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(54) STEEL SHEET, MEMBER, AND METHODS FOR PRODUCING SAID STEEL SHEET AND SAID MEMBER

(57) Provided are a high strength steel sheet having good delayed fracture resistance and a method for manufacturing the same.

The steel sheet contains, in mass %, C: 0.15 to 0.45%, Si: 1.5% or less, Mn: 1.7% or less, P: 0.03% or less, S: less than 0.0020%, sol Al: 0.20% or less, N: 0.005% or less, B: 0.0015 to 0.0100%, and at least one of Nb and Ti in a total amount of 0.005 to 0.080%, with the balance being Fe and incidental impurities. The area fraction of martensite with respect to the total area of the microstructure is 95 to 100%, and the diameter of prior γ grains is less than 11.0 um. The number density A of precipitates having an equivalent circular diameter of 500 nm or more satisfies the formula: A (particles / mm^2) $\leq$ 8.5 $\times$ 10^5 $\times$ [B].

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Description

Technical Field

[0001] The present invention relates to a steel sheet such as a high strength steel sheet for cold press forming that is to be subjected to cold press forming before being used for automobiles, etc. and also relates to a member using the steel sheet and methods for manufacturing the same.

Background Art

[0002] In recent years, steel sheets having a tensile strength TS of 1310 MPa grade or higher are being increasingly used for automobile frame members for the purpose of crash safety and weight reduction of automobiles. Steel sheets having a tensile strength TS of 1470 MPa grade or higher are being increasingly used for bumpers, impact beams, etc.

[0003] When a high strength steel sheet having a tensile strength TS of 1470 MPa grade or higher is subjected to cold press forming to produce a component, delayed fracture may occur due to an increase in residual stress in the component or deterioration of the delayed fracture resistance of the steel sheet itself.

[0004] The delayed fracture is a phenomenon described below. When a component with high stress applied thereto is placed in a hydrogen-intrusion environment, hydrogen enters a steel sheet included in the component. This causes a reduction in interatomic bonding force and local deformation, and microcracks are thereby formed. The microcracks grow, and fracture thereby occurs.

[0005] One technique for improving the delayed fracture characteristics is based on, for example, the knowledge that, by reducing the number of coarse precipitates that can serve as starting points of delayed fracture, the delayed fracture resistance is improved. Patent Literature 1 discloses a high strength steel sheet having good delayed fracture resistance. The steel sheet has a chemical composition containing, in mass %, C: 0.13% or more and 0.40% or less, Si: 0.02% or more and 1.5% or less, Mn: 0.4% or more and 1.7% or less, P: 0.030% or less, S: 0.0002% or more and less than 0.0010%, sol. Al: 0.01% or more and 0.20% or less, N: 0.0055% or less, O: 0.0025% or less, Nb: 0.002% or more and 0.035% or less, and Ti: 0.002% or more and 0.040% or less, with the balance being Fe and incidental impurities, wherein Nb and Ti are contained so as to satisfy formulas (1) and (2), wherein the steel sheet has a steel microstructure in which the total area fraction of martensite and bainite with respect to the total area of the microstructure is 95% or more and 100% or less, with the balance being one or two of ferrite and retained austenite, in which prior austenite grains have an average grain diameter of more than 5 um, and in which inclusion clusters satisfying conditions below and having a major axis of 20 to 80 um are present at 5 clusters / mm^2, and wherein the steel sheet has a tensile strength of 1320 MPa or more,

$$[\%\mathrm{Ti}] + [\%\mathrm{Nb}] > 0.007 \qquad (1)$$

$$[\%\mathrm{Ti}] \times [\%\mathrm{Nb}]^2 \leq 7.5 \times 10^{-6} \qquad (2)$$

where [%Nb] and [%Ti] are the content (%) of Nb and the content (%) of Ti, respectively.

[0006] Patent Literature 2 discloses a high strength cold rolled steel sheet having good hydrogen embrittlement resistance and good workability. The steel sheet has a chemical composition containing, in mass%, C: 0.05% to 0.30%, Si: 2.0% or less (including 0%), Mn: more than 0.1% and 2.8% or less, P: 0.1% or less, S: 0.005% or less, N: 0.01% or less, and Al: 0.01 to 0.50% or less and further containing one or two or more of Nb, Ti, and Zr in a total amount of 0.01% or more such that $[\%C] - [\%Nb] / 92.9 \times 12 - [\%Ti] / 47.9 \times 12 - [\%Zr] / 91.2 \times 12 > 0.03$ is satisfied, with the balance being iron and incidental impurities. The steel sheet has a microstructure containing tempered martensite at an area fraction of 50% or more (including 100%) with the balance being ferrite. Precipitates in tempered martensite are distributed such that the number of precipitates having an equivalent circular diameter of 1 to 10 nm is 20 or more per 1 μm^2 of the tempered martensite, that the number of precipitates having an equivalent circular diameter of 20 nm or more and containing one or two or more of Nb, Ti, and Zr is 10 or less per 1 μm^2 in the tempered martensite, and that the average grain diameter of ferrite grains surrounded by high-angle grain boundaries with a misorientation of 15° or more is 5 um or less.

Citation List

Patent Literature

[0007]

PTL 1: Japanese Patent No. 6388085
PTL 2: Japanese Patent No. 4712882

Summary of Invention

Technical Problem

[0008] However, the conventional techniques are not sufficient for obtaining a tensile strength TS of 1470 MPa or more and good delayed fracture resistance.

[0009] The present invention has been made to solve the foregoing problem, and it is an object to provide a steel sheet having a tensile strength of 1470 MPa or more (TS ≥ 1470 MPa) and good delayed fracture resistance, a member, and methods for manufacturing the same.

[0010] The good delayed fracture resistance means good delayed fracture resistance determined by the following evaluation.

(1) First, a strip-shaped test specimen is cut from a steel sheet (coil) obtained. Specifically, the test specimen has dimensions of 100 mm in a direction orthogonal to a rolling direction and 30 mm in the rolling direction and is cut from a position 1/4 of the width of the coil from a widthwise edge of the coil.

(2) To obtain the long-side end faces of the test specimen that have a length of 100 mm, the steel sheet is sheared, and the as-sheared test specimen (without machining for removing burrs) is subjected to bending such that the burrs are present on the outer peripheral side of the bend and fixed with a bolt while the shape at the time of bending is maintained.

[0011] In the shearing, the clearance is set to 13%, and the rake angle is set to 1°. The bending is performed such that the corner bending radius is 10 mm and the inner apex angle of the bend is 90° (V bending).

[0012] The punch used has a tip radius equal to the corner bending radius R described above and has a U-shape (the round tip portion of the punch has a semicircular shape, and the barrel portion of the punch has a thickness of 2R). The die used has a corner R of 30 mm. The depth when the punch pushes the steel sheet is adjusted, and the steel sheet is subjected to shaping such that the corner bending angle (the inner apex angle of the bend) is 90° (the steel sheet has a V shape).

[0013] The test specimen is clamped with a hydraulic jack such that the distance between flange ends of straight portions of the bent test specimen is the same as that at the time of the bending (such that an increase in the opening angle between the straight portions due to springback is canceled out), and then the test specimen in this state is fixed with the bolt. The bolt is inserted into elliptical holes (minor axis: 10 mm, major axis: 15 mm) formed in advance at positions 10 mm inward from the short side edges of the strip-shaped test specimen to thereby fix the test specimen.

[0014] (3) The bolted test specimen is immersed in a solution prepared by mixing a 0.1% by mass aqueous ammonium thiocyanate solution and a McIlvaine buffer solution at a ratio of 1:1 and having a pH adjusted to 8.0, and a delayed fracture resistance evaluation test is performed. The temperature of the solution is 20°C, and the amount of the solution per 1 cm^3 of the surface area of the test specimen is 20 mL.

[0015] (4) The presence or absence of a visually observable crack (having a length of 1 mm or more) is checked after a lapse of 24 hours. A test specimen with no crack observed is considered to have good delayed fracture resistance.

Solution to Problem

[0016] The inventors of the present invention have conducted extensive studies in order to solve the foregoing problem and found that, when all the following conditions are satisfied, the delayed fracture resistance can be significantly improved.

i) The area fraction of martensite is 95% or more.
ii) The average grain diameter of prior austenite grains (prior γ gain diameter) is less than 11.0 μm.
iii) The number density A of precipitates having an equivalent circular diameter of 500 nm or more satisfies the following condition.

$$A\ (\text{particles}\ /\ \text{mm}^2) \leq 8.5 \times 10^5 \times [B]$$

[0017] Here, [B] is the content of B (% by mass).

[0018] The present invention has been completed as a result of further studies based on the above findings and is summarized as follows.

[1] A steel sheet having a chemical composition containing, in mass %,

C: 0.15% or more and 0.45% or less,
Si: 1.5% or less,
Mn: 1.7% or less,
P: 0.03% or less,
S: less than 0.0020%,
sol. Al: 0.20% or less,
N: 0.005% or less,
B: 0.0015% or more and 0.0100% or less, and
at least one of Nb and Ti in a total amount of 0.005% or more and 0.080% or less,
with the balance being Fe and incidental impurities,
wherein the steel sheet has a microstructure in which the area of martensite with respect to the total area of the microstructure is 95% or more and 100% or less,
wherein prior austenite grains have an average grain diameter of less than 11.0 um, and
wherein the number density A of precipitates having an equivalent circular diameter of 500 nm or more satisfies formula (1) below:

$$A\ (\text{particles}\ /\ \text{mm}^2) \leq 8.5 \times 10^5 \times [B] \quad \text{formula (1)}$$

where [B] represents the content of B (% by mass).

[2] The steel sheet according to [1], wherein the chemical composition further contains, in mass %, one or two selected from Cu: 1.0% or less and Ni: 1.0% or less.
[3] The steel sheet according to [1] or [2], wherein the chemical composition further contains, in mass %, one or two or more selected from Cr: 1.0% or less, Mo: less than 0.3%, V: 0.5% or less, Zr: 0.2% or less, and W: 0.2% or less.
[4] The steel sheet according to any of [1] to [3], wherein the chemical composition further contains, in mass %, one or two or more selected from Ca: 0.0030% or less, Ce: 0.0030% or less, La: 0.0030% or less, REMs (excluding Ce and La): 0.0030% or less, and Mg: 0.0030% or less.
[5] The steel sheet according to any of [1] to [4], wherein the chemical composition further contains, in mass %, one or two selected from Sb: 0.1% or less and Sn: 0.1% or less.
[6] The steel sheet according to any of [1] to [5], wherein the steel sheet includes a coated layer on a surface thereof.
[7] A member formed using the steel sheet according to any of [1] to [6].
[8] A method for manufacturing a steel sheet, the method including:

heating a steel slab having the chemical composition according to any of [1] to [5] such that the surface temperature of the slab is increased from 1000°C to a heat holding temperature of 1250°C or higher at an average heating rate of 10°C/minute or less and then holding the steel slab at the heat holding temperature for 30 minutes or longer;
then setting a residence time at 900 to 1000°C to 20 seconds or longer and 150 seconds or shorter and performing hot finish rolling under the condition of a finish rolling temperature of 850°C or higher;
performing cooling at an average cooling rate of 40°C/second or more in a range from the finish rolling temperature to 650°C;
then performing coiling at a coiling temperature of 650°C or lower to obtain a hot rolled steel sheet;
subjecting the hot rolled steel sheet to cold rolling at a rolling reduction of 40% or more to obtain a cold rolled steel sheet; and
subjecting the cold rolled steel sheet to continuous annealing including
heating the cold rolled steel sheet from 400°C to an annealing temperature of 830 to 950°C at an average heating rate of 1.0°C/second or more,
holding the cold rolled steel sheet at the annealing temperature for 600 seconds or shorter,

cooling the cold rolled steel sheet from a cooling start temperature of 680°C or higher to a finish cooling temperature of 260°C or lower at an average cooling rate of 70°C/second or more, and
then holding the cold rolled steel sheet at a holding temperature of 150 to 260°C for 20 to 1500 seconds to thereby manufacture a steel sheet.

[9] The method for manufacturing a steel sheet according to [8], the method further including, after the continuous annealing, subjecting a surface of the steel sheet to coating treatment.
[10] A method for manufacturing a member, the method including the step of subjecting the steel sheet according to any of [1] to [6] to at least one of forming and joining to thereby obtain a member.

Advantageous Effects of Invention

[0019] According to the present invention, a steel sheet and a member having high strength and good delayed fracture resistance and methods for manufacturing the same are provided.

Description of Embodiments

[0020] Embodiments of the present invention will next be described.

[0021] The steel sheet of the present invention has a chemical composition containing, in mass %, C: 0.15% or more and 0.45% or less, Si: 1.5% or less, Mn: 1.7% or less, P:0.03% or less, S: less than 0.0020%, sol. Al: 0.20% or less, N: 0.005% or less, B: 0.0015% or more and 0.0100% or less, and at least one of Nb and Ti in a total amount to 0.005% or more and 0.080% or less, with the balance being Fe and incidental impurities. The steel sheet has a microstructure in which the area fraction of martensite with respect to the total area of the microstructure is 95% or more and 100% or less, and prior austenite grains (which hereinafter may be referred to also as prior γ grains) have an average grain diameter (prior γ grain diameter) of less than 11.0 um. The number density A of precipitates having an equivalent circular diameter of 500 nm or more satisfies formula (1) below.

$$A\ (\text{particles}\ /\ \text{mm}^2) \leq 8.5 \times 10^5 \times [B] \qquad \text{formula (1)}$$

[0022] Here, [B] represents the content of B (% by mass).

Chemical composition

[0023] A description will be given of the reasons for the limitations on the ranges of the chemical composition of the steel sheet of the present invention. "%" for the content of a component is "% by mass."

C: 0.15% or more and 0.45% or less

[0024] C is contained in order to improve hardenability to thereby obtain a martensite steel microstructure and in order to increase the strength of the martensite. To obtain a tensile strength of 1470 MPa or more (hereinafter denoted also as TS ≥ 1470 MPa), the content of C is 0.15% or more. From the viewpoint of increasing the tensile strength to thereby reduce the weight of automobile frame members, the content of C is preferably 0.20% or more and more preferably 0.27% or more. An excess portion of the C added may form iron carbide or segregate at grain boundaries and may cause deterioration of delayed fracture resistance. From the above points of view, the content of C is limited to 0.45% or less. The content of C is preferably 0.40% or less and more preferably 0.37% or less.

Si: 1.5% or less

[0025] Si is an element for strengthening through solid solution strengthening and is contained from the viewpoint of reducing the formation of film-shaped carbides when the steel sheet is tempered in a temperature range of 200°C or higher to thereby improve the delayed fracture resistance. Si is contained also from the viewpoint of reducing segregation of Mn in a thicknesswise central portion to thereby reduce the formation of MnS. Moreover, Si is contained in order to prevent decarbonization and deboronation due to oxidation of a surface layer during annealing in a continuous annealing line (CAL). The lower limit of the content of Si is not specified. However, from the viewpoint of obtaining the above effects, it is preferable that Si is contained in an amount of 0.02% or more. The content of Si is preferably 0.10% or more and more preferably 0.20% or more. When the content of Si is excessively large, a significant increase in a rolling load in hot rolling and cold rolling and a reduction in toughness occur. From the above points of view, the content of Si is 1.5%

or less (including 0%). The content of Si is preferably 1.2% or less and more preferably 1.0% or less.

Mn: 1.7% or less

[0026] Mn is contained in order to improve the hardenability of the steel and to adjust the area fraction of martensite within the prescribed range so that the desired strength is obtained. When the content of Mn is excessively large, segregation of Mn increases, and the workability and weldability deteriorate. Therefore, Mn is 1.7% or less. The content of Mn is preferably 1.5% or less and more preferably 1.3% or less. The lower limit of the content of Mn is not specified. To obtain the desired martensite area fraction in an industrially stable manner, it is preferable that Mn is contained in an amount of 0.2% or more.

P: 0.03% or less

[0027] P is an element that strengthens the steel. However, when the content of P is large, P segregates at grain boundaries to reduce the grain boundary strength, and therefore the delayed fracture resistance and spot weldability deteriorate significantly. From the above point of view, the content of P is 0.03% or less. The content of P is preferably 0.02% or less and more preferably 0.01% or less. The lower limit of the content of P is not specified. However, the practical lower limit that is at present industrially achievable is 0.002%.

S: Less than 0.0020%

[0028] S forms coarse MnS that can serve as a starting point of delayed fracture and therefore causes significant deterioration of the delayed fracture resistance. Therefore, to reduce the amount of MnS, the content of S must be at most less than 0.0020%. From the viewpoint of improving the delayed fracture resistance, the content of S is preferably less than 0.0010%, more preferably 0.0008% or less, and still more preferably 0.0006% or less. The lower limit of the content of S is not specified. However, the practical lower limit that is at present industrially achievable is 0.0002%.

Sol. Al: 0.20% or less

[0029] Al is contained in order to achieve sufficient deoxidization and reduce the number of inclusions in the steel. The lower limit of sol. Al is not particularly specified. To achieve deoxidization stably, the content of sol. Al is preferably 0.005% or more. The content of sol. Al is more preferably 0.01% or more and still more preferably 0.02% or more. When the content of sol. Al exceeds 0.20%, cementite formed during coiling is unlikely to dissolve in the annealing process, and the delayed fracture resistance deteriorates. Therefore, the content of sol. Al is 0.20% or less. The content of sol. Al is preferably 0.10% or less and more preferably 0.05% or less.

N: 0.005% or less

[0030] N forms precipitates such as TiN, (Nb,Ti)(C,N) in the steel and reduces the amounts of NbC, TiC, and (Nb,Ti)C that are effective in reducing the size of prior austenite grains through the formation of the precipitates. These precipitates hinder adjustment to the steel microstructure required in the present invention and adversely affect the delayed fracture resistance. To reduce the adverse effect, the content of N is 0.005% or less. The content of N is preferably 0.0040% or less. The lower limit of the content of N is not specified. However, the practical lower limit that is at present industrially achievable is 0.0006%.

B: 0.0015% or more and 0.0100% or less

[0031] B is an element that improves the hardenability of the steel and has an advantage in that martensite can be formed at the prescribed area fraction even when the content of Mn is small. B segregates at grain boundaries to increase the bonding force at the grain boundaries and reduces the segregation of P that causes a reduction in the grain boundary strength to thereby improve the delayed fracture resistance. When an excessively large amount of B is added, the amounts of $Fe_{23}(C,B)_6$ and BN increase. These precipitates serve as a starting point of delayed fracture, and the delayed fracture resistance rather deteriorates. Therefore, to obtain the effect of improving the delayed fracture resistance by the addition of B, it is necessary to increase the amount of solute B at the grain boundaries and reduce the number of B-based precipitates simultaneously. To obtain a sufficient amount of solute B at the grain boundaries in the steel with a prior γ grain diameter of 10 um or less, the content of B is 0.0015% or more. The content of B is preferably 0.0025% or more and more preferably 0.0040% or more. When the amount of B contained is more than 0.0100%, it is difficult to reduce the number of the B-based precipitates even when the hot rolling conditions and the annealing conditions are controlled. Therefore, the content of B is 0.0100% or less. The content of B is preferably 0.0090% or less and more preferably 0.0080% or less.

[0032] At least one of Nb and Ti in total amount of 0.005% or more and 0.080% or less

Nb and Ti contribute to an increase in strength through refinement of the internal structure of martensite and reduce the size of prior γ grains to thereby improve the delayed fracture resistance. From the above point of view, at least one of Nb and Ti is contained in a total amount of 0.005% or more. The total content of Nb and Ti is preferably 0.010% or more and more preferably 0.020% or more. When the total amount of at least one of Nb and Ti is more than 0.080%, Nb and Ti do not completely dissolve during reheating of the slab. In this case, the number of precipitates such as TiN, Ti(C,N), NbN, Nb(C,N), and (Nb,Ti)(C,N) having an equivalent circular diameter of 500 nm or more increases, and the precipitates serve as starting points of delayed fracture, so that the delayed fracture resistance rather deteriorates. Therefore, the upper limit of the total content of Nb and Ti is 0.080%. The total content of Nb and Ti (Ti + Nb) is preferably 0.07% or less and more preferably 0.06% or less.

[0033] The chemical composition of the steel sheet of the present invention contains the above components as basic components, with the balance being iron (Fe) and incidental impurities. Preferably, the steel sheet of the present invention has the chemical composition containing the basic components described above, with the balance being iron (Fe) and incidental impurities.

[0034] In the present invention, the chemical composition may contain one or two or more selected from the following (A) to (D).

(A) One or two selected from Cu: 1.0% or less and Ni: 1.0% or less in terms of % by mass.
(B) One or two or more selected from Cr: 1.0% or less, Mo: less than 0.3%, V: 0.5% or less, Zr: 0.2% or less, and W: 0.2% or less in terms of % by mass.
(C) One or two or more selected from Ca: 0.0030% or less, Ce: 0.0030% or less, La: 0.0030% or less, REMs (excluding Ce and La): 0.0030% or less, and Mg: 0.0030% or less in terms of % by mass.
(D) One or two selected from Sb: 0.1% or less and Sn: 0.1% or less in terms of % by mass.

Cu: 1.0% or less

[0035] Cu improves corrosion resistance in the use environment of automobiles. When Cu is contained, corrosion products cover the surface of the steel sheet, and the effect of preventing intrusion of hydrogen into the steel sheet is obtained. Cu is an element that is mixed when scrap is used as a raw material. When mixing of Cu is permissible, recycled materials can be used as raw materials, and the manufacturing cost can be reduced. From the above point of view, it is preferable that Cu is contained in an amount of 0.01% or more. From the viewpoint of improving the delayed fracture resistance, the content of Cu is preferably 0.05% or more. The content of Cu is more preferably 0.10% or more. However, when the content of Cu is excessively large, Cu causes surface defects. Therefore, the content of Cu is preferably 1.0% or less. As described above, when Cu is contained, the content of Cu is 1.0% or less. The content of Cu is more preferably 0.50% or less and still more preferably 0.30% or less.

Ni: 1.0% or less

[0036] Ni also is an element that has the effect of improving the corrosion resistance. Moreover, Ni has the effect of reducing surface defects that are likely to occur when Cu is contained. Therefore, from the above point of view, it is preferable that Ni is contained in an amount of 0.01% or more. The content of Ni is more preferably 0.05% or more and still more preferably 0.10% or more. When the content of Ni is excessively large, the formation of scales in a heating furnace is non-uniform. This causes surface defects, and a significant increase in cost occurs. Therefore, when Ni is contained, the content of Ni is 1.0% or less. The content of Ni is more preferably 0.50% or less and still more preferably 0.30% or less.

Cr: 1.0% or less

[0037] Cr may be added in order to obtain the effect of improving the hardenability of the steel. To obtain this effect, it is preferable that Cr is contained in an amount of 0.01% or more. The content of Cr is more preferably 0.05% or more and still more preferably 0.10% or more. However, when the content of Cr exceeds 1.0%, the rate of dissolution of cementite during annealing is reduced, and undissolved cementite remains present, so that the delayed fracture resistance at sheared end faces deteriorates. Moreover, pitting corrosion resistance deteriorates. In addition, chemical convertibility deteriorates. Therefore, when Cr is contained, the content of Cr is 1.0% or less. The delayed fracture resistance, the pitting corrosion resistance, and the chemical convertibility tend to deteriorate when the content of Cr exceeds 0.2%. From the viewpoint of preventing the deterioration of these properties, the content of Cr is more preferably 0.2% or less.

Mo: Less than 0.3%

[0038] Mo may be added in order to obtain the effect of improving the hardenability of the steel, the effect of forming fine carbides containing Mo and serving as hydrogen trapping sites, and the effect of improving the delayed fracture resistance through a reduction in the size of martensite grains. When large amounts of Nb and Ti are added, coarse precipitates of these elements are formed, and the delayed fracture resistance rather deteriorates. However, the solubility limit of Mo is larger than those of Nb and Ti. When Mo is added in combination with Nb and Ti, fine precipitates of Mo combined with Nb and Ti are formed, and the effect of refining the microstructure is obtained. Therefore, by adding Mo in combination with small amounts of Nb and Ti, the microstructure can be refined with no coarse precipitates remaining therein, and a large number of fine carbides can be dispersed in the microstructure, so that the delayed fracture resistance can be improved. To obtain this effect, it is preferable that Mo is contained in an amount of 0.01% or more. The content of Mo is more preferably 0.03% or more and still more preferably 0.05% or more. However, when Mo is contained in an amount of 0.3% or more, the chemical convertibility deteriorates. Therefore, when Mo is contained, the content of Mo is less than 0.3%. The content of Mo is preferably 0.2% or less.

V: 0.5% or less

[0039] V may be added in order to obtain the effect of improving the hardenability of the steel, the effect of forming fine carbides containing V and serving as hydrogen trapping sites, and the effect of improving the delayed fracture resistance through a reduction in the size of martensite grains. To obtain this effect, the content of V is preferably 0.003% or more. The content of V is more preferably 0.03% or more and still more preferably 0.05% or more. However, when V is contained in an amount of more than 0.5%, castability deteriorates significantly. Therefore, when V is contained, the content of V is 0.50 or less. The content of V is more preferably 0.3% or less and still more preferably 0.2% or less. The content of V is yet more preferably 0.1% or less.

Zr: 0.2% or less

[0040] Zr contributes to an increase in strength through a reduction in the size of prior γ grains and refinement of the internal structure of martensite and improves the delayed fracture resistance. Moreover, Zr forms fine Zr-based carbides and carbonitrides serving as hydrogen trapping sites to thereby increase the strength and improve the delayed fracture resistance. In addition, Zr improves the castability. From these points of view, the content of Zr is preferably 0.005% or more. The content of Zr is more preferably 0.010% or more and preferably 0.015% or more. However, when a large amount of Zr is added, the number of undissolved coarse ZrN- and ZrS-based precipitates remaining during heating of the slab in a hot rolling step increases, and the delayed fracture resistance of the sheared end faces deteriorates. Therefore, when Zr is contained, the content of Zr is 0.2% or less. The content of Zr is more preferably 0.1% or less and still more preferably 0.04% or less.

W: 0.2% or less

[0041] W contributes to an increase in strength and an improvement in the delayed fracture resistance through the formation of fine W-based carbides and carbonitrides serving as hydrogen trapping sites. From this point of view, it is preferable that W is contained in an amount of 0.005% or more. The content of W is more preferably 0.010% or more and still more preferably 0.030% or more. However, when a large amount of W is contained, the number of undissolved coarse precipitates remaining during heating of the slab in the hot rolling step increases, and the delayed fracture resistance of the sheared end faces deteriorates. Therefore, when W is contained, the content of W is 0.2% or less. The content of W is more preferably 0.1% or less.

Ca: 0.0030% or less

[0042] Ca fixes S as CaS and improves the delayed fracture resistance. To obtain this effect, it is preferable that Ca is contained in an amount of 0.0002% or more. The content of Ca is more preferably 0.0005% or more and still more preferably 0.0010% or more. However, when a large amount of Ca is added, the surface quality and the bendability deteriorate. Therefore, the content of Ca is preferably 0.0030% or less. As described above, when Ca is contained, the content of Ca is 0.0030% or less. The content of Ca is more preferably 0.0025% or less and still more preferably 0.0020% or less.

Ce: 0.0030% or less

[0043] Ce also fixes S and improves the delayed fracture resistance. To obtain this effect, it is preferable that Ce is contained in an amount of 0.0002% or more. The content of Ce is more preferably 0.0003% or more and still more preferably 0.0005% or more. However, when a large amount of Ce is added, the surface quality and the bendability deteriorate. Therefore, the content of Ce is preferably 0.0030% or less. As described above, when Ce is contained, the content of Ce is 0.0030% or less. The content of Ce is more preferably 0.0020% or less and still more preferably 0.0015% or less.

La: 0.0030% or less

[0044] La also fixes S and improves the delayed fracture resistance. To obtain this effect, it is preferable that La is contained in an amount of 0.0002% or more. The content of La is more preferably 0.0005% or more and still more preferably 0.0010% or more. However, when a large amount of La is added, the surface quality and the bendability deteriorate. Therefore, the content of La is preferably 0.0030% or less. As described above, when La is contained, the content of La is 0.0030% or less. The content of La is more preferably 0.0020% or less and still more preferably 0.0015% or less.

REMs: 0.0030% or less

[0045] REMs also fix S and improve the delayed fracture resistance. To obtain this effect, it is preferable that REMs are contained in an amount of 0.0002% or more. The content of REMs is more preferably 0.0003% or more and still more preferably 0.0005% or more. However, when a large amount of REMs is added, the surface quality and the bendability deteriorate. Therefore, the content of REMs is preferably 0.0030% or less. As descried above, when REMs are contained, the content of REMs is 0.0030% or less. The content of REMs is more preferably 0.0020% or less and still more preferably 0.0015% or less.

[0046] The REMs in the present invention are elements including scandium (Sc) with an atomic number of 21, yttrium (Y) with an atomic number of 39, lanthanoid elements from lanthanum (La) with an atomic number of 57 to lutetium (Lu) with an atomic number of 71 except for Ce and La. The concentration of REMs in the present invention is the total content of one or two or more elements selected from the REMs described above.

Mg: 0.0030% or less

[0047] Mg fixes O as MgO and improves the delayed fracture resistance. To obtain this effect, it is preferable that Mg is contained in an amount of 0.0002% or more. The content of Mg is more preferably 0.0005% or more and still more preferably 0.0010% or more. However, when a large amount of Mg is added, the surface quality and the bendability deteriorate. Therefore, the content of Mg is preferably 0.0030% or less. As described above, when Mg is contained, the content of Mg is 0.0030% or less. The content of Mg is more preferably 0.0020% or less and still more preferably 0.0015% or less.

Sb: 0.1% or less

[0048] Sb reduces oxidation and nitridation of the surface layer, and a reduction in the amounts of C and B is thereby prevented. Since the reduction in the amounts of C and B is prevented, the formation of ferrite in the surface layer is reduced, and therefore Sb contributes to an increase in strength and an improvement in the delayed fracture resistance. From these points of view, the content of Sb is preferably 0.002% or more. The content of Sb is more preferably 0.004% or more and still more preferably 0.006% or more. However, when the content of Sb exceeds 0.1%, the castability deteriorates. Moreover, Sb segregates at prior γ grain boundaries, and the delayed fracture resistance of the sheared end faces deteriorates. Therefore, the content of Sb is preferably 0.1% or less. As described above, when Sb is contained, the content of Sb is 0.1% or less. The content of Sb is more preferably 0.05% or less and still more preferably 0.02% or less.

Sn: 0.1% or less

[0049] Sn reduces oxidation and nitridation of the surface layer, and a reduction in the amounts of C and B is thereby prevented. Since the reduction in the amounts of C and B is prevented, the formation of ferrite in the surface layer is reduced, and therefore Sn contributes to an increase in strength and an improvement in the delayed fracture resistance. From these points of view, the content of Sn is preferably 0.002% or more. The content of Sn is preferably 0.003% or more. However, when the content of Sn exceeds 0.1%, the castability deteriorates, and Sn segregates at prior γ grain boundaries, so that the delayed fracture resistance of the sheared end faces deteriorates. Therefore, when Sn is contained, the content of Sn is 0.1% or less. The content of Sn is more preferably 0.05% or less and still more preferably 0.01% or less.

[0050] When any of the above elements is contained in an amount of less than its preferred lower limit, the element is considered to be contained as an incidental impurity.

Steel microstructure

[0051] The steel microstructure of the steel sheet of the present invention has the following structural features.

(Structural feature 1) The area fraction of martensite with respect to the total area of the microstructure is 95% or more and 100% or less.
(Structural feature 2) The average grain diameter of the prior austenite grains is less than 11.0 um.
(Structural feature 3) The number density A of precipitates having an equivalent circular diameter of 500 nm or more satisfies the following formula (1).

$$A\ (\text{particles} / \text{mm}^2) \leq 8.5 \times 10^5 \times [B] \qquad \text{formula (1)}$$

[0052] Here, [B] represents the content of B (% by mass).

[0053] Each of the structural features will be described.

(Structural feature 1) Area fraction of martensite with respect to total area of microstructure is 95% or more and 100% or less

[0054] To achieve a high strength of TS ≥ 1470 MPa and good delayed fracture resistance simultaneously, the area fraction of martensite in the steel microstructure is 95% or more. The area fraction is more preferably 99% or more and still more preferably 100%. When microstructures other than martensite are contained, the remaining microstructures include bainite, ferrite, and retained austenite (retained γ). Materials other than these microstructures are small numbers of carbides, sulfides, nitrides, and oxides. The area fraction of the remaining microstructures is 5% or less and preferably 1% or less. The martensite includes martensite that has not undergone tempering, which is the process of holding the steel sheet at about 150°C or higher for a prescribed time and includes self-tempering during the continuous cooling. In the steel microstructure, the area fraction of the martensite may be 100% with no other microstructures.

(Structural feature 2) Average grain diameter of prior austenite grains is less than 11.0 um

[0055] In steel having the steel microstructure in which the area fraction of martensite is 95% or more, the fracture surface of delayed fracture is often an intergranular fracture surface, and it is considered that the starting point of the delayed fracture and the initial crack growth path of the delayed fracture are on prior austenite grain boundaries. To prevent intergranular fracture, reducing the size of the prior austenite grains is effective. The reduction in the size of the prior austenite grains improves the delayed fracture resistance significantly. The mechanism of the improvement may be as follows. The reduction in the size of the prior austenite grains increases the area fraction of the prior austenite grain boundaries, and the concentrations of impurity elements such as P, which are grain boundary embrittlement elements, on the prior austenite grain boundaries may decrease. The reduction in the size of the prior austenite grains also contributes to an improvement in the tensile strength. From the viewpoint of the delayed fracture resistance and the strength, the average grain diameter of the prior austenite grains (the prior γ grain diameter) is less than 11.0 um. This average grain diameter is preferably 10 um or less, more preferably 7.0 um or less, and still more preferably 5.0 um or less.

[0056] (Structural feature 3) Number density A of precipitates having equivalent circular diameter of 500 nm or more satisfies formula below

$$A\ (\text{particles} / \text{mm}^2) \leq 8.5 \times 10^5 \times [B] \qquad \text{formula (1)}$$

[0057] Here, [B] represents the content of B (% by mass).

[0058] To control intergranular fracture in steel having a high strength of TS ≥ 1470 MPa, it is effective to reduce the size of the prior austenite grains and to segregate B at the grain boundaries to strengthen the grain boundaries. However, when the amount of B is simply increased, not only the amount of B segregating at the grain boundaries but also the number of B-based precipitates composed mainly of $Fe_{23}(C,B)_6$ and serving as starting points of delayed fracture increase, and therefore the delayed fracture resistance rather deteriorates. The inventors of the present invention have found that, when the hot-rolling conditions are controlled to reduce the number density A of precipitates having an equivalent circular diameter of 500 nm or more so that the following condition is satisfied, the improvement in the delayed fracture resistance through grain boundary strengthening by B and prevention of fracture starting from the precipitates can be achieved simultaneously.

$$A\ (\text{particles} / \text{mm}^2) \leq 8.5 \times 10^5 \times [B],$$

preferably A (particles / mm^2) $\leq 5.0 \times 10^5 \times$ [B], and more preferably A (particles / mm^2) $\leq 2.0 \times 10^5 \times$ [B].

[0059] Methods for measuring the structural features in the steel microstructure will be described.

[0060] The area fractions of martensite, bainite, and ferrite are measured as follows. An L cross section of a steel sheet (its cross section parallel to the rolling direction and perpendicular to the surfaces of the steel sheet (the cross section is hereinafter referred to also as a vertical cross section parallel to the rolling direction)) is polished and etched with nital. The cross section is observed at positions 1/4 of the thickness from a surface of the steel sheet under an SEM at a magnification of 2000X to capture microstructure photographs in four viewing areas. The captured microstructure photographs are subjected to image analysis to measure the area fractions. The martensite and bainite appear as gray or white microstructures under the SEM. The ferrite appears as dark contrast regions under the SEM. The martensite and bainite include thereinside small numbers of carbides, nitrides, sulfides, and oxides. However, since it is difficult to remove these particles, the area fractions of the martensite and bainite are the area fractions of regions including these particles.

[0061] The bainite has the following features. Specifically, the bainite is in the form of a plate having an aspect ratio of 2.5 or more and is a slightly black microstructure than the martensite. The width of the plate is 0.3 to 1.7 um. The distribution density of carbides having a diameter of 10 to 200 nm and present inside the bainite is 0 to 3 particles / μm^2.

[0062] The retained austenite (retained γ) is measured as follows. The surface layer of the steel sheet is chemically polished with oxalic acid to a depth of 200 um, and the area fraction of the retained austenite on the sheet surface is determined by an X-ray diffraction intensity method. The area fraction is computed from the integrated intensities of peaks from $(200)\alpha$, $(211)\alpha$, $(220)\alpha$, $(200)\gamma$, $(220)\gamma$, and $(311)\gamma$ diffraction planes that are measured using the Mo-Kα line.

[0063] The average grain diameter of the prior austenite grains (the prior γ grain diameter) is measured as follows. An L cross section of the steel sheet (its vertical cross section parallel to the rolling direction) is polished and etched with a chemical solution capable of etching the prior γ grain boundaries (for example, a saturated aqueous picric acid solution or a solution prepared by adding ferric chloride to the saturated aqueous picric acid solution). The cross section is observed at positions 1/4 of the thickness from a surface of the steel sheet under an optical microscope at a magnification of 500X to capture photographs in four viewing areas. In each of the obtained photographs, 15 lines are drawn in the thickness direction at intervals of 10 um or more in actual length, and 15 lines are drawn in the rolling direction at intervals of 10 um or more in actual length. Then the number of intersections of the grain boundaries and the lines is counted. A value obtained by dividing the total line length by the number of intersections is multiplied by 1.13, and the prior γ grain diameter (the average grain diameter of the prior austenite grains) can thereby be measured.

[0064] The number density A of the precipitates having an equivalent circular diameter of 500 nm or more is determined as follows. An L cross section of the steel sheet (its vertical cross section parallel to the rolling direction) is polished. In a region extending from a position 1/5 of the thickness of the steel sheet to a position 4/5 of the thickness, i.e., in a region extending from the position 1/5 of the thickness from a surface of the steel sheet to the position 4/5 of the thickness with the thicknesswise center positioned therebetween, images of 2 mm^2 regions are continuously captured under an SEM. The number density A is determined by counting the number of the above-described precipitates in the captured SEM photographs. The magnification of the captured images is 2000X. When each of the inclusion particles is subjected to component analysis, the inclusion particle is magnified by a factor of 10000 to analyze the precipitate. The precipitates having an equivalent circular diameter of 500 or more are precipitates containing B such as $Fe_{23}(C,B)_6$. Elemental analysis by energy dispersive X-ray spectrometry (EDS) using an acceleration voltage of 3 kV is performed to check for the presence of a peak of B. When a peak of B is observed, it is determined that the above-described precipitates are present.

[0065] When reheating of the slab is insufficient, the number of precipitates containing Nb and Ti increases, and these precipitates adversely affect the delayed fracture characteristics.

[0066] The equivalent circular diameter of a precipitate is the diameter of a perfect circle having the same area as the precipitate computed in an SEM photograph.

Tensile strength (TS): 1470 MPa or more

[0067] The deterioration of the delayed fracture resistance of a steel sheet is significant when the tensile strength of the steel sheet is 1470 MPa or more. One feature of the present invention is that the delayed fracture resistance is good even when the tensile strength is 1470 MPa or more. Therefore, in the present invention, it is necessary that the tensile strength be 1470 MPa or more. From the viewpoint of reducing the weight of automobile frame members, the tensile strength is preferably 1700 MPa or more. The tensile strength of the steel sheet of the present invention may be 2100 MPa or less.

[0068] The tensile strength can be measured as follows. A JIS No. 5 tensile test piece is cut from a position 1/4 of the coil width such that a direction orthogonal to the rolling direction is the longitudinal direction of the test piece, and the tensile strength is measured using a tensile test according to JIS Z 2241.

[0069] The steel sheet of the present invention may be a steel sheet having a coated layer on a surface thereof. The coated layer may be a zinc coating or may be a coating of another metal. The coated layer may be a hot-dip coated layer or an electroplated layer.

[0070] Next, a method for manufacturing the steel sheet of the present invention will be described.

[0071] The method for manufacturing the steel sheet of the present invention includes: heating a steel slab having the chemical composition described above such that the surface temperature of the slab is increased from 1000°C to a heat holding temperature of 1250°C or higher at an average heating rate of 10°C/minute or less and then holding the steel slab at the heat holding temperature for 30 minutes or longer; then setting a residence time at 900 to 1000°C to 20 seconds or longer and 150 seconds or shorter and performing hot finish rolling under the condition of a finish rolling temperature of 850°C or higher; performing cooling at an average cooling rate of 40°C/second or more in the range from the finish rolling temperature to 650°C; performing coiling at a coiling temperature of 650°C or lower to obtain a hot rolled steel sheet; subjecting the hot rolled steel sheet to cold rolling at a rolling reduction of 40% or more to obtain a cold rolled steel sheet; and subjecting the cold rolled steel sheet to continuous annealing including heating the cold rolled steel sheet from 400°C to an annealing temperature of 830 to 950°C at an average heating rate of 1.0°C/second or more, holding the cold rolled steel sheet at the annealing temperature for 600 seconds or shorter, cooling the cold rolled steel sheet from a cooling start temperature of 680°C or higher to a finish cooling temperature of 260°C or lower at an average cooling rate of 70°C/second or more, and then holding the cold rolled steel sheet at a holding temperature of 150 to 260°C for 20 to 1500 seconds.

Hot rolling

[0072] In the heating of the slab before the hot rolling, the average heating rate in the range of from 1000°C to the heat holding temperature of 1250°C or higher is 10°C/minute or less. In this manner, dissolution of sulfides is facilitated, and the number of inclusions and their size are reduced. Since the dissolution temperatures of Nb and Ti are high, the heat holding temperature is set such that the surface temperature of the slab reaches 1250°C or higher, and the holding time is set to 30 minutes or longer. In this manner, the dissolution of Nb and Ti is facilitated, and the number of inclusions and their size are reduced. The heat holding temperature is preferably 1300°C or higher. The heat holding temperature is more preferably 1350°C or higher.

[0073] The average heating rate is "(the temperature at the end of the slab heating (the heat holding temperature) (°C) - the temperature at the start of the slab heating (°C) (1000°C)) / the heating time from the start of the heating to the end of the heating (minutes)."

[0074] Then the slab is held at 900 to 1000°C for 20 seconds or longer and 150 seconds or shorter. When the residence time in the temperature range of 900 to 1000°C is increased, precipitates composed mainly of BN are formed and coarsened. The precipitates formed in this temperature range do not easily dissolve by anneal heating and cause a reduction in the amount of solute B after annealing. Therefore, when the residence time exceeds 150 seconds, the amount of solute B effective in preventing delayed fracture cannot be obtained. Thus, the residence time is 150 seconds or shorter and is preferably 120 seconds or shorter and more preferably 100 seconds or shorter. When the residence time is shorter than 20 seconds, the microstructure may be nonuniform. Therefore, the residence time is 20 seconds or longer and is preferably 30 seconds or longer and more preferably 40 seconds or longer.

[0075] In the hot finish rolling, the finish rolling temperature (FT) is set to 850°C or higher in order to reduce the precipitation of Nb, Ti, B, etc. The finish rolling temperature is preferably 930°C or lower.

[0076] After the hot finish rolling, cooling is performed at an average cooling rate of 40°C/second or more in the range from the finish rolling temperature to 650°C. When the average cooling rate is lower than 40°C/second, Nb carbonitrides and Ti carbonitrides are coarsened. In this case, the number of carbonitride particles having an equivalent circular diameter of 1.0 um or more increases, and the desired delayed fracture resistance cannot be obtained. The average cooling rate is preferably 250°C/second or lower and more preferably 200°C/second or lower.

[0077] The average cooling rate in the hot rolling step is "(the temperature at the start of the cooling (the finish rolling temperature) (°C) - the temperature at the end of the cooling (°C) (650°C)) / the cooling time from the start of the cooling to the end of the cooling (seconds)."

[0078] After the cooling to 650°C, the steel slab is coiled while being cooled as needed. In this case, when the coiling temperature is higher than 650°C, only coarsening of fine Nb- and Ti-based precipitates precipitated in the austenite range proceeds. Therefore, the number of coarse precipitates increases, and the delayed fracture characteristics deteriorate. Therefore, the coiling temperature is set to 650°C or lower. The coiling temperature is preferably 500°C or higher.

Cold rolling

[0079] In the cold rolling, when the rolling reduction (cold rolling reduction ratio) is 40% or more, the recrystallization behavior and the texture orientation in the subsequent continuous annealing can be stabilized. When the rolling reduction is less than 40%, some of austenite grains are coarsened during annealing, and the strength may decrease. The cold rolling reduction is preferably 80% or less.

Continuous annealing

[0080] The cold-rolled steel sheet is subjected to annealing in a continuous annealing line (CAL) and optionally subjected to tempering and temper-rolling.

[0081] $Fe_{23}(C,B)_6$ is formed and coarsened in the ferrite range during anneal heating. Therefore, to reduce the amount of $Fe_{23}(C,B)_6$ to thereby obtain the effect of grain boundary strengthening by B sufficiently, it is very important to increase the average heating rate at 400°C or higher. Moreover, also from the viewpoint of reducing the diameter of the prior γ grains to less than 11.0 um, it is necessary to increase the heating rate. From the above points of view, the average heating rate at 400°C or higher is set to 1.0°C/second or more. The average heating rate at 400°C or higher is preferably 1.5°C/second or more and more preferably 3.0°C/second or more.

[0082] The average heating rate is preferably 10°C/second or lower.

[0083] The average heating rate is "the annealing temperature (°C) described later - 400 (°C)) / the heating time from 400°C to the annealing temperature (minutes)."

[0084] To sufficiently reduce the number of undissolved precipitates such as $Fe_{23}(C,B)_6$ remaining after the annealing, the annealing is performed at a high temperature for a long time. Specifically, it is necessary to set the annealing temperature to 830°C or higher.

[0085] When the annealing is performed at higher than 950°C, the prior γ grains are coarsened, and the target microstructure is not obtained. Therefore, the annealing temperature is 950°C or lower. When the annealing is performed at higher than 900°C, BN is precipitated at the grain boundaries, and the delayed fracture resistance may deteriorate. Therefore, the annealing temperature is more preferably 900°C or lower. When the soaking time (holding time) at the annealing temperature is increased, the diameter of the prior γ grains increases excessively. Therefore, the soaking time is 600 seconds or shorter. The soaking time is preferably 10 seconds or longer.

[0086] Then, to reduce the amounts of ferrite and retained austenite to adjust the area fraction of martensite to 95% or more, cooling is performed from the cooling start temperature of 680°C or higher to the finish cooling temperature of 260°C or lower at an average cooling rate of 70°C/second or more.

[0087] The average cooling rate is "the cooling start temperature (°C) of 680°C or higher - the finish cooling temperature (°C) of 260°C or lower) / the cooling time (seconds) from the cooling start temperature (°C) of 680°C or higher to the finish cooling temperature of 260°C or lower. "

[0088] When the cooling start temperature is lower than 680°C, the area fraction of martensite cannot be adjusted to 95% or more. Therefore, the cooling start temperature is set to 680°C or higher. The cooling start temperature is preferably 800°C or lower.

[0089] When the average cooling rate is less than 70°C/second, large amounts of ferrite and bainite are formed, and sufficient strength is not obtained. Therefore, the average cooling rate is set to 70°C/second or more. The average cooling rate is preferably 700°C/second or more.

[0090] When the finish cooling temperature exceeds 260°C, a problem arises in that upper bainite and lower bainite are formed and the amounts of retained austenite and fresh martensite increase. Therefore, the finish cooling temperature is 260°C or lower.

[0091] Carbides distributed inside the martensite are carbides formed when the steel sheet is held in the low-temperature range after the quenching. It is necessary to control the formation of the carbides appropriately such that good delayed fracture resistance and a tensile strength of 1470 MPa or more ($TS \geq 1470$ MPa) can be obtained.

[0092] To achieve this, it is necessary to control the holding time at a holding temperature of 150 to 260°C to 20 to 1500 seconds.

[0093] When the holding temperature is lower than the lower limit, i.e., 150°C, or the holding time is short, the distribution density of carbides in the transformed phase is insufficient, and the delayed fracture resistance deteriorates. When the holding temperature is higher than the upper limit, i.e., 260°C, the carbides in the grains and at the block grain boundaries are coarsened significantly, and the delayed fracture resistance may deteriorate. When the holding time exceeds 1500 seconds, the carbides in the grains and at the block grain boundaries are coarsened significantly, and the delayed fracture resistance may deteriorate. Therefore, in the present invention, the steel sheet is held in the continuous annealing at a holding temperature of 150 to 260°C for 20 to 1500 seconds.

[0094] From the viewpoint of stabilizing press formability by adjusting the surface roughness, flattening the shape of the sheet, etc., the thus-obtained steel sheet may be subjected to skin pass rolling. In this case, the skin pass elongation rate is preferably 0.1% or more. The skin pass elongation rate is preferably 0.6% or less. In this case, from the viewpoint of flattening the shape of the steel sheet, it is preferable that the skin pass roll used is a dull roll and that the roughness Ra of the steel sheet is adjusted to 0.8 um or more. It is also preferable that the roughness Ra of the steel sheet is adjusted to 1.8 um or less.

[0095] The steel sheet obtained may be subjected to coating treatment. Specifically, after the continuous annealing, the surface of the steel sheet may be subjected to coating treatment. The steel sheet subjected to the coating treatment has a coated layer on its surface.

[0096] As described above, according to the present invention, the delayed fracture resistance of the high strength cold rolled steel sheet is significantly improved, and the application of the high strength steel sheet to a component contributes to an improvement in the strength of the component and a reduction in the weight of the component. The steel sheet of the present invention has a thickness of preferably 0.5 mm or more. The thickness is preferably 2.0 mm or less.

[0097] Next, the member of the present invention and a method for manufacturing the member will be described.

[0098] The member of the present invention is prepared by subjecting the steel sheet of the present invention to at least one of forming and joining. The method for manufacturing the member of the present invention includes the step of subjecting the steel sheet of the present invention to at least one of forming and joining.

[0099] The steel sheet of the present invention has a tensile strength of 1470 MPa or more and has good delayed fracture resistance. Therefore, the member obtained using the steel sheet of the present invention also has high strength and has better delayed fracture resistance than conventional high strength members. By using the member of the present invention, a reduction in weight can be achieved. Therefore, the member of the present invention can be preferably used, for example, for a vehicle body frame member.

[0100] The forming used may be any common working method such as press forming. The joining used may be any of common welding such as spot or arc welding, riveting, and crimping.

EXAMPLES

[0101] Examples in the present invention will next be described.

[0102] Molten steel having a chemical composition shown in Table 1 was prepared and cast into a slab.

[0103] The slab was subjected to heat treatment and rolling shown in Table 2 to thereby obtain a steel sheet having a thickness of 1.4 mm.

[0104] Specifically, a slab having one of the chemical compositions was heated such that the surface temperature of the slab was increased to a heat holding temperature shown in Table 2 at an average heating rate of 6°C/minute and then held for a heat holding time shown in Table 2. Then the slab was held at 900 to 1000°C for a residence time shown in Table 2, subjected to hot finish rolling at a finish rolling temperature of 870°C, and cooled at an average cooling rate of 50°C/second in the range from the finish rolling temperature to 650°C.

[0105] Then the resulting slab was cooled and coiled at a coiling temperature of 550°C to thereby obtain a hot rolled steel sheet, and the hot rolled steel sheet was cold rolled at a rolling reduction (cold rolling reduction) of 50% to thereby obtain a cold rolled steel sheet.

[0106] Then the cold rolled steel sheet was heated from 400°C to an annealing temperature shown in Table 2 at an average heating rate shown in Table 2 and soaked at the annealing temperature for a soaking time shown in Table 2.

[0107] Then the resulting cold rolled steel sheet was subjected to continuous annealing. Specifically, the cold rolled steel sheet was cooled from a cooling start temperature shown in Table 2 to a finish cooling temperature shown in Table 2 at an average cooling rate shown in Table 2, optionally reheated, and then held at a holding temperature shown in Table 2 for a holding time shown in Table 2.

[0108] As for No. 13, the steel sheet obtained was subjected to electroplating to thereby obtain a steel sheet having a Zn coated layer formed thereon.

[Table 1]

Steel grade	Chemical composition (% by mass)												Remarks
	C	Si	Mn	P	S	sol. Al	N	Ti	Nb	B	others	Ti + Nb	
A	0.34	0.80	1.1	0.007	0.0009	0.02	0.0028	0.030	0.012	0.0030	-	0.042	Suitable
B	0.33	0.50	1.0	0.008	0.0007	0.02	0.0027	0.025	0.021	0.0040	-	0.046	Suitable
C	0.30	0.21	1.3	0.008	0.0007	0.05	0.0021	0.014	0.007	0.0030	-	0.021	Suitable
D	0.37	0.49	1.4	0.007	0.0007	0.04	0.0041	0.048	0.007	0.0040	-	0.055	Suitable
E	0.33	0.32	0.7	0.028	0.0005	0.03	0.0032	0.012	0.005	0.0050	-	0.017	Suitable
F	0.31	0.72	0.9	0.024	0.0002	0.03	0.0033	0.018	0.018	0.0060	Cu: 0.10, Cr: 0.15	0.036	Suitable
G	0.32	0.97	0.3	0.014	0.0003	0.04	0.0016	0.007	0.020	0.0040	Ni:0.30,Mg :0.0010	0.027	Suitable
H	0.35	1.24	1.3	0.018	0.0005	0.04	0.0020	0.012	0.013	0.0030	Mo: 0.20, V: 0.100, Zr: 0.050	0.025	Suitable
I	0.33	1.10	1.3	0.024	0.0008	0.04	0.0030	0.030	0.016	0.0090	Ca:0.0020, Ce :0.0010	0.046	Suitable
J	0.34	1.20	0.5	0.023	0.0005	0.03	0.0040	0.041	0.006	0.0030	La: 0.0010, REMs: 0.0010	0.047	Suitable
K	0.28	1.01	1.5	0.029	0.0008	0.03	0.0042	0.010	0.005	0.0040	Sb: 0.020	0.015	Suitable
L	0.28	1.05	0.6	0.027	0.0006	0.03	0.0035	0.008	0.002	0.0040	Zr: 0.020, Sn: 0.003, W:0.050	0.010	Suitable
M	0.29	1.30	1.3	0.004	0.0003	0.04	0.0044	0.060	0.004	0.0050	Sn: 0.010	0.064	Suitable
N	0.12	0.26	0.8	0.023	0.0004	0.04	0.0036	0.035	0.008	0.0060	-	0.043	Comparative
O	0.46	0.25	1.0	0.021	0.0008	0.02	0.0035	0.021	0.020	0.0040	-	0.041	Comparative
P	0.38	0.70	1.0	0.070	0.0007	0.05	0.0038	0.041	0.008	0.0040	-	0.049	Comparative
Q	0.34	0.49	1.0	0.009	0.0020	0.05	0.0032	0.018	0.012	0.0030	-	0.030	Comparative
R	0.35	0.72	0.5	0.021	0.0003	0.23	0.0026	0.023	0.022	0.0025	-	0.045	Comparative
S	0.34	0.49	0.3	0.009	0.0009	0.05	0.0080	0.018	0.012	0.0040	-	0.030	Comparative
T	0.33	0.70	1.2	0.020	0.0005	0.02	0.0035	0.001	0.001	0.0030	-	0.002	Comparative
U	0.31	1.00	0.8	0.010	0.0008	0.02	0.0038	0.052	0.030	0.0035	-	0.082	Comparative

(continued)

Steel grade	Chemical composition (% by mass)												Remarks
	C	Si	Mn	P	S	sol. Al	N	Ti	Nb	B	others	Ti + Nb	
V	0.30	1.00	1.0	0.020	0.0005	0.03	0.0040	0.019	0.010	0.0115	-	0.029	Comparative
W	0.33	0.70	1.2	0.020	0.0008	0.02	0.0035	0.010	0.020	0.0008	-	0.030	Comparative
* The balance other than the above components includes Fe and incidental impurities.													

[Table 2]

Steel sheet No.	Steel grade	Hot rolling			Continuous annealing								Coating treatment	Remarks
		Heat holding temperature (°C)	Heat holding time (min)	Residence time at 900 to 1000°C (sec)	Annealing temperature (°C)	Average heating rate (°C/sec)	Soaking time (sec)	Cooling start temperature (°C)	Average cooling rate (°C/sec)	Finish cooling temperature (°C)	Holding temperature (°C)	Holding time (sec)		
1	A	1250	120	120	920	2.0	360	760	820	30	180	600	No	Suitable
2	B	1250	120	120	920	2.0	360	760	820	30	180	600	No	Suitable
3	C	1250	120	120	920	2.0	360	760	815	30	180	600	No	Suitable
4	D	1270	120	120	920	2.0	360	760	816	30	180	600	No	Suitable
5	E	1270	150	120	920	2.0	360	780	789	30	180	780	No	Suitable
6	F	1270	150	120	920	2.0	360	780	796	30	190	780	No	Suitable
7	G	1300	150	120	900	2.0	360	780	775	30	190	780	No	Suitable
8	H	1300	150	120	900	2.0	420	780	802	30	190	780	No	Suitable
9	I	1300	150	120	900	2.0	420	780	800	30	190	820	No	Suitable
10	J	1360	100	120	900	2.0	420	800	779	30	190	820	No	Suitable
11	K	1360	100	120	900	2.0	420	800	787	190	190	820	No	Suitable
12	L	1360	100	120	900	2.0	420	800	813	30	190	900	No	Suitable
13	M	1300	60	120	900	2.0	420	800	824	25	200	900	Yes	Suitable
14	N	1300	60	120	900	2.0	420	720	864	25	200	680	No	Comparative
15	O	1300	60	120	900	2.0	420	720	900	25	200	680	No	Comparative
16	P	1300	60	120	900	2.0	420	690	846	25	200	680	No	Comparative
17	Q	1250	80	120	900	2.0	480	720	864	25	200	680	No	Comparative
18	R	1250	80	120	900	2.0	480	720	823	25	200	680	No	Comparative
19	S	1320	120	120	890	2.0	480	720	891	25	200	1080	No	Comparative
20	T	1320	120	120	890	2.0	480	720	880	25	200	1080	No	Comparative
21	U	1320	120	120	890	2.0	480	720	890	25	200	750	No	Comparative
22	V	1320	120	120	890	2.0	480	720	810	25	200	750	No	Comparative

(continued)

Steel sheet No.	Steel grade	Hot rolling			Continuous annealing								Coating treatment	Remarks
		Heat holding temperature (°C)	Heat holding time (min)	Residence time at 900 to 1000°C (sec)	Annealing temperature (°C)	Average heating rate (°C/sec)	Soaking time (sec)	Cooling start temperature (°C)	Average cooling rate (°C/sec)	Finish cooling temperature (°C)	Holding temperature (°C)	Holding time (sec)		
23	W	1320	120	120	890	2.0	480	720	820	25	200	750	No	Comparative
24	A	1200	120	120	890	2.0	480	750	851	25	210	750	No	Comparative
25	A	1250	20	120	890	2.0	480	750	823	25	210	880	No	Comparative
26	A	1250	100	300	890	2.0	480	750	810	25	210	880	No	Comparative
27	A	1250	100	120	890	0.4	540	830	809	25	210	880	No	Comparative
28	A	1300	100	120	890	2.0	900	830	809	23	190	600	No	Comparative
29	A	1300	100	120	890	2.0	540	660	793	23	190	600	No	Comparative
30	A	1300	100	120	890	2.0	540	830	34	23	200	600	No	Comparative

[0109] For each of the obtained steel sheets, the metallic microstructures were quantified using the methods described above, and a tensile test and a delayed fracture resistance evaluation test were performed.

[0110] Specifically, the microstructures were measured using the following methods.

[0111] The area fractions of martensite, bainite, and ferrite were measured as follows. An L cross section of a steel sheet (its vertical cross section parallel to the rolling direction) was polished and etched with nital. The cross section was observed at positions 1/4 of the thickness from a surface of the steel sheet under an SEM at a magnification of 2000X to capture microstructure photographs in four viewing areas. The captured microstructure photographs were subjected to image analysis to measure the area fractions. The martensite and bainite appear as gray or white microstructures under the SEM. The bainite has the following features. Specifically, the bainite is in the form of a plate having an aspect ratio of 2.5 or more and is a slightly black microstructure than the martensite. The width of the plate is 0.3 to 1.7 um. The distribution density of carbides having a diameter of 10 to 200 nm and present inside the bainite is 0 to 3 particles / μm^2. The ferrite appears as dark contrast regions under the SEM. The martensite and bainite include thereinside small numbers of carbides, nitrides, sulfides, and oxides. However, since it is difficult to remove these particles, the area fractions of the martensite and bainite are the area fractions of regions including these particles.

[0112] The retained austenite (retained γ) was measured as follows. The surface layer of the steel sheet was chemically polished with oxalic acid to a depth of 200 um, and the area fraction of the retained austenite on the sheet surface was determined by an X-ray diffraction intensity method. The area fraction was computed from the integrated intensities of peaks from $(200)\alpha$, $(211)\alpha$, $(220)\alpha$, $(200)\gamma$, $(220)\gamma$, and $(311)\gamma$ diffraction planes that were measured using the Mo-Kα line.

[0113] The average grain diameter of the prior austenite grains (the prior γ grain diameter) was measured as follows. An L cross section of the steel sheet (its vertical cross section parallel to the rolling direction) was polished and etched with a chemical solution capable of etching the prior γ grain boundaries (for example, a saturated aqueous picric acid solution or a solution prepared by adding ferric chloride to the saturated aqueous picric acid solution). The cross section was observed at positions 1/4 of the thickness from a surface of the steel sheet under an optical microscope at a magnification of 500X to capture photographs in four viewing areas. In each of the obtained photographs, 15 lines were drawn in the thickness direction at intervals of 10 um or more in actual length, and 15 lines were drawn in the rolling direction at intervals of 10 um or more in actual length. Then the number of intersections of the grain boundaries and the lines was counted. A value obtained by dividing the total line length by the number of intersections was multiplied by 1.13, and the prior γ grain diameter was thereby determined.

[0114] The number density A of the precipitates having an equivalent circular diameter of 500 nm or more was determined as follows. An L cross section of the steel sheet (its vertical cross section parallel to the rolling direction) was polished. In a region extending from a position 1/5 of the thickness of the steel sheet to a position 4/5 of the thickness, i.e., in a region extending from the position 1/5 of the thickness from a surface of the steel sheet to the position 4/5 of the thickness with the thicknesswise center positioned therebetween, images of 2 mm^2 regions were continuously captured under an SEM. The number density A was determined by counting the number of precipitates described above in the captured SEM photographs. The magnification of the captured images is 2000X. When each of the inclusion particles was subjected to component analysis, the inclusion particle was magnified by a factor of 10000 to analyze the precipitate. The precipitates having an equivalent circular diameter of 500 nm or more are precipitates containing B such as $Fe_{23}(C,B)_6$. Elemental analysis by energy dispersive X-ray spectrometry (EDS) using an acceleration voltage of 3 kV was performed to check for the presence of a peak of B. When a peak of B was observed, it was determined that the above-described precipitates were present.

[0115] A tensile test was performed as follows. A JIS No. 5 tensile test piece was cut from a position 1/4 of the coil width such that a direction orthogonal to the rolling direction was the longitudinal direction of the test piece, and the tensile test (according to JIS Z 2241) was performed to evaluate the YP, TS, and El.

[0116] The delayed fracture resistance was evaluated as follows.

[0117] A strip-shaped test specimen was cut from a steel sheet (coil) obtained. Specifically, the test specimen had dimensions of 100 mm in a direction orthogonal to the rolling direction and 30 mm in the rolling direction and was cut from a position 1/4 of the width of the steel sheet (coil) in the width direction of the coil. Then the evaluation was performed. To obtain the long-side end faces of the test specimen that had a length of 100 mm, the steel sheet was sheared, and the as-sheared test specimen (without machining for removing burrs) was subjected to bending such that the burrs were present on the outer peripheral side of the bend and fixed with a bolt while the shape at the time of bending was maintained. In the shearing, the clearance was set to 13%, and the rake angle was set to 1°. The bending was performed such that the corner bending radius was 10 mm and the inner apex angle of the bend was 90° (V bending). The punch used had a tip radius equal to the corner bending radius R described above and had a U-shape (the round tip portion of the punch had a semicircular shape, and the barrel portion of the punch had a thickness of 2R). The die used had a corner R of 30 mm. The depth when the punch pushed the steel sheet was adjusted, and the steel sheet was subjected to shaping such that the corner bending angle (the inner apex angle of the bend) was 90° (the steel sheet had a V shape). The test specimen was clamped with a hydraulic jack such that the distance between flange ends of straight portions of the bent test specimen was the same as that at the time of the bending (such that an increase in the opening angle between the straight portions due to springback was canceled out), and then the test specimen in this state was fixed with the bolt. The bolt was inserted into elliptical holes (minor axis: 10 mm, major axis: 15 mm) formed in advance at positions 10 mm inward from the short side edges of the strip-shaped test specimen to thereby fix the test specimen. The bolted test specimen was immersed in a solution prepared by mixing a 0.1% by mass aqueous ammonium thiocyanate solution and a McIlvaine buffer solution at a ratio of 1:1 and having a pH adjusted to 8.0, and a delayed fracture resistance evaluation test was performed. The temperature of the solution was 20°C, and the amount of the solution per 1 cm^3 of the surface area of the test specimen was 20 mL. The presence or absence of a visually observable crack (having a length of 1 mm or more) was checked after a lapse of 24 hours. A test specimen with no crack observed was considered to have good delayed fracture resistance.

[0118] The microstructure and characteristics of each of the steel sheets obtained are shown in Table 3.

[Table 3]

Steel sheet No.	Steel grade	Area fraction of martensite (%)	Area fraction of remaining microstructures (%) (*1)	Diameter of prior γ grains (μm) (*2)	A (particles / mm^2) (*3)	A / [B] ($\times 10^5$) (*4)	TS (MPa)	Delayed fracture characteristics	Remarks
1	A	100	0	5.3	1354	4.51	1956	Not cracked	Suitable
2	B	100	0	5.1	2083	5.21	1923	Not cracked	Suitable
3	C	100	0	7.8	1429	4.76	1842	Not cracked	Suitable
4	D	100	0	4.1	2034	5.09	1990	Not cracked	Suitable
5	E	100	0	7.7	2860	5.72	1935	Not cracked	Suitable
6	F	100	0	5.2	3690	6.15	1818	Not cracked	Suitable
7	G	100	0	5.1	2102	5.26	1842	Not cracked	Suitable
8	H	100	0	5.5	1345	4.48	1822	Not cracked	Suitable
9	I	97	3	4.3	6540	7.27	1724	Not cracked	Suitable
10	J	100	0	3.9	1432	4.77	1904	Not cracked	Suitable
11	K	100	0	6.7	2140	5.35	1735	Not cracked	Suitable
12	L	100	0	8.3	2016	5.04	1728	Not cracked	Suitable
13	M	100	0	3.5	2871	5.74	1725	Not cracked	Suitable
14	N	100	0	6.0	3750	6.25	1250	Not cracked	Comparative
15	O	100	0	4.4	2010	5.03	2180	Cracked	Comparative
16	P	100	0	4.4	2075	5.19	1976	Cracked	Comparative
17	Q	100	0	6.5	1392	4.64	1850	Cracked	Comparative
18	R	100	0	5.3	1135	4.54	1879	Cracked	Comparative
19	S	100	0	6.4	2040	5.10	1872	Cracked	Comparative
20	T	100	0	14.9	1365	4.55	1836	Cracked	Comparative
21	U	100	0	3.6	1801	5.15	2896	Cracked	Comparative
22	V	100	0	5.4	10300	8.96	1760	Cracked	Comparative
23	W	100	0	5.0	221	2.76	1839	Cracked	Comparative
24	A	100	0	11.0	2865	9.55	1828	Cracked	Comparative

(continued)

Steel sheet No.	Steel grade	Area fraction of martensite (%)	Area fraction of remaining microstructures (%) (*1)	Diameter of prior γ grains (μm) (*2)	A (particles / mm^2) (*3)	A / [B] ($\times 10^5$) (*4)	TS (MPa)	Delayed fracture characteristics	Remarks
25	A	100	0	13.2	3440	11.47	1819	Cracked	Comparative
26	A	100	0	5.9	3111	10.37	1835	Cracked	Comparative
27	A	100	0	12.5	2633	8.78	1821	Cracked	Comparative
28	A	100	0	11.0	1821	6.07	1884	Cracked	Comparative
29	A	91	9	4.3	2087	6.96	1659	Cracked	Comparative
30	A	85	15	4.9	1793	5.98	1652	Cracked	Comparative

(*1) Area fraction of remaining microstructures: Total area fraction of bainite, ferrite, and retained austenite.
(*2) Diameter of prior γ grains: Average grain diameter of prior austenite grains.
(*3) A: The number density of precipitates having an equivalent circular diameter of 500 nm or more.
(*4) [B]:The content of B (% by mass).

[0119] Steel sheets within the scope of the present invention had high strength and had good delayed fracture resistance.

[0120] However, in No. 14 (steel N), the content of C was lower than the lower limit of the value specified in the present invention, and the TS was insufficient.

[0121] In No. 15 (steel O), the content of C was higher than the upper limit of the value specified in the present invention, and sufficient delayed fracture resistance was not obtained.

[0122] In No. 16 (steel P), the content of P was higher than the upper limit of the value specified in the present invention, and sufficient delayed fracture resistance was not obtained.

[0123] In No. 17 (steel Q), the content of S was higher than the upper limit of the value specified in the present invention, and sufficient delayed fracture resistance was not obtained.

[0124] In No. 18 (steel R), the content of sol. Al was higher than the upper limit of the value specified in the present invention, and sufficient delayed fracture resistance was not obtained.

[0125] In No. 19 (steel S), the content of N was higher than the upper limit of the value specified in the present invention, and sufficient delayed fracture resistance was not obtained.

[0126] In No. 20 (steel T), the content of Nb and Ti was lower than the lower limit of the value specified in the present invention. Therefore, the diameter of the prior γ grains was large, and sufficient delayed fracture resistance was not obtained.

[0127] In No. 21 (steel U), the content of Nb and Ti was higher than the upper limit of the value specified in the present invention, and sufficient delayed fracture resistance was not obtained.

[0128] In No. 22 (steel V), the content of B was higher than the upper limit of the value specified in the present invention. Therefore, the number of coarse precipitates was large, and sufficient delayed fracture resistance was not obtained.

[0129] In No. 23 (steel W), the content of B was lower than the lower limit of the value specified in the present invention, and sufficient delayed fracture resistance was not obtained.

[0130] In No. 24 (steel A), the heating temperature (slab surface temperature (SRT)) was lower than the lower limit of the value specified in the present invention. Therefore, the diameter of the prior γ grains was large, and the number density A of the precipitates was excessively large, so that sufficient delayed fracture resistance was not obtained.

[0131] In No. 25 (steel A), the holding time for the slab heating was shorter than the lower limit of the value specified in the present invention. Therefore, the diameter of the prior γ grains was large, and the number density A of the precipitates was excessively large, so that sufficient delayed fracture resistance was not obtained.

[0132] In No. 26 (steel A), the residence time at 900 to 1000°C was longer than the upper limit of the value specified in the present invention. Therefore, the number density A of the precipitates was excessively large, and sufficient delayed fracture resistance was not obtained.

[0133] In No. 27 (steel A), the average heating rate during the annealing was lower than the lower limit of the value specified in the present invention. Therefore, the diameter of the prior γ grains was large, and the number density A of the precipitates was excessively large, so that sufficient delayed fracture resistance was not obtained.

[0134] In No. 28 (steel A), the soaking time during the annealing was longer than the upper limit of the value specified in the present invention. Therefore, the diameter of the prior γ grains was large, and sufficient delayed fracture resistance was not obtained.

[0135] In No. 29 (steel A), the cooling start temperature during the annealing was lower than the lower limit of the value specified in the present invention. Therefore, the formation of martensite was insufficient, and sufficient delayed fracture resistance was not obtained.

[0136] In No. 30 (steel A), the average cooling rate during the annealing was lower than the lower limit of the value specified in the present invention. Therefore, the formation of martensite was insufficient, and sufficient delayed fracture resistance was not obtained.

[0137] Members obtained by subjecting the steel sheets in Inventive Examples to forming and members obtained by subjecting the steel sheets in the Inventive Examples to joining had high strength and had good delayed fracture resistance, as did the steel sheets in the Inventive Examples, because the steel sheets in the Inventive Examples had high strength and had good delayed fracture resistance.

Claims

1. A steel sheet having a chemical composition comprising, in mass %,

C: 0.15% or more and 0.45% or less,
Si: 1.5% or less,
Mn: 1.7% or less,
P: 0.03% or less,

S: less than 0.0020%,
sol. Al: 0.20% or less,
N: 0.005% or less,
B: 0.0015% or more and 0.0100% or less, and
at least one of Nb and Ti in a total amount of 0.005% or more and 0.080% or less,
with the balance being Fe and incidental impurities,
wherein the steel sheet has a microstructure in which the area fraction of martensite with respect to the total area of the microstructure is 95% or more and 100% or less,
wherein prior austenite grains have an average grain diameter of less than 11.0 um, and
wherein the number density A of precipitates having an equivalent circular diameter of 500 nm or more satisfies formula (1) below:

$$A\ (\text{particles} / \text{mm}^2) \leq 8.5 \times 10^5 \times [B] \qquad \text{formula (1)}$$

where [B] represents the content of B (% by mass).

2. The steel sheet according to claim 1, wherein the chemical composition further comprises, in mass %, one or two selected from Cu: 1.0% or less and Ni: 1.0% or less.

3. The steel sheet according to claim 1 or 2, wherein the chemical composition further comprises, in mass %, one or two or more selected from Cr: 1.0% or less, Mo: less than 0.3%, V: 0.5% or less, Zr: 0.2% or less, and W: 0.2% or less.

4. The steel sheet according to any of claims 1 to 3, wherein the chemical composition further comprises, in mass %, one or two or more selected from Ca: 0.0030% or less, Ce: 0.0030% or less, La: 0.0030% or less, REMs (excluding Ce and La): 0.0030% or less, and Mg: 0.0030% or less.

5. The steel sheet according to any of claims 1 to 4, wherein the chemical composition further comprises, in mass %, one or two selected from Sb: 0.1% or less and Sn: 0.1% or less.

6. The steel sheet according to any of claims 1 to 5, wherein the steel sheet comprises a coated layer on a surface thereof.

7. A member formed using the steel sheet according to any of claims 1 to 6.

8. A method for manufacturing a steel sheet, the method comprising:

heating a steel slab having the chemical composition according to any of claims 1 to 5 such that the surface temperature of the slab is increased from 1000°C to a heat holding temperature of 1250°C or higher at an average heating rate of 10°C/minute or less and then holding the steel slab at the heat holding temperature for 30 minutes or longer;
then setting a residence time at 900 to 1000°C to 20 seconds or longer and 150 seconds or shorter and performing hot finish rolling under the condition of a finish rolling temperature of 850°C or higher;
performing cooling at an average cooling rate of 40°C/second or more in a range from the finish rolling temperature to 650°C;
then performing coiling at a coiling temperature of 650°C or lower to obtain a hot rolled steel sheet;
subjecting the hot rolled steel sheet to cold rolling at a rolling reduction of 40% or more to obtain a cold rolled steel sheet; and
subjecting the cold rolled steel sheet to continuous annealing including
heating the cold rolled steel sheet from 400°C to an annealing temperature of 830 to 950°C at an average heating rate of 1.0°C/second or more,
holding the cold rolled steel sheet at the annealing temperature for 600 seconds or shorter,
cooling the cold rolled steel sheet from a cooling start temperature of 680°C or higher to a finish cooling temperature of 260°C or lower at an average cooling rate of 70°C/second or more, and
then holding the cold rolled steel sheet at a holding temperature of 150 to 260°C for 20 to 1500 seconds to thereby manufacture a steel sheet.

9. The method for manufacturing a steel sheet according to claim 8, the method further comprising, after the continuous annealing, subjecting a surface of the steel sheet to coating treatment.

10. A method for manufacturing a member, the method comprising the step of subjecting the steel sheet according to any of claims 1 to 6 to at least one of forming and joining to thereby obtain a member.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/024963

A. CLASSIFICATION OF SUBJECT MATTER

C21D 9/46(2006.01)i; ***C22C 38/00***(2006.01)i; ***C22C 38/14***(2006.01)i; ***C22C 38/60***(2006.01)i
FI: C22C38/00 301S; C22C38/00 301T; C22C38/14; C22C38/60; C21D9/46 G; C21D9/46 J

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)

C21D9/46; C22C38/00; C22C38/14; C22C38/60

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 2020/170667 A1 (JFE STEEL CORP.) 27 August 2020 (2020-08-27)	1-10
A	WO 2018/062381 A1 (JFE STEEL CORP.) 05 April 2018 (2018-04-05)	1-10

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search **26 August 2022**	Date of mailing of the international search report **13 September 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/024963

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2020/170667 A1	27 August 2020	EP 3929321 A1	
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		CN 109642295 A	
		KR 10-2019-0034265 A	

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

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- JP 6388085 B **[0007]**
- JP 4712882 B **[0007]**