less.

C-concentrated region: Length of 100 nm or more in direction parallel to martensitic grain boundary

[0059] To achieve excellent bendability and yield ratio, it is important to strengthen the martensitic grain boundary into a network by C segregation. Therefore, the C-concentrated region is formed with a length of 100 nm or more in a direction parallel to the martensitic grain boundary. When the length of the C-concentrated region is less than 100 nm, fracture and yielding occur from breaks in the C-concentrated region. The C-concentrated region preferably exists with a length of 120 nm or more in the direction parallel to the martensitic grain boundary. No upper limit is placed on the length of the C-concentrated region along the martensitic grain boundary. The C-concentrated region may exist so as to cover the entire length of the martensitic grain boundary.

[0060] The C concentration, concentration width, and length of the C-concentrated region are measured as follows. A thin film sample is prepared from the region including the martensite grain boundary by the SEM-FIB method and the area analysis of C is performed by STEM and energy dispersive X-ray spectroscopy (EDS). An analytical transmission electron microscope Talos F200X (made by FEI) is used for the analysis. The thin film sample is tilted so that the martensitic grain boundary is parallel to the electron beam, and the area analysis in a region of 200 nm × 500 nm is performed. The analysis length in the direction parallel to the martensitic grain boundary (direction along the martensitic grain boundary) is 500 nm. The area analysis data is integrated in the direction parallel to the martensitic grain boundary to obtain a line profile with a length of 200 nm in the direction perpendicular to the martensitic grain boundary. In the line profile of C concentration, the half value of the maximum value of the line profile is determined, and the width that is equal to or more than the half value on the line profile is considered as the concentration width of the C-concentrated region. The C concentration in the C-concentrated region is determined by quantitative analysis of EDS for the concentration width. The length of the C-concentrated region is measured in the direction parallel to the martensitic grain boundary in the area analysis of C. The obtained length is considered as the length of the C-concentrated region along the martensitic grain boundary.

[0061] According to this disclosure, it is possible to provide a high strength steel sheet with a tensile strength of 1180 MPa or higher. The tensile strength of the high strength steel sheet is preferably 1250 MPa or higher.

[0062] The above-described high strength steel sheet may have a coated or plated layer on at least one surface. One of a hot-dip galvanized layer, a galvanized layer, and an electrogalvanized layer is preferred as the coated or plated layer. No particular limitation is placed on the composition of the coated or plated layer. Any known composition can be used.

[0063] No particular limitation is placed on the composition of the hot-dip galvanized layer. A common composition may be used. In an example, the coated or plated layer contains: Fe: 20 mass% or less; and Al: 0.001 mass% or more and 1.0 mass% or less, and further contains one or two or more selected from the group consisting of Pb, Sb, Si, Sn, Mg, Mn, Ni, Cr, Co, Ca, Cu, Li, Ti, Be, Bi, and REM by the total content thereof in the range of 0 mass% or more and 3.5 mass% or less, with the balance being Zn and inevitable impurities. When the coated or plated layer is a hot-dip galvanized layer, in an example, the Fe content in the coated or plated layer is less than 7 mass%. When the coated or plated layer is a galvanized layer, in an example, the Fe content in the coated or plated layer is 7 mass% or more and 15 mass% or less. More preferably, the Fe content in the coated or plated layer is 8 mass% or more, and the Fe content in the coated or plated layer is 13 mass% or less.

[0064] No particular limitation is placed on the coating weight. However, the coating weight per one surface of the high strength steel sheet is preferably 20 g/m² or more, and the coating weight per one surface of the high strength steel sheet is preferably 80 g/m² or less. In an example, the coated or plated layer is formed on the front and back surfaces of the high strength steel sheet.

[0065] Next, a method of producing a high strength steel sheet will be described.

[0066] First, a steel slab having the above-described chemical composition is produced. Steel materials are first smelted to produce molten steel having the above-described chemical composition. No particular limitation is placed on

the smelting method. Any of known smelting methods, such as converter smelting and electric furnace smelting, can be applied. The resulting molten steel is solidified to produce a steel slab (slab). No particular limitation is placed on the method of producing a steel slab from molten steel. Continuous casting, ingot casting, thin slab casting, or other methods can be used. The steel slab may be cooled once and then heated again before hot rolling, or a casted steel slab may be continuously hot rolled without cooling it to room temperature. In consideration of rolling load and scale generation, the slab heating temperature is preferably 1100 °C or higher, and the slab heating temperature is preferably 1300 °C or lower. No particular limitation is placed on the slab heating method. For example, the slab can be heated in a heating furnace in accordance with a conventional method.

[Hot rolling]

[0067] Next, the heated steel slab is hot rolled to form a hot-rolled sheet. No particular limitation is placed on the hot rolling. Hot rolling may be performed in accordance with a conventional method. No particular limitation is placed on the cooling after hot rolling. The hot-rolled sheet is cooled to a coiling temperature. The hot-rolled sheet is then coiled in a coil form. The coiling temperature is preferably 400 °C or higher. This is because coiling is easier without increasing the strength of the hot-rolled sheet when the coiling temperature is 400 °C or higher. The coiling temperature is more preferably 550 °C or higher. The coiling temperature is preferably 750 °C or lower to suitably prevent generation of thick scale and to further improve yield. Before pickling, the hot-rolled sheet may be subjected to heat treatment to be softened.

[Pickling]

[0068] Optionally, scale is removed from the hot-rolled sheet that has been coiled in a coil form. No particular limitation is placed on the method of removing scale. However, pickling is preferably performed while rewinding the hot-rolled coil to completely remove scale. No particular limitation is placed on the pickling method. Pickling may be performed in accordance with a conventional method.

[Cold rolling]

[0069] The hot-rolled sheet, which has been optionally descaled, is cleaned as appropriate, and then cold-rolled to form a cold-rolled sheet. No particular limitation is placed on the method of cold rolling. Cold rolling may be performed in accordance with a conventional method.

[Annealing]

[0070] Next, an annealing process is performed, in which the cold-rolled sheet is heated to a first heating temperature of 850 °C or higher and 920 °C or lower and held for 10 seconds or longer, then the temperature is raised to a second heating temperature of 1000 °C or higher and 1200 °C or lower at an average heating rate of 50 °C/s or more, and the sheet is cooled to 500 °C or lower at a cooling rate of 50 °C/s or more within 5 seconds after reaching the second heating temperature.

First heating temperature of 850 °C or higher and 920 °C or lower

[0071] The cold-rolled sheet is then heated to the first heating temperature of 850 °C or higher and 920 °C or lower and held for 10 seconds or longer. To obtain a martensite and bainite-dominated microstructure, annealing is performed at the first heating temperature in the austenite single phase region. When the first heating temperature is less than 850 °C, ferrite is generated, and strength is reduced. On the other hand, when the first heating temperature exceeds 920 °C, the austenite grain size exceeds 10 μm, and bendability, toughness, and yield ratio are reduced because the subsequent processes cannot reduce the grain size. The first heating temperature is preferably 860 °C or higher. The first heating temperature is preferably 900 °C or lower.

Holding time at first heating temperature: 10 seconds or longer

[0072] The holding time at the first heating temperature is 10 seconds or longer. By holding the sheet at the first heating temperature for 10 seconds or longer, the growth of austenite grain size is balanced by pinning by Nb carbides or growth inhibition by solute Nb. When the holding time is less than 10 seconds, the austenite grains are in the process of growing, and the effect of pinning by Nb carbides or growth inhibition by solute Nb does not occur during the subsequent rapid heating, and the prior austenite grain size exceeds 10 μm. No particular upper limit is placed on the holding time at the first heating temperature. However, from the viewpoint of productivity, the holding time at the first heating tem-

perature is preferably 60 seconds or shorter. The holding time at the first heating temperature is preferably 20 seconds or longer.

Second heating temperature of 1000 °C or higher and 1200 °C or lower

[0073] After holding the sheet at the first heating temperature, the sheet is annealed at high temperature while maintaining the austenite grain boundary at 10 μm or less to cause a sufficient amount of B to segregate at the grain boundary. When the second heating temperature is less than 1000 °C, B diffusion is slow, and grain boundary segregation is insufficient. When the second heating temperature exceeds 1200 °C, austenite grain growth is rapid, and the austenite grain size exceeds 10 μm. The second heating temperature is preferably 1020 °C or higher. The second heating temperature is preferably 1150 °C or lower.

Average heating rate: 50 °C/s or more

[0074] An average heating rate from the first heating temperature to the second heating temperature is 50 °C/s or more. When the average heating rate from the first heating temperature to the second heating temperature is less than 50 °C/s, the austenite grain size grows to more than 10 μm. No particular upper limit is placed on the average heating rate from the first heating temperature to the second heating temperature. However, the average heating rate is preferably 120 °C/s or less because excessive rapid heating is difficult to control. The average heating rate from the first heating temperature to the second heating temperature is preferably 80 °C/s or more.

Cooling at average cooling rate of 50 °C/s or more to 500 °C or lower within 5 seconds after reaching second heating temperature

[0075] After reaching the second heating temperature, rapid cooling is started within 5 seconds after reaching the second heating temperature without holding the sheet at the second heating temperature, and the rapid cooling is performed at an average cooling rate of 50 °C/s or more to 500 °C or lower. This can produce a steel microstructure with an austenite grain size of 10 μm or less and B segregated at the grain boundary by 0.1 % or more. Cooling is started immediately after the second heating temperature is reached because grain growth starts quickly after holding the sheet at the second heating temperature.

Average cooling rate: 50 °C/s or more

[0076] In the cooling after reaching the second heating temperature, an average cooling rate from the second heating temperature to 500 °C or lower is 50 °C/s or more. When the average cooling rate from the second heating temperature to 500 °C or lower is less than 50 °C/s, grain growth occurs during cooling. No particular upper limit is placed on the average cooling rate from the second heating temperature to 500 °C or lower. However, the average cooling rate is preferably 120 °C/s or less to facilitate control. The average cooling rate from the second heating temperature to 500 °C or lower is preferably 80 °C/s or more.

Cooling stop temperature: 500 °C or lower

[0077] To inhibit ferrite transformation, rapid cooling is performed to a cooling stop temperature of 500 °C or lower. The cooling stop temperature is preferably 450 °C or lower. No particular lower limit is placed on the cooling stop temperature. However, the cooling stop temperature is preferably 100 °C or higher.

[0078] After the above-described annealing process and before a reheating process, a coating or plating process may be performed, in which at least one surface of the high strength steel sheet is subjected to coating or plating treatment to obtain a high strength coated or plated steel sheet. After the coating or plating process, the high strength coated or plated steel sheet may be subjected to heat treatment to alloy the coated or plated layer of the high strength coated or plated steel sheet, resulting in a galvanized steel sheet.

After annealing process, rolling process in which rolling with an elongation rate of 0.5% or more is performed

[0079] After the above-described annealing process, a rolling process is performed, in which the cold-rolled sheet is rolled at an elongation rate of 0.5 % or more to obtain a second cold-rolled sheet. The cold-rolled sheet obtained in the preceding process contains many mobile dislocations. In this rolling process, the mobile dislocations accumulate at the grain boundary and become entangled to form immobile dislocations. When the elongation rate is less than 0.5 %, the effect is small. The elongation rate in the rolling process is preferably 0.6 % or more. No particular upper limit is placed

on the elongation rate in the rolling process. However, the elongation rate is preferably 2 % or less, for example, to reduce the load on the equipment.

After rolling process, reheating process in which second cold-rolled sheet is held at reheating temperature of 70 °C or higher and 200 °C or lower for 600 seconds or longer

[0080] After the above-described rolling process, the second cold-rolled sheet is tempered at low temperature in order to segregate C on the dislocations accumulated near the grain boundary or to generate clusters. When the reheating temperature is less than 70 °C, C diffusion is slow, and C is not concentrated near the grain boundary to a sufficient amount. On the other hand, when the reheating temperature exceeds 200 °C, tempering excessively proceeds, and cementite precipitates. The cementite precipitated at the grain boundary is likely to be a fracture origin, and the C concentration of the matrix phases around the cementite is reduced, resulting in reduced bendability and toughness. The reheating temperature is preferably 90 °C or higher. The reheating temperature is preferably 190 °C or lower.

Holding time at reheating temperature: 600 seconds or longer

[0081] When the holding time at the reheating temperature is less than 600 seconds, C diffusion is slow, and a sufficient amount of C concentration is not obtained. No particular upper limit is placed on the holding time at the reheating temperature. However, the holding time is preferably 43200 seconds (0.5 days) or shorter to prevent cementite precipitation. The holding time at the reheating temperature is preferably 800 seconds or longer.

[0082] In the case of reheating without the rolling process, C segregates at the grain boundary, and toughness is improved. However, the concentration width is narrow and regions except for the grain boundary is not strengthened, resulting in poor bendability. In addition, dislocations remain mobile dislocations, resulting in poor YR.

[0083] Production conditions other than those described above can be determined in accordance with conventional methods.

[Member]

[0084] It is possible to provide a member formed using the above-described high strength steel sheet or high strength coated or plated steel sheet, for at least a portion thereof. The above-described high strength steel sheet or high strength coated or plated steel sheet can be formed into a desired shape by press working, in an example, to form an automotive part. The automotive part may contain steel sheets other than the high strength steel sheet or high strength coated or plated steel sheet according to this embodiment, as its materials. According to this embodiment, it is possible to provide a high strength steel sheet with a TS of 1180 MPa or higher, bendability, toughness, and a high yield ratio. Therefore, the high strength steel sheet or high strength coated or plated steel sheet according to this embodiment is suitable for automotive parts that contribute to weight reduction of the automotive body. This high strength steel sheet or high strength coated or plated steel sheet can be suitably used for automotive parts, in particular, members used as skeletal structural parts or reinforcement parts in general.

EXAMPLES

[0085] Steel having the chemical compositions presented in Table 1, with the balance being Fe and inevitable impurities, was smelted in a converter furnace to form steel slabs. The resulting slabs were reheated, hot rolled, and then coiled to obtain hot-rolled coils. The hot-rolled coils were then subjected to pickling treatment while being rewound, and then cold rolled. The thickness of the hot-rolled sheets was 3.0 mm, and the thickness of the cold-rolled sheets was 1.2 mm. Annealing was performed in a continuous hot-dip galvanizing line under the conditions presented in Table 2 to obtain cold-rolled steel sheets, hot-dip galvanized steel sheets (GI), and galvanized steel sheets (GA). The hot-dip galvanized steel sheets were immersed in a plating bath at 460 °C to achieve a coating weight of 35 g/m² per surface. The galvanized steel sheets were produced by adjusting the coating weight to 45 g/m² per surface, followed by alloying treatment at 520 °C for 40 seconds. The resulting steel sheets were subjected to rolling and reheat treatment under the conditions presented in Table 2.

[0086] For each resulting steel sheet, the total area ratio of martensite and bainite, the prior austenite grain size, the B concentration at the prior austenite grain boundary, the C concentration in the C-concentrated region at the martensitic grain boundary (mass%)/the C content in the steel (mass%), the concentration width of the C-concentrated region, and the length along the martensite grain boundary in the C-concentrated region were evaluated according to the above-described methods. The tensile strength, yield ratio, toughness, and bendability were also evaluated according to the methods described below. The results are presented in Table 3.

[Tensile test]

[0087] The resulting steel sheets were subjected to a tensile test in accordance with JIS Z 2241. JIS No. 5 tensile test specimens were taken having a longitudinal direction perpendicular to the rolling direction, and the tensile test was conducted to measure the tensile strength (TS) and yield stress (YS). The tensile strength was considered good when the tensile strength TS was 1180 MPa or higher. A ratio of yield stress to tensile strength, $YR = YS/TS$, of 0.80 or higher indicates a high yield ratio.

[Charpy test]

[0088] Charpy impact test was conducted in accordance with JIS Z 2242. From each resulting steel sheet, a test specimen with a width of 10 mm, a length of 55 mm, and a 90° V-notch with a notch depth of 2 mm at the center of the length was taken such that the direction perpendicular to the rolling direction of the steel sheet was a V-notching direction. The Charpy impact test was then conducted in a test temperature range of -120 °C to +120 °C. The transition curve was determined from the obtained percent brittle fracture, and the temperature at which the percent brittle fracture reaches 50 % was determined as a brittle-ductile transition temperature. The toughness was considered good when the brittle-ductile transition temperature obtained from the Charpy test was -40 °C or lower. In the table, brittle-ductile transition temperatures of -40 °C or lower were indicated as "Excellent" for toughness, and brittle-ductile transition temperatures exceeding -40 °C were indicated as "Poor" for toughness.

[Bend test]

[0089] Bend test was conducted in accordance with JIS Z 2248. From each resulting steel sheet, a strip test specimen with a width of 30 mm and a length of 100 mm was taken such that the direction parallel to the rolling direction of the steel sheet was the axial direction in the bend test. Then, 90° V-bend test was conducted under a set of conditions including a pushing load of 100 kN and a pressing holding time of 5 seconds. The bendability was evaluated by the pass rate in the bend test. The bend test for five samples was conducted at the maximum R where R/t , the value obtained by dividing the bend radius (R) by the sheet thickness (t), is 5 or less (e.g., when the sheet thickness is 1.2 mm, the bend radius is 7.0 mm). Next, the presence of cracks at the ridge of the tip of the bending test specimen was evaluated. The bendability was considered good only when none of the five samples cracked, i.e., when the pass rate was 100 %. In the table, only cases when the pass rate was 100 % are indicated as "Excellent" for bendability and other cases are indicated as "Poor" for bendability. The presence of cracks was evaluated by measuring the ridge of the tip of the bending test specimen using a digital microscope (RH-2000: made by Hirox Co., Ltd.) with a magnification of 40x.

[Table 1]

[0090]

Table 1

Steel sample ID	Chemical composition (mass%)											([%N]/14)/([%Ti]/47.9)
	C	Si	Mn	P	S	Al	N	Ti	Nb	B	Other	
A	0.15	1.10	3.2	0.011	0.0010	0.040	0.0041	0.018	0.011	0.0012		0.78
B	<u>0.09</u>	0.95	2.9	0.015	0.0018	0.036	0.0035	0.021	0.015	0.0018		0.57
C	<u>0.34</u>	1.03	3.3	0.021	0.0020	0.042	0.0052	0.020	0.022	0.0018		0.89
D	0.19	0.65	3.5	0.018	0.0012	0.038	0.0038	0.018	<u>0.001</u>	0.0016		0.72
E	0.22	0.66	3.4	0.022	0.0016	0.040	0.0036	0.022	<u>0.082</u>	0.0017		0.56
F	0.24	0.82	3.0	0.016	0.0009	0.042	0.0044	0.021	0.035	<u>0.0001</u>		0.72
G	0.20	1.10	2.9	0.012	0.0014	0.039	0.0033	0.017	0.042	<u>0.0084</u>		0.66
H	0.19	0.78	3.4	0.016	0.0010	0.036	0.0058	0.015	0.027	0.0022		<u>1.32</u>

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(continued)

Steel sample ID	Chemical composition (mass%)											([%N]/14)/([%Ti]/47.9)
	C	Si	Mn	P	S	Al	N	Ti	Nb	B	Other	
I	0.16	0.85	3.2	0.011	0.0012	0.037	0.0042	0.022	0.031	0.0020	Cr 0.21, Mo 0.272	0.65
J	0.12	1.01	3.7	0.012	0.0009	0.039	0.0033	0.024	0.005	0.0021	V 0.080	0.47
K	0.22	0.81	2.8	0.018	0.0021	0.045	0.0061	0.032	0.018	0.0016	Cu 0.11, Ca 0.0005	0.65
L	0.27	0.96	2.7	0.010	0.0008	0.029	0.0032	0.015	0.032	0.0020	Ni 0.12, Ta 0.007	0.73
M	0.18	0.99	2.9	0.008	0.0015	0.039	0.0028	0.020	0.023	0.0015	Sb 0.009, Mg 0.0010	0.48
N	0.18	0.76	3.1	0.011	0.0009	0.039	0.0040	0.021	0.011	0.0022	Sn 0.008, Co 0.008	0.65
O	0.25	0.92	2.9	0.012	0.0014	0.044	0.0033	0.018	0.041	0.0021	REM 0.0022	0.63
P	0.17	0.91	3.1	0.013	0.0011	0.038	0.0028	0.021	0.021	0.0017	W 0.122, Zr 0.0018	0.46
Q	0.18	0.99	3.2	0.012	0.0013	0.035	0.0036	0.020	0.024	0.0022		0.62
R	0.19	0.85	2.9	0.011	0.0012	0.040	0.0038	0.018	0.016	0.0019	Te 0.005, Hf 0.02, Bi 0.002	0.72
Underlines indicate outside the appropriate range of this disclosure.												

[Table 2]

[0091]

Table 2

No.	Steel sample ID	First heating temperature (°C)	Holding time (s)	Second heating temperature (°C)	Average heating rate from first heating temperature to second heating temperature (°C/s)	Average cooling rate from second heating temperature to 500 °C or lower (°C/s)	Coating or plating	Elongation rate (%)	Reheating temperature (°C)	Holding time (s)	Remarks
1	A	870	40	1110	80	80	Without	1.2	170	1200	Example
2	A	860	30	1100	60	60	GI	1.4	180	800	Example
3	A	900	30	1140	80	80	GA	1.0	90	10800	Example
4	A	830	50	1150	80	80	GI	1.2	120	3600	Comparative Example
5	A	880	5	1120	80	80	Without	1.2	180	1500	Comparative Example
6	A	900	20	980	80	80	Without	1.0	150	2400	Comparative Example
7	A	890	40	1210	80	80	GA	0.8	140	3600	Comparative Example
8	A	860	40	1100	40	80	Without	0.6	100	7200	Comparative Example
9	A	870	30	1190	80	40	Without	0.8	150	2400	Comparative Example
10	B	860	30	1100	80	80	GA	0.8	160	1200	Comparative Example
11	C	880	40	1120	80	80	GI	0.6	120	3000	Comparative Example
12	D	900	40	1060	80	80	GA	1.2	170	1800	Comparative Example
13	E	910	50	1070	80	80	GA	0.6	100	10800	Comparative Example

(continued)

No.	Steel sample ID	First heating temperature (°C)	Holding time (s)	Second heating temperature (°C)	Average heating rate from first heating temperature to second heating temperature (°C/s)	Average cooling rate from second heating temperature to 500 °C or lower (°C/s)	Coating or plating	Elongation rate (%)	Reheating temperature (°C)	Holding time (s)	Remarks
14	<u>F</u>	900	30	1140	80	80	GA	1.2	150	2400	Comparative Example
15	<u>G</u>	890	40	1130	80	80	GA	0.6	120	1800	Comparative Example
16	<u>H</u>	890	40	1050	80	80	GA	0.8	140	2400	Comparative Example
17	<u>I</u>	860	50	1180	80	80	GA	1.2	180	700	Example
18	<u>J</u>	910	50	1150	80	80	GI	1.2	80	10800	Example
19	<u>K</u>	890	30	1130	80	80	GI	0.6	130	7200	Example
20	<u>L</u>	870	50	1030	80	80	Without	0.6	120	7200	Example
21	<u>M</u>	890	40	1130	80	80	GA	0.8	150	3600	Example
22	<u>N</u>	900	50	1140	80	80	GA	0.8	160	1500	Example
23	<u>O</u>	880	30	1040	80	80	GA	0.6	120	7200	Example
24	<u>P</u>	870	40	1110	80	80	GA	1.0	150	3600	Example
25	<u>Q</u>	900	40	1060	80	80	GA	1.0	140	3600	Example
26	<u>Q</u>	880	50	1120	80	80	GA	0.8	60	7200	Comparative Example
27	<u>Q</u>	910	40	1150	80	80	GA	0.8	150	500	Comparative Example
28	<u>Q</u>	900	40	1110	80	80	GA	1.0	230	1800	Comparative Example
29	<u>Q</u>	880	30	1040	80	80	GA	0.2	180	1200	Comparative Example

(continued)

No.	Steel sample ID	First heating temperature (°C)	Holding time (s)	Second heating temperature (°C)	Average heating rate from first heating temperature to second heating temperature (°C/s)	Average cooling rate from second heating temperature to 500 °C or lower (°C/s)	Coating or plating	Elongation rate (%)	Reheating temperature (°C)	Holding time (s)	Remarks
30	Q	900	40	1060	80	80	GA	<u>None</u>	140	3600	Comparative Example
31	R	890	40	1120	80	80	Without	0.8	160	900	Example
Underlines indicate outside the appropriate range of this disclosure.											

[Table 3]

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[0092]

Table 3

No.	Steel sample ID	Total area ratio of martensite and bainite (%)	Residual microstructure	Prior austenite grain size (μm)	B concentration at prior austenite grain boundary (mass%)	Concentration width of C-concentrated region (nm)	C concentration in C-concentrated region (mass%)/ C content in steel (mass%)	Length of C-concentrated region (nm)	TS (MPa)	YS (MPa)	YR	Toughness	Brittle-ductile transition temperature ($^{\circ}\text{C}$)	Bendability	Remarks
1	A	99	Residual γ	6	0.25	15	52	320	1283	1102	0.86	Excellent	-80	Excellent	Example
2	A	99	Residual γ	5	0.31	22	4.8	220	1318	1142	0.87	Excellent	-60	Excellent	Example
3	A	99	Residual γ	6	0.22	8	4.8	180	1291	1089	0.84	Excellent	-60	Excellent	Example
4	A	88	Ferrite	6	0.25	24	4.3	220	1052	793	0.75	Excellent	-80	Excellent	Comparative Example
5	A	99	Residual γ	12	0.43	15	42	310	1233	1022	0.83	Poor	-20	Poor	Comparative Example
6	A	99	Residual γ	8	0.07	10	4.6	280	1303	1084	0.83	Poor	0	Poor	Comparative Example
7	A	99	Residual γ	14	0.44	12	4.5	190	1228	984	0.80	Poor	-10	Poor	Comparative Example
8	A	99	Residual γ	15	0.38	8	4.2	260	1212	994	0.82	Poor	-20	Poor	Comparative Example
9	A	99	Residual γ	12	0.42	22	4.8	170	1233	1008	0.82	Poor	-30	Poor	Comparative Example
10	B	87	Ferrite	7	0.32	14	5.2	140	1030	721	0.70	Excellent	-60	Excellent	Comparative Example
11	C	99	Residual γ	8	0.06	28	4.1	200	1581	1320	0.83	Poor	0	Poor	Comparative Example
12	D	99	Residual γ	18	0.37	17	4.1	180	1333	1126	0.84	Poor	-20	Poor	Comparative Example

(continued)

No.	Steel sample ID	Total area ratio of martensite and bainite (%)	Residual microstructure	Prior austenite grain size (μm)	B concentration at prior austenite grain boundary (mass%)	Concentration width of C-concentrated region (nm)	C concentration in C-concentrated region (mass%)/ C content in steel (mass%)	Length of C-concentrated region (nm)	TS (MPa)	YS (MPa)	YR	Toughness	Brittle-ductile transition temperature ($^{\circ}\text{C}$)	Bendability	Remarks
13	E	99	Residual γ	5	0.28	16	4.9	230	1509	1288	0.85	Poor	-20	Poor	Comparative Example
14	F	99	Residual γ	6	0.00	10	4.4	220	1521	1289	0.85	Poor	0	Poor	Comparative Example
15	G	99	Residual γ	7	0.52	13	4.8	130	1490	1225	0.82	Poor	0	Poor	Comparative Example
16	H	99	Residual γ	12	0.04	14	4.7	180	1455	1206	0.83	Poor	0	Poor	Comparative Example
17	I	99	Residual γ	6	0.26	11	5.1	250	1236	1061	0.86	Excellent	-60	Excellent	Example
18	J	99	Residual γ	7	0.33	6	6.2	240	1202	1011	0.84	Excellent	-70	Excellent	Example
19	K	99	Residual γ	6	0.29	10	4.4	160	1521	1276	0.84	Excellent	-50	Excellent	Example
20	L	99	Residual γ	7	0.29	13	42	180	1522	1264	0.83	Excellent	-50	Excellent	Example
21	M	99	Residual γ	6	0.27	18	4.6	190	1366	1118	0.82	Excellent	-80	Excellent	Example
22	N	99	Residual γ	7	0.31	21	5.1	120	1229	1020	0.83	Excellent	-80	Excellent	Example
23	O	99	Residual γ	6	0.40	5	4.2	200	1502	1263	0.84	Excellent	-50	Excellent	Example
24	P	99	Residual γ	7	0.35	12	4.9	240	1202	1021	0.85	Excellent	-80	Excellent	Example
25	Q	99	Residual γ	8	0.34	13	52	230	1341	1130	0.84	Excellent	-60	Excellent	Example
26	Q	99	Residual γ	7	0.33	2	4.9	120	1386	1029	0.74	Poor	0	Poor	Comparative Example
27	Q	99	Residual γ	7	0.29	64	3.4	200	1404	1084	0.77	Poor	-20	Poor	Comparative Example

(continued)

No.	Steel sample ID	Total area ratio of martensite and bainite (%)	Residual microstructure	Prior austenite grain size (μm)	B concentration at prior austenite grain boundary (mass%)	Concentration width of C-concentrated region (nm)	C concentration in C-concentrated region (mass%)/ C content in steel (mass%)	Length of C-concentrated region (nm)	TS (MPa)	YS (MPa)	YR	Toughness	Brittle-ductile transition temperature ($^{\circ}\text{C}$)	Bendability	Remarks
28	Q	99	Residual γ	7	0.31	<u>130</u>	<u>1.8</u>	220	1306	975	0.75	Poor	0	Poor	Comparative Example
29	Q	99	Residual γ	7	0.42	4	4.1	<u>70</u>	1442	1081	0.75	Excellent	-60	Poor	Comparative Example
30	Q	99	Residual γ	8	0.29	2	<u>2.7</u>	<u>60</u>	1335	1021	0.76	Excellent	-50	Poor	Comparative Example
31	R	99	Residual γ	6	0.32	18	4.6	210	1290	1071	0.83	Excellent	-80	Poor	Example
Underlines indicate outside the appropriate range of this disclosure															

[0093] Table 3 presents that the examples each have a TS of 1180 MPa or higher, a yield ratio of 0.80 or higher, and excellent bendability and toughness. On the other hand, one or more of the TS, yield ratio, bendability, and toughness are poor in the comparative examples.

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Claims

1. A high strength steel sheet comprising a chemical composition containing, in mass%:

10 C: 0.10 % or more and 0.30 % or less;
 Si: 0.20 % or more and 1.20 % or less;
 Mn: 2.5 % or more and 4.0 % or less;
 P: 0.050 % or less;
 S: 0.020 % or less;
 15 Al: 0.10 % or less;
 N: 0.01 % or less;
 Ti: 0.100 % or less;
 Nb: 0.002 % or more and 0.050 % or less; and
 B: 0.0005 % or more and 0.0050 % or less,

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with the balance being Fe and inevitable impurities, and satisfying the following formula (1), wherein

the total area ratio of martensite and bainite is 95 % or more,
 the average grain size of prior austenite grains is 10 μm or less,
 25 the B concentration at a prior austenite grain boundary is 0.10 % or more in mass%,
 a C-concentrated region is provided along a martensitic grain boundary,
 the C concentration in the C-concentrated region is 4.0 times or more than the C content in the steel, and
 the C-concentrated region has a concentration width of 3 nm or more and 100 nm or less in a direction perpen-
 dicular to the martensitic grain boundary and a length of 100 nm or more in a direction parallel to the martensitic
 30 grain boundary:

$$([\%N]/14)/([\%Ti]/47.9) < 1.0 \dots (1),$$

35 in the formula (1), [%N] and [%Ti] indicate the N content and the Ti content in the steel in mass%, respectively.

2. The high strength steel sheet according to claim 1, wherein the chemical composition further contains at least one element selected from, in mass%:

40 V: 0.100 % or less;
 Mo: 0.500 % or less;
 Cr: 1.00 % or less;
 Cu: 1.00 % or less;
 Ni: 0.50 % or less;
 45 Sb: 0.200 % or less;
 Sn: 0.200 % or less;
 Ta: 0.200 % or less;
 W: 0.400 % or less;
 Zr: 0.0200 % or less;
 50 Ca: 0.0200 % or less;
 Mg: 0.0200 % or less;
 Co: 0.020 % or less;
 REM: 0.0200 % or less;
 Te: 0.020 % or less;
 55 Hf: 0.10 % or less; or
 Bi: 0.200 % or less.

3. A high strength coated or plated steel sheet having a coated or plated layer on at least one surface of the high

strength steel sheet according to claim 1 or 2.

4. A method of producing a high strength steel sheet, comprising:

hot rolling a steel slab having the chemical composition according to claim 1 or 2 to form a hot-rolled sheet;
cold rolling the hot-rolled sheet to form a cold-rolled sheet;
performing an annealing process in which the cold-rolled sheet is heated to a first heating temperature of 850 °C or higher and 920 °C or lower and held for 10 seconds or longer, the temperature is then raised to a second heating temperature of 1000 °C or higher and 1200 °C or lower at an average heating rate of 50 °C/s or more, and the sheet is cooled to 500 °C or lower at an average cooling rate of 50 °C/s or more within 5 seconds after reaching the second heating temperature,
after the annealing process, performing a rolling process in which the cold-rolled sheet is rolled at an elongation rate of 0.5 % or more to obtain a second cold-rolled sheet, and
after the rolling process, performing a reheating process in which the second cold-rolled sheet is held at a reheating temperature of 70 °C or higher and 200 °C or lower for 600 seconds or longer to obtain a high strength steel sheet.

5. A method of producing a high strength coated or plated steel sheet, comprising a coating or plating process in which, after the annealing process according to claim 4 and before the reheating process, at least one surface of the high strength steel sheet is subjected to coating or plating treatment to obtain a high strength coated or plated steel sheet.

6. A member formed using the high strength steel sheet according to claim 1 or 2 for at least a portion thereof.

7. A member formed using the high strength coated or plated steel sheet according to claim 3 for at least a portion thereof.

FIG. 1A

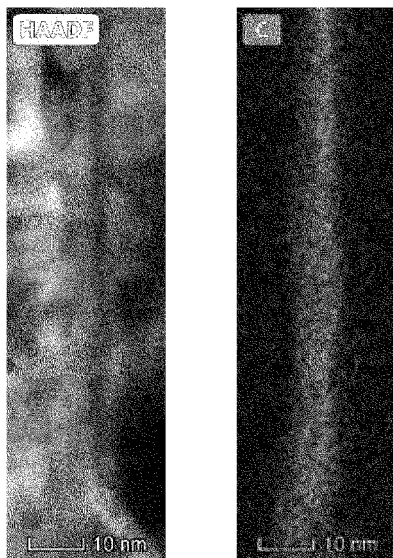
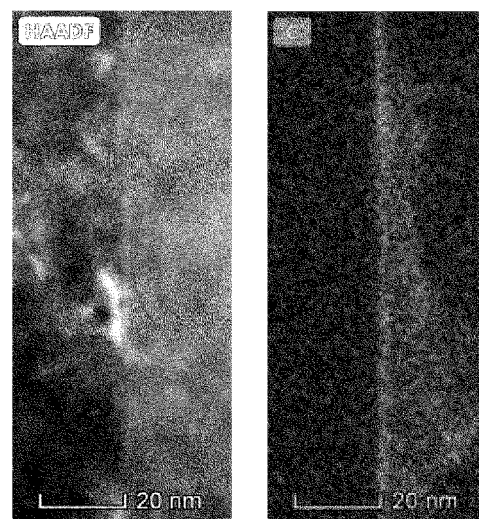


FIG. 1B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/024762

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; C21D 9/46(2006.01)i; C22C 38/14(2006.01)i; C22C 38/60(2006.01)i

FI: C22C38/00 301S; C21D9/46 G; C21D9/46 J; C22C38/00 301T; C22C38/00 301Z; C22C38/14; C22C38/60

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; C21D9/46-9/48

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 1971-2022

Registered utility model specifications of Japan 1996-2022

Published registered utility model applications of Japan 1994-2022

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 2021/033407 A1 (JFE STEEL CORP) 25 February 2021 (2021-02-25) claims, paragraphs [0008], [0023], [0055]	1-7
A	WO 2018/062380 A1 (JFE STEEL CORP) 05 April 2018 (2018-04-05) claims	1-7
A	JP 2013-104081 A (KOBE STEEL LTD) 30 May 2013 (2013-05-30) claims, tables 5, 6	1-7
A	WO 2020/162561 A1 (NIPPON STEEL CORP) 13 August 2020 (2020-08-13) claims	1-7

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

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

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/024762

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2021/033407 A1	25 February 2021	EP 3988679 A1 claims, paragraphs [0008], [0023], [0055] CN 114269961 A JP 6879441 B1	
WO 2018/062380 A1	05 April 2018	EP 3489382 A1 claims US 2019/0194775 A1 CN 109642294 A JP 6354921 B1	
JP 2013-104081 A	30 May 2013	(Family: none)	
WO 2020/162561 A1	13 August 2020	EP 3922745 A1 claims US 2022/0119908 A1 CN 113330133 A JP 6750772 B1	

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 5728108 B [0003] [0004]
- JP 6597939 B [0003] [0004]
- JP 6700398 B [0003] [0004]