



(11)

EP 4 421 198 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:

28.08.2024 Bulletin 2024/35

(51) International Patent Classification (IPC):

C22C 38/00 (2006.01) C22C 38/60 (2006.01)

C21D 9/46 (2006.01)

(21) Application number: 22883670.6

(52) Cooperative Patent Classification (CPC):

C22C 38/00; C22C 38/60; C21D 9/46

(22) Date of filing: 21.10.2022

(86) International application number:

PCT/JP2022/039377

(87) International publication number:

WO 2023/068368 (27.04.2023 Gazette 2023/17)

(84) Designated Contracting States:

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

Designated Extension States:

BA

Designated Validation States:

KH MA MD TN

(30) Priority: 21.10.2021 JP 2021172425

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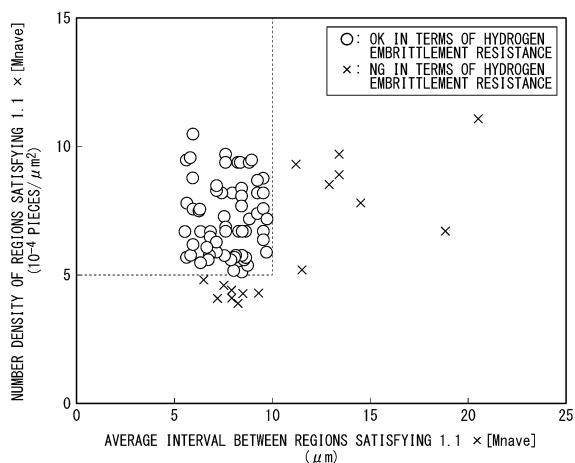
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(54) STEEL PLATE

(57) What is provided is a steel sheet having a pre-determined chemical composition, in which a microstructure includes, by area ratio, ferrite: 5.0% or less, martensite and tempered martensite: more than 90.0% in total, and a remainder: one or two or more of bainite, pearlite, and residual austenite, in a cross section in a sheet thickness direction, regions having an Mn content of $1.1 \times [\text{Mnave}]$ or more, where the $[\text{Mnave}]$ is an average Mn content throughout the sheet thickness direction, have a number density of 5.0×10^{-4} pieces/ μm^2 or more and are present so that the average interval between closest regions having an Mn content of $1.1 \times [\text{Mnave}]$ or more is 10.0 μm or less, and a tensile strength is 1,500 MPa or more.

FIG. 1



Description

[Technical Field of the Invention]

5 [0001] The present invention relates to a steel sheet.

[0002] Priority is claimed on Japanese Patent Application No. 2021-172425, filed on October 21, 2021, the content of which is incorporated herein by reference.

[Related Art]

10 [0003] Today, as industrial technology fields are highly divided, materials used in each technology field require special and advanced performance. In particular, with regard to steel sheets for a vehicle, in order to reduce the weight of a vehicle body and improve fuel efficiency in consideration of the global environment, there is a significantly increasing demand for high strength steel sheets. However, most metal materials deteriorate in various properties with high strengthening and particularly, the hydrogen embrittlement susceptibility increases. It is known that the hydrogen embrittlement susceptibility particularly increases when the tensile strength of a steel member is 1,200 MPa or more, and there is a case of hydrogen embrittlement cracking in bolt steel for which high strengthening has progressed in the vehicle field. Therefore, for high strength steel sheets having a tensile strength of 1,500 MPa or more, there is a strong demand for a radical solution to hydrogen embrittlement.

15 [0004] In many cases, the microstructure of a high strength steel sheet having a tensile strength of 1,500 MPa or more mainly includes martensite or tempered martensite. In such a high strength steel sheet, hydrogen intruding into the steel segregates to grain boundaries of martensite and causes grain boundary embrittlement (decreases the grain boundary strength), whereby cracking occurs (hydrogen embrittlement occurs). Since the intrusion of hydrogen also occurs at room temperature, there is no method for completely suppressing the intrusion of hydrogen, and it is necessary to modify the internal structure of steel in order to obtain a radical solution.

20 [0005] So far, many proposals have been made for technologies for improving the hydrogen embrittlement resistance (may be referred to as hydrogen embrittlement resistance properties) of high strength steel sheets (for example, see Patent Documents 1 to 6).

25 [0006] Patent Document 1 discloses, as an ultra-high strength thin steel sheet having excellent hydrogen embrittlement resistance properties and workability, an ultra-high strength thin steel sheet containing, by mass%, C: more than 0.25% to 0.60%, Si: 1.0% to 3.0%, Mn: 1.0% to 3.5%, P: 0.15% or less, S: 0.02% or less, Al: 1.5% or less (not including 0%), Mo: 1.0% or less (not including 0%), Nb: 0.1% or less (not including 0%), and a remainder consisting of iron and unavoidable impurities, in which a metallographic structure after stretch working at a working ratio of 3% includes residual austenite structure: 1% or more, bainitic ferrite and martensite: 80% or more in total, and ferrite and pearlite: 9% or less (including 0%) in total by area ratio with respect to the whole structure, crystal grains of the residual austenite have an average axial ratio (major axis/minor axis) of 5 or higher, and the tensile strength is 1,180 MPa or more.

30 [0007] Patent Document 2 discloses, as a high strength steel sheet having a tensile strength of 1,500 MPa or more, a high strength steel sheet excellent in delayed fracture resistance properties and bendability in a rolling direction, that contains Si + Mn as steel components: 1.0% or more, and in which in a primary phase structure, ferrite and carbides form layers, a carbide has an aspect ratio of 10 or more, a layered structure in which an interval between the layers is 50 nm or less occupies 65% or more of the whole structure by volume percentage, and among the carbides that form layers with ferrite, a fraction of carbides having an aspect ratio of 10 or more and an angle of 25° or less with respect to the rolling direction is 75% or more by area ratio.

35 [0008] Patent Document 3 discloses, as a thin ultra-high strength cold-rolled steel sheet having excellent bendability and delayed fracture resistance properties, an ultra-high strength cold-rolled steel sheet having excellent bendability, that contains, by mass%, C: 0.15% to 0.30%, Si: 0.01% to 1.8%, Mn: 1.5% to 3.0%, P: 0.05% or less, S: 0.005% or less, Al: 0.005% to 0.05%, N: 0.005% or less, and a remainder consisting of Fe and unavoidable impurities, and in which a soft steel sheet surface layer portion meeting the relationship represented by "hardness of soft steel sheet surface layer portion/hardness of center portion of steel sheet ≤ 0.8 " is provided, the ratio of the soft steel sheet surface layer portion to the sheet thickness is 0.10 or more and 0.30 or less, the volume percentage of tempered martensite is 90% or more in the soft steel sheet surface layer portion, the structure of the center portion of the steel sheet includes tempered martensite, and the tensile strength is 1,270 MPa or more.

40 [0009] Patent Document 4 discloses, as a cold-rolled steel sheet having a tensile strength of 1,470 MPa or more and excellent bending workability and delayed fracture resistance properties, a cold-rolled steel sheet that contains, by mass%, C: 0.15% to 0.20%, Si: 1.0% to 2.0%, Mn: 1.5% to 2.5%, P: 0.020% or less, S: 0.005% or less, Al: 0.01% to 0.05%, N: 0.005% or less, Ti: 0.1% or less, Nb: 0.1% or less, B: 5 to 30 ppm, and a remainder consisting of Fe and unavoidable impurities, in which in a metallographic structure, the volume percentage of a tempered martensite is 97% or more and the volume percentage of a residual austenite is less than 3%.

[0010] Patent Document 5 discloses, as an ultra-high strength steel sheet capable of exhibiting excellent delayed fracture resistance properties even at a cut end portion, an ultra-high strength steel sheet having a tensile strength of 1,470 MPa or more containing, as a composition, by mass%, C: 0.15% to 0.4%, Mn: 0.5% to 3.0%, Al: 0.001% to 0.10%, and a remainder consisting of iron and unavoidable impurities of which P, S, and N are limited so that P: 0.1% or less, S: 0.01% or less, and N: 0.01% or less are satisfied, in which a structure including martensite: 90% or more and residual austenite: 0.5% or more by area ratio with respect to the whole structure is provided, a region where a local Mn concentration is 1.1 times or more the Mn content of the entire steel sheet exists in an area ratio of 2% or more, and the tensile strength is 1,470 MPa or more.

[0011] Patent Document 6 discloses, as an ultra-high strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance properties and a tensile strength of 1,300 MPa or more, an ultra-high strength cold-rolled steel sheet having a steel structure containing C: 0.150% to 0.300%, Si: 0.001% to 2.0%, Mn: 2.10% to 4.0%, P: 0.05% or less, S: 0.01% or less, N: 0.01% or less, Al: 0.001% to 1.0%, Ti: 0.001% to 0.10%, and B: 0.0001% to 0.010%, in which values of a solid solution B amount solB [mass%] and a prior austenite grain size D_y [μm] satisfy the relationship represented by $\text{solB} \cdot D_y \geq 0.0010$, polygonal ferrite is 10% or less, bainite is 30% or less, residual austenite is 6% or less, tempered martensite is 60% or more, the number density of Fe carbides in the tempered martensite is 1×10^6 pieces/ mm^2 or more, the average dislocation density of the entire steel is 1.0×10^{15} to 2.0×10^{16} pieces/ m^2 , and a crystal grain size is 7.0 μm or less.

[Prior Art Document]

[Patent Document]

[0012]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2006-207019

[Patent Document 2] Japanese Unexamined Patent Application, First Publication No. 2010-138489

[Patent Document 3] Japanese Unexamined Patent Application, First Publication No. 2011-179030

[Patent Document 4] Japanese Unexamined Patent Application, First Publication No. 2010-215958

[Patent Document 5] Japanese Unexamined Patent Application, First Publication No. 2016-153524

[Patent Document 6] Japanese Unexamined Patent Application, First Publication No. 2016-050343

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0013] As described above, several technologies for improving the hydrogen embrittlement resistance properties (hydrogen embrittlement resistance) of a high strength steel sheet have been proposed. However, in Patent Document 1, only the hydrogen embrittlement resistance properties when a stress of 1,000 MPa is applied are disclosed, and no technical solution guidelines are provided for the hydrogen embrittlement resistance properties when a higher stress is applied.

[0014] In addition, as described above, hydrogen embrittlement occurs when hydrogen accumulates at grain boundaries and decreases the bonding strength of the grain boundaries. Therefore, for this reason, in order to prevent the hydrogen embrittlement, it is effective to uniformly and finely disperse regions having a higher attracting interaction with hydrogen (H) than prior austenite grain boundaries in the steel, thereby preventing H from accumulating at the prior γ grain boundaries. However, Patent Documents 1 to 6 do not consider a method of improving the hydrogen embrittlement resistance properties based on such a viewpoint. In recent years, it has been stringently necessary to obtain hydrogen embrittlement resistance properties, and Patent Documents 1 to 6 may not be able to meet such stringent requirements.

[0015] That is, in the related art, in high strength steel sheets having a microstructure mainly including martensite and tempered martensite, there is room for improvement in hydrogen embrittlement resistance properties.

[0016] Therefore, an object of the present invention is to provide a steel sheet having a high strength and excellent hydrogen embrittlement resistance properties.

[Means for Solving the Problem]

[0017] As described above, the hydrogen embrittlement is considered to be cracking occurring from grain boundaries due to a decrease in bonding strength of the grain boundaries by segregation of hydrogen in steel to the grain boundaries (mainly prior austenite grain boundaries in a case of a microstructure mainly including martensite and tempered martensite).

[0018] Therefore, the present inventors have considered preventing the accumulation of H at prior γ grain boundaries by uniformly and finely dispersing regions having a higher attracting interaction with hydrogen (H) than the prior austenite grain boundaries in the steel, and focused on a method of utilizing the attracting interaction of Mn with H.

[0019] As a result, the following findings were obtained.

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- a) By dispersing regions having an Mn content higher than the average Mn content at predetermined intervals, the accumulation of H at the prior austenite grain boundaries can be suppressed.
- b) In order to disperse regions having a higher Mn content than average in a high strength steel sheet having a microstructure mainly including martensite and tempered martensite, it is important to control the dispersion state of cementite by optimizing rolling conditions for a hot rolling step and coiling conditions, and then to control annealing conditions and cooling conditions after annealing.

[0020] The present invention was made in view of the above findings. The gist of the present invention is as follows.

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[1] A steel sheet according to one aspect of the present invention containing, as a chemical composition, by mass%: C: 0.150% to 0.400%; Si: 0.01% to 2.00%; Mn: 0.8% to 2.0%; P: 0.0001% to 0.0200%; S: 0.0001% to 0.0200%; Al: 0.001% to 1.000%; N: 0.0001% to 0.0200%; O: 0.0001% to 0.0200%; Co: 0% to 0.500%; Ni: 0% to 1.000%; Mo: 0% to 1.000%; Cr: 0% to 2.000%; Ti: 0% to 0.500%; B: 0% to 0.0100%; Nb: 0% to 0.500%; V: 0% to 0.500%; Cu: 0% to 0.500%; W: 0% to 0.100%; Ta: 0% to 0.100%; Mg: 0% to 0.050%; Ca: 0% to 0.050%; Y: 0% to 0.050%; Zr: 0% to 0.050%; La: 0% to 0.050%; Ce: 0% to 0.050%; Sn: 0% to 0.050%; Sb: 0% to 0.050%; As: 0% to 0.050%; and a remainder: Fe and impurities, in which a microstructure includes, by area ratio, ferrite: 5.0% or less, martensite and tempered martensite: more than 90.0% in total, and a remainder: one or two or more of bainite, pearlite, and residual austenite, in a cross section in a sheet thickness direction, regions having an Mn content of $1.1 \times [Mnave]$ or more, where the [Mnave] is an average Mn content throughout the sheet thickness direction, have a number density of 5.0×10^{-4} pieces/ μm^2 or more and are present so that an average interval between closest regions having an Mn content of $1.1 \times [Mnave]$ or more is 10.0 μm or less, and a tensile strength is 1,500 MPa or more.

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[2] In the steel sheet according to [1], the chemical composition may contain one or two or more selected from the group consisting of Co: 0.01% to 0.500%, Ni: 0.01% to 1.000%, Mo: 0.01% to 1.000%, Cr: 0.001% to 2.000%, Ti: 0.001% to 0.500%, B: 0.0001% to 0.0100%, Nb: 0.001% to 0.500%, V: 0.001% to 0.500%, Cu: 0.001% to 0.500%, W: 0.001% to 0.100%, Ta: 0.001% to 0.100%, Mg: 0.0001% to 0.050%, Ca: 0.001% to 0.050%, Y: 0.001% to 0.050%, Zr: 0.001% to 0.050%, La: 0.001% to 0.050%, Ce: 0.001% to 0.050%, Sn: 0.001% to 0.050%, Sb: 0.001% to 0.050%, and As: 0.001% to 0.050%.

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[3] In the steel sheet according to [1] or [2], a coating layer containing zinc, aluminum, magnesium, or an alloy of these metals may be provided on a surface.

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[Effects of the Invention]

[0021] According to the aspect of the present invention, it is possible to provide a steel sheet having a high strength and excellent hydrogen embrittlement resistance properties.

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[Brief Description of the Drawings]

[0022] FIG. 1 is a graph showing influences of the average interval between regions satisfying $1.1 \times [Mnave]$ and a number density of regions satisfying $1.1 \times [Mnave]$ on hydrogen embrittlement resistance.

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[Embodiments of the Invention]

[0023] Hereinafter, a steel sheet according to an embodiment of the present invention (the steel sheet according to the present embodiment) will be described.

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[0024] The steel sheet according to the present embodiment has a predetermined chemical composition, in which a microstructure includes, by area ratio, ferrite: 5.0% or less, martensite and tempered martensite: more than 90.0% in total, and a remainder: one or two or more of bainite, pearlite, and residual austenite, in a cross section in a sheet thickness direction, regions having an Mn content of $1.1 \times [Mnave]$ or more, where the [Mnave] is an average Mn content throughout the sheet thickness direction, have a number density of 5.0×10^{-4} pieces/ μm^2 or more and are present so that the average interval between closest regions having an Mn content of $1.1 \times [Mnave]$ or more is 10.0 μm or less, and the tensile strength is 1,500 MPa or more.

<Chemical Composition>

[0025] First, the content range of each of the elements constituting the chemical composition of the steel sheet according to the present embodiment will be described. Hereinafter, "%" regarding the amount of each element means "mass%".
 5 In addition, ranges shown using "to" include values at both ends thereof as a lower limit and an upper limit.

C: 0.150% to 0.400%

[0026] C is an effective element for increasing the tensile strength at a low cost. In a case where the C content is less than 0.150%, a target tensile strength cannot be obtained, and the fatigue properties of a weld deteriorate. Therefore, the C content is set to 0.150% or more. The C content may be 0.160% or more, 0.180% or more, or 0.200% or more.
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[0027] Meanwhile, in a case where the C content is more than 0.400%, the hydrogen embrittlement resistance properties and the weldability decrease. Therefore, the C content is set to 0.400% or less. The C content may be 0.350% or less, 0.300% or less, or 0.250% or less.
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Si: 0.01% to 2.00%

[0028] Si is an element that acts as a deoxidizing agent and affects the morphology of carbide and residual austenite after a heat treatment. In a case where the Si content is less than 0.01%, it is difficult to suppress the formation of coarse oxides. The coarse oxides serve as crack initiation points, and the cracking propagates in the steel, leading to a deterioration in hydrogen embrittlement resistance properties. Therefore, the Si content is set to 0.01% or more. The Si content may be 0.05% or more, 0.10% or more, or 0.30% or more.
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[0029] Meanwhile, in a case where the Si content is more than 2.00%, the local ductility may decrease and the hydrogen embrittlement resistance properties may deteriorate. Therefore, the Si content is set to 2.00% or less. The Si content may be 1.80% or less, 1.60% or less, or 1.40% or less.
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Mn: 0.8% to 2.0%

[0030] Mn is an effective element for increasing the strength of the steel sheet. In a case where the Mn content is less than 0.8%, the effect cannot be sufficiently obtained. Therefore, the Mn content is set to 0.8% or more. The Mn content may be 1.0% or more or 1.2% or more.
 30

[0031] Meanwhile, in a case where the Mn content is more than 2.0%, Mn may not only promote co-segregation with P and S, but also deteriorate the corrosion resistance and the hydrogen embrittlement resistance properties. Therefore, the Mn content is set to 2.0% or less. The Mn content may be 1.9% or less or 1.8% or less.
 35

P: 0.0001% to 0.0200%

[0032] P is an element that strongly segregates to ferrite grain boundaries and promotes grain boundary embrittlement. In a case where the P content is more than 0.0200%, the hydrogen embrittlement resistance properties significantly decrease due to the grain boundary embrittlement. Therefore, the P content is set to 0.0200% or less. The P content may be 0.0180% or less, 0.0150% or less, or 0.0120% or less.
 40

[0033] The P content is preferably as small as possible. However, in a case where the P content is less than 0.0001%, the time required for refining increases and this leads to a significant increase in cost. Therefore, the P content is set to 0.0001% or more. The P content may be 0.0005% or more, 0.0010% or more, or 0.0020% or more.
 45

S: 0.0001% to 0.0200%

[0034] S is an element that forms non-metallic inclusions such as MnS in the steel. In a case where the S content is more than 0.0200%, non-metallic inclusions which serve as crack initiation points in cold working are noticeably formed. In this case, cracking occurs from the non-metallic inclusions, and the cracking propagates in the steel, leading to a deterioration in hydrogen embrittlement resistance properties. Therefore, the S content is set to 0.0200% or less. The S content may be 0.0180% or less, 0.0150% or less, or 0.0120% or less.
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[0035] The S content is preferably as small as possible. However, in a case where the S content is less than 0.0001%, the time required for refining increases and this leads to a significant increase in cost. Therefore, the S content is set to 0.0001% or more. The S content may be 0.0005% or more, 0.0010% or more, or 0.0020% or more.
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Al: 0.001% to 1.000%

[0036] Al is an element that acts as a deoxidizing agent for steel and stabilizes ferrite. In a case where the Al content is less than 0.001%, the effect cannot be sufficiently obtained. Therefore, the Al content is set to 0.001% or more. The Al content may be 0.005% or more, 0.010% or more, or 0.020% or more.

[0037] Meanwhile, in a case where the Al content is more than 1.000%, coarse Al oxides are formed. The coarse oxides serve as crack initiation points. Therefore, in a case where coarse Al oxides are formed, cracking occurs in the coarse oxides, and the cracking propagates in the steel, leading to a deterioration in hydrogen embrittlement resistance properties. Therefore, the Al content is set to 1.000% or less. The Al content may be 0.950% or less, 0.900% or less, or 0.800% or less.

N: 0.0001% to 0.0200%

[0038] N is an element that forms coarse nitrides in the steel sheet and decreases the hydrogen embrittlement resistance properties of the steel sheet. In addition, N is an element that causes the generation of blowholes during welding.

[0039] In a case where the N content is more than 0.0200%, the hydrogen embrittlement resistance properties deteriorate, and the generation of blowholes is noticeable. Therefore, the N content is set to 0.0200% or less. The N content may be 0.0180% or less, 0.0160% or less, or 0.0120% or less.

[0040] Meanwhile, in a case where the N content is set to less than 0.0001%, the manufacturing cost increases significantly. Therefore, the N content is set to 0.0001% or more. The N content may be 0.0005% or more, 0.0010% or more, or 0.0020% or more.

O: 0.0001% to 0.0200%

[0041] O is an element that forms oxides and deteriorates the hydrogen embrittlement resistance properties. In particular, the oxides are present as inclusions in many cases. In a case where the oxides are present in a punched end surface or a cut surface, notch-like scratches or coarse dimples are formed on the end surface, which cause stress concentration during intensive working. These serve as crack initiation points and significantly deteriorate the workability. In a case where the O content is more than 0.0200%, the above-described tendency of deterioration in workability is noticeable. Therefore, the O content is set to 0.0200% or less. The O content may be 0.0180% or less, 0.0150% or less, or 0.0100% or less.

[0042] The O content is preferably low. However, from the economic perspective, it is not preferable the O content be less than 0.0001% due to an excessive increase in cost. Therefore, the O content is set to 0.0001% or more. The O content may be 0.0005% or more, 0.0010% or more, or 0.0015% or more.

[0043] The base elements of the chemical composition of the steel sheet according to the embodiment of the present invention are as described above. That is, the chemical composition of the steel sheet according to the present embodiment may contain the above elements and a remainder comprising Fe and impurities. Meanwhile, the chemical composition of the steel sheet according to the present embodiment may contain, instead of a part of Fe in the remainder, one or more of Co, Ni, Mo, Cr, Ti, B, Nb, V, Cu, W, Ta, Mg, Ca, Y, Zr, La, Ce, Sn, Sb, and As as an optional component in order to improve various properties.

[0044] Since these elements do not necessarily need to be contained, the lower limits thereof in content are 0%. In addition, even in a case where the following elements are contained as impurities, the effects of the steel sheet according to the present embodiment are not impaired.

Co: 0% to 0.500%

[0045] Co is an effective element for controlling the morphology of carbide and increasing the strength of the steel sheet. Therefore, Co may be contained. To sufficiently obtain the effect, the Co content is preferably set to 0.010% or more. The Co content may be 0.020% or more, 0.050% or more, or 0.100% or more.

[0046] Meanwhile, in a case where the Co content is more than 0.500%, coarse Co carbides are precipitated. In this case, the hydrogen embrittlement resistance properties may deteriorate. Therefore, the Co content is set to 0.500% or less. The Co content may be 0.450% or less, 0.400% or less, or 0.300% or less.

Ni: 0% to 1.000%

[0047] Ni is an effective element for increasing the strength of the steel sheet. In addition, Ni is also an effective element for improving the wettability and promoting an alloying reaction. Therefore, Ni may be contained. In order to obtain the above effect, the Ni content is preferably set to 0.010% or more. The Ni content may be 0.020% or more, 0.050% or

more, or 0.100% or more.

[0048] Meanwhile, in a case where the Ni content is more than 1.000%, the hydrogen embrittlement resistance properties may decrease. Therefore, the Ni content is set to 1.000% or less. The Ni content may be 0.900% or less, 0.800% or less, or 0.600% or less.

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Mo: 0% to 1.000%

[0049] Mo is an effective element for increasing the strength of the steel sheet. In addition, Mo is an element having an effect of suppressing ferritic transformation that occurs during a heat treatment in continuous annealing equipment or continuous hot-dip galvanizing equipment. Therefore, Mo may be contained. In order to obtain the above effect, the Mo content is preferably set to 0.010% or more. The Mo content may be 0.020% or more, 0.050% or more, or 0.080% or more.

[0050] Meanwhile, in a case where the Mo content is more than 1.000%, the effect of suppressing ferritic transformation is saturated. Therefore, the Mo content is set to 1.000% or less. The Mo content may be 0.900% or less, 0.800% or less, or 0.600% or less.

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Cr: 0% to 2.000%

[0051] Cr is an effective element for suppressing pearlitic transformation, thereby increasing the strength of steel, similar to Mn. Therefore, Cr may be contained. In order to obtain the above effect, the Cr content is preferably set to 0.001% or more. The Cr content may be 0.005% or more, 0.010% or more, or 0.050% or more.

[0052] Meanwhile, in a case where the Cr content is more than 2.000%, coarse Cr carbides may be formed in a center segregation portion and the hydrogen embrittlement resistance properties may decrease. Therefore, the Cr content is set to 2.000% or less. The Cr content may be 1.800% or less, 1.500% or less, or 1.000% or less.

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Ti: 0% to 0.500%

[0053] Ti is an element that contributes to an increase in strength of the steel sheet by precipitation strengthening, grain refinement strengthening by suppressing the growth of ferrite crystal grains, and dislocation strengthening by suppressing recrystallization. Therefore, Ti may be contained. In order to obtain the above effect, the Ti content is preferably set to 0.001% or more. The Ti content may be 0.003% or more, 0.010% or more, or 0.050% or more.

[0054] Meanwhile, in a case where the Ti content is more than 0.500%, the precipitation of carbonitrides may increase and the hydrogen embrittlement resistance properties may deteriorate. Therefore, the Ti content is set to 0.500% or less. The Ti content may be 0.450% or less, 0.400% or less, or 0.300% or less.

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B: 0% to 0.0100%

[0055] B is an element that suppresses the formation of ferrite and pearlite in the course of cooling from an austenite temperature range and promotes the formation of a low temperature transformation structure such as bainite or martensite. In addition, B is an element useful for high strengthening of steel. Therefore, B may be contained. In order to obtain the above effect, the B content is preferably set to 0.0001% or more. The B content may be 0.0003% or more, 0.0005% or more, or 0.0010% or more.

[0056] Meanwhile, in a case where the B content is more than 0.0100%, coarse B oxides are formed in the steel. Since the oxides serve as initiation points where voids are generated in cold working, the hydrogen embrittlement resistance properties may deteriorate due to the formation of coarse B oxides. Therefore, the B content is set to 0.0100% or less. The B content may be 0.0080% or less, 0.0060% or less, or 0.0050% or less.

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Nb: 0% to 0.500%

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[0057] Similar to Ti, Nb is an effective element for controlling the morphology of carbide and is also an effective element for improving the toughness by refining the structure. Therefore, Nb may be contained. In order to obtain the above effect, the Nb content is preferably set to 0.001% or more. The Nb content may be 0.002% or more, 0.010% or more, or 0.020% or more.

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[0058] Meanwhile, in a case where the Nb content is more than 0.500%, coarse Nb carbides are noticeably formed. Since cracking is likely to occur in the coarse Nb carbides, the hydrogen embrittlement resistance properties may deteriorate due to the formation of the coarse Nb carbides. Therefore, the Nb content is set to 0.500% or less. The Nb content may be 0.450% or less, 0.400% or less, or 0.300% or less.

V: 0% to 0.500%

[0059] V is an element that contributes to an increase in strength of the steel sheet by precipitation strengthening, grain refinement strengthening by suppressing the growth of ferrite crystal grains, and dislocation strengthening by suppressing recrystallization. Therefore, V may be contained. In order to obtain the above effect, the V content is preferably set to 0.001% or more. The V content may be 0.002% or more, 0.010% or more, or 0.020% or more.

[0060] Meanwhile, in a case where the V content is more than 0.500%, the precipitation of carbonitrides may increase and the hydrogen embrittlement resistance properties may deteriorate. Therefore, the V content is set to 0.500% or less. The V content may be 0.450% or less, 0.400% or less, or 0.300% or less.

Cu: 0% to 0.500%

[0061] Cu is an effective element for improving the strength of the steel sheet. In a case where the Cu content is less than 0.001%, it is not possible to sufficiently obtain the effect. Therefore, in order to obtain the above effect, the Cu content is preferably set to 0.001% or more. The Cu content may be 0.002% or more, 0.010% or more, or 0.030% or more.

[0062] Meanwhile, in a case where the Cu content is more than 0.500%, the hydrogen embrittlement resistance properties may deteriorate. In addition, in a case where the Cu content is large, the steel may embrittle during hot rolling and it may not be possible to perform the hot rolling. Therefore, the Cu content is set to 0.500% or less. The Cu content may be 0.450% or less, 0.400% or less, or 0.300% or less.

W: 0% to 0.100%

[0063] W is an effective element for increasing the strength of the steel sheet. In addition, W is an element that forms precipitates or crystallized substances. Since the precipitates and crystallized substances containing W act as hydrogen trap sites, W is an effective element for improving the hydrogen embrittlement resistance properties. Therefore, W may be contained. In order to obtain the above effect, the W content is preferably set to 0.001% or more. The W content may be 0.002% or more, 0.005% or more, or 0.010% or more.

[0064] Meanwhile, in a case where the W content is more than 0.100%, coarse W precipitates or crystallized substances are noticeably formed. Cracking is likely to occur in the coarse W precipitates or crystallized substances, and the cracking propagates in the steel with a low load stress. Therefore, in a case where coarse W precipitates or crystallized substances are formed, the hydrogen embrittlement resistance properties may deteriorate. Therefore, the W content is set to 0.100% or less. The W content may be 0.080% or less, 0.060% or less, or 0.050% or less.

Ta: 0% to 0.100%

[0065] Similar to Nb, V, and W, Ta is an effective element for controlling the morphology of carbide and increasing the strength of the steel sheet. Therefore, Ta may be contained. In order to obtain the above effect, the Ta content is preferably set to 0.001% or more. The Ta content may be 0.002% or more, 0.005% or more, or 0.010% or more.

[0066] Meanwhile, in a case where the Ta content is more than 0.100%, a large number of fine Ta carbides may be precipitated and the strength of the steel sheet may increase. With this, the ductility may decrease or the bending resistance and the hydrogen embrittlement resistance properties may decrease. Therefore, the Ta content is set to 0.100% or less. The Ta content may be 0.080% or less, 0.060% or less, or 0.050% or less.

Mg: 0% to 0.050%

[0067] Mg is an element capable of controlling the morphology of sulfide when contained in a small amount. Therefore, Mg may be contained. In order to obtain the above effect, the Mg content is preferably set to 0.001% or more. The Mg content may be 0.005% or more, 0.010% or more, or 0.020% or more.

[0068] Meanwhile, in a case where the Mg content is more than 0.050%, coarse inclusions may be formed and the hydrogen embrittlement resistance properties may decrease. Therefore, the Mg content is set to 0.050% or less. The Mg content may be 0.040% or less, 0.030% or less, or 0.020% or less.

Ca: 0% to 0.050%

[0069] Ca is an element that is useful as a deoxidizing element and is also effective in controlling the morphology of sulfide. Therefore, Ca may be contained. In order to obtain the above effect, the Ca content is preferably set to 0.001% or more. The Ca content may be 0.002% or more, 0.004% or more, or 0.006% or more.

[0070] Meanwhile, in a case where the Ca content is more than 0.050%, coarse inclusions may be formed and the

hydrogen embrittlement resistance properties may decrease. Therefore, the Ca content is set to 0.050% or less. The Ca content may be 0.040% or less, 0.030% or less, or 0.020% or less.

Y: 0% to 0.050%

[0071] Similar to Mg and Ca, Y is an element capable of controlling the morphology of sulfide when contained in a small amount. Therefore, Y may be contained. In order to obtain the above effect, the Y content is preferably set to 0.001% or more. The Y content may be 0.002% or more, 0.004% or more, or 0.006% or more.

[0072] Meanwhile, in a case where the Y content is more than 0.050%, coarse Y oxides may be formed and the hydrogen embrittlement resistance properties may decrease. Therefore, the Y content is set to 0.050% or less. The Y content may be 0.040% or less, 0.030% or less, or 0.020% or less.

Zr: 0% to 0.050%

[0073] Similar to Mg, Ca, and Y, Zr is an element capable of controlling the morphology of sulfide when contained in a small amount. Therefore, Zr may be contained. In order to obtain the above effect, the Zr content is preferably set to 0.001% or more. The Zr content may be 0.002% or more, 0.004% or more, or 0.006% or more.

[0074] Meanwhile, in a case where the Zr content is more than 0.050%, coarse Zr oxides may be formed and the hydrogen embrittlement resistance properties may decrease. Therefore, the Zr content is set to 0.050% or less. The Zr content may be 0.040% or less, 0.030% or less, or 0.020% or less.

La: 0% to 0.050%

[0075] Similar to Mg, Ca, Y, and Zr, La is an element capable of controlling the morphology of sulfide when contained in a small amount. Therefore, La may be contained. In order to obtain the above effect, the La content is preferably set to 0.001% or more. The La content may be 0.002% or more, 0.004% or more, or 0.006% or more.

[0076] Meanwhile, in a case where the La content is more than 0.050%, La oxides may be formed and the hydrogen embrittlement resistance properties may decrease. Therefore, the La content is set to 0.050% or less. The La content may be 0.040% or less, 0.030% or less, or 0.020% or less.

Ce: 0% to 0.050%

[0077] Similar to La, Ce is an element capable of controlling the morphology of sulfide when contained in a small amount. Therefore, Ce may be contained. In order to obtain the above effect, the Ce content is preferably set to 0.001% or more. The Ce content may be 0.002% or more, 0.004% or more, or 0.006% or more.

[0078] Meanwhile, in a case where the Ce content is more than 0.050%, Ce oxides may be formed and the hydrogen embrittlement resistance properties may decrease. Therefore, the Ce content is set to 0.050% or less. The Ce content may be 0.040% or less, 0.030% or less, or 0.020% or less.

Sn: 0% to 0.050%

[0079] Sn is an element that is contained in the steel in a case where a scrap is used as a raw material. In a case where the Sn content is large, the hydrogen embrittlement resistance properties may decrease due to grain boundary embrittlement. In a case where the Sn content is more than 0.050%, the adverse effect is particularly noticeable. Therefore, the Sn content is set to 0.050% or less. The Sn content may be 0.040% or less, 0.030% or less, or 0.020% or less.

[0080] The Sn content is preferably as small as possible and may be 0%. However, in a case where the Sn content is less than 0.001%, the refining cost increases. Therefore, the Sn content may be set to 0.001% or more. The Sn content may be 0.002% or more, 0.005% or more, or 0.010% or more.

Sb: 0% to 0.050%

[0081] Similar to Sn, Sb is an element that is contained in a case where a scrap is used as a raw material. Sb is an element that strongly segregates to grain boundaries and causes the grain boundary embrittlement and a decrease in ductility. In a case where the Sb content is more than 0.050%, the adverse effect is particularly noticeable. Therefore, the Sb content is set to 0.050% or less. The Sb content may be 0.040% or less, 0.030% or less, or 0.020% or less.

[0082] The Sb content is preferably as small as possible and may be 0%. However, in a case where the Sb content is less than 0.001%, the refining cost increases. Therefore, the Sb content may be set to 0.001% or more. The Sb content may be 0.002% or more, 0.005% or more, or 0.008% or more.

As: 0% to 0.050%

[0083] Similar to Sn and Sb, As is an element that is contained in a case where a scrap is used as a raw material, strongly segregates to grain boundaries, and causes the grain boundary embrittlement and a decrease in ductility. In a case where the As content is large, the hydrogen embrittlement resistance properties may decrease. In a case where the As content is more than 0.050%, the adverse effect is particularly noticeable. Therefore, the As content is set to 0.050% or less. The As content may be 0.040% or less, 0.030% or less, or 0.020% or less.

[0084] The As content is preferably as small as possible and may be 0%. However, in a case where the As content is less than 0.001%, the refining cost increases. Therefore, the As content may be set to 0.001% or more. The As content may be 0.002% or more, 0.003% or more, or 0.005% or more.

[0085] As described above, the chemical composition of the steel sheet according to the present embodiment may contain base elements and a remainder comprising Fe and impurities, or may contain base elements, one or more optional elements, and a remainder consisting of Fe and impurities.

[0086] The chemical composition of the steel sheet according to the present embodiment may be measured by a general method. For example, the measurement may be performed on chips using inductively coupled plasma-atomic emission spectrometry (ICP-AES) according to JISG1201: 2014. In this case, the chemical composition is the average content of (throughout) the whole sheet thickness. C and S, that cannot be measured by ICP-AES, may be measured using a combustion-infrared absorption method, N may be measured using an inert gas fusion-thermal conductivity method, and O may be measured using an inert gas fusion-nondispersive infrared absorption method. The Mn content obtained here is also used as [Mnave] to be described later.

[0087] In a case where the steel sheet is provided with a coating layer on the surface, the chemical composition may be analyzed after removing the coating layer by mechanical grinding or the like. In a case where the coating layer is a plating layer, the coating layer may be removed by dissolving the plating layer in an acid solution to which an inhibitor suppressing the corrosion of the steel sheet is added.

<Microstructure (Metallographic Structure)>

[0088] Next, the microstructure of the steel sheet according to the present embodiment will be described. In the present embodiment, the microstructure is a microstructure at a position ranging from 1/8 to 318 (t/4 portion) of the sheet thickness in the sheet thickness direction from the surface of the steel sheet. The reason why the microstructure is regulated in the t/4 portion is that it is a representative microstructure of the steel sheet and has a high correlation with the properties of the steel sheet.

[0089] In addition, the fraction (%) of each of the following phases is an area ratio unless otherwise specified.

Ferrite: 5.0% or less

[0090] Ferrite has an influence on the deformability of steel whose structure mainly includes martensite and tempered martensite. As the area ratio of ferrite increases, the local deformability and hydrogen embrittlement resistance properties decrease. In particular, in a case where the area ratio of ferrite is more than 5.0%, the hydrogen embrittlement resistance properties may decrease due to fractures in elastic deformation under stress loading. Therefore, the area ratio of ferrite is set to 5.0% or less. The area ratio of ferrite may be 4.0% or less, 3.0% or less, or 2.0% or less.

[0091] The area ratio of ferrite may be 0%. However, in order to control the area ratio to less than 1.0%, a high degree of control is required in the manufacturing, and this leads to a decrease in yield. Therefore, the area ratio of ferrite may be set to 1.0% or more.

Martensite and Tempered Martensite: more than 90.0% in total

[0092] The total area ratio of martensite (so-called fresh martensite) and tempered martensite has an influence on the strength of steel. As the area ratio increases, the tensile strength increases. In a case where the total area ratio of martensite and tempered martensite is 90.0% or less, the target tensile strength cannot be achieved. Moreover, fractures may be caused during elastic deformation under stress loading or the hydrogen embrittlement resistance properties may decrease. Therefore, the total area ratio of martensite and tempered martensite is set to more than 90.0%. The total area ratio of martensite and tempered martensite may be 95.0% or more, 97.0% or more, 99.0% or more, or 100.0%.

55 Remainder: one or two or more of bainite, pearlite, and residual austenite

[0093] The area ratio of the structure (the remainder in microstructure) other than the above-described structure may be 0%, but in a case where the remainder in microstructure is present, the remainder in microstructure includes one or

two or more of bainite, pearlite, and residual austenite.

[0094] In a case where the area ratio of the remainder in microstructure is more than 8.0%, the hydrogen embrittlement resistance properties may decrease due to fractures in elastic deformation under stress loading. Therefore, the area ratio of the remainder in microstructure is preferably 8.0% or less, and more preferably 7.0% or less. Of these, particularly, 5 pearlite and residual austenite are structures that deteriorate the local ductility of the steel, and are preferably as small as possible.

[0095] Meanwhile, a high degree of control is required in the manufacturing in order to control the area ratio of the remainder in microstructure to 0%, and this may lead to a decrease in yield. Therefore, the area ratio of the remainder in microstructure may be 1.0% or more.

[0096] The area ratio of each phase in the microstructure of the steel sheet according to the present embodiment can 10 be obtained by the following method.

(Method of Evaluating Area Ratio of Ferrite)

[0097] The area ratio of ferrite is obtained by observing a t/4 portion (ranging from 1/8 to 318 of the sheet thickness, 15 in which a 1/4 position of the sheet thickness is centered in the sheet thickness direction from the surface) of an electron channeling contrast image for which a field emission-scanning electron microscope (FE-SEM) is used. The electron channeling contrast image relates to a method of detecting a crystal orientation difference in crystal grains as a difference in contrast in an image, and in the image, a part that appears with uniform contrast in a structure determined to be ferrite rather than pearlite, bainite, martensite, or residual austenite is polygonal ferrite. The area ratio of polygonal ferrite is 20 calculated in each of 8 visual fields in a 35 $\mu\text{m} \times 25 \mu\text{m}$ electron channeling contrast image by an image analysis method, and the average value thereof is defined as the area ratio of ferrite.

(Method of Evaluating Total Area Ratio of Martensite and Tempered Martensite)

[0098] The total area ratio of martensite and tempered martensite is also obtained from an image taken with the above-described electron channeling contrast. These structures are more difficult to etch than ferrite and are thus present as protrusions on the structure observation section. Tempered martensite is an aggregate of lath-shaped crystal grains and contains iron-based carbides having a major axis of 20 nm or more therein, and the carbides belong to a plurality 30 of variants, that is, a plurality of iron-based carbide groups elongated in different directions. In addition, residual austenite is also present as protrusions on the structure observation section. Therefore, by subtracting, from the area ratio of the protrusions obtained by the above procedure, the area ratio of residual austenite measured by a procedure to be described later, the total area ratio of martensite and tempered martensite can be accurately measured.

(Method of Evaluating Total Area Ratio of Bainite, Pearlite, and Residual Austenite)

[0099] The area ratio of residual austenite can be calculated by measurement using X-rays. That is, a portion from 40 the sheet surface of a sample to a 1/4 position of the sheet thickness in the sheet thickness direction is removed by mechanical polishing and chemical polishing. The microstructural fraction of residual austenite is calculated from the integrated intensity ratio of the diffraction peaks of (200) and (211) of a bcc phase and (200), (220), and (311) of an fcc phase obtained from the polished sample using MoK α rays as characteristic X rays, and this is defined as the area ratio of residual austenite.

[0100] In addition, the area ratio of pearlite is obtained from an image taken with the above-described electron channeling contrast. Pearlite is a structure in which platelike carbides and ferrite are arranged.

[0101] In addition, bainite is an aggregate of lath-shaped crystal grains, contains no iron-based carbide having a major 45 axis of 20 nm or more therein or contains iron-based carbides having a major axis of 20 nm or more therein, and the carbides belong to a single variant, that is, an iron-based carbide group elongated in the same direction. Here, the iron-based carbide group elongated in the same direction means a group in which a difference in elongation direction of the iron-based carbide group is within 5°.

50 (Regions Having Mn Content of $1.1 \times [\text{Mnave}]$ or More Have Number Density of 5.0×10^{-4} Pieces/ μm^2 or More and are Present So That Average Interval Between Closest Regions Having Mn Content of $1.1 \times [\text{Mnave}]$ or More is 10.0 μm or Less)

[0102] Mn has an attracting interaction with H. Thus, in a case where the dispersion state thereof is controlled, it is possible to suppress the accumulation of H at prior austenite grain boundaries, and as a result, it is possible to obtain 55 a steel sheet having excellent hydrogen embrittlement resistance properties.

[0103] In the steel sheet according to the present embodiment, in a cross section in a sheet thickness direction, a

plurality of regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more, where the $[Mn_{ave}]$ is the average Mn content throughout the (whole) sheet thickness direction, are dispersed as regions having a higher attracting interaction with H than the prior austenite grain boundaries.

[0104] Meanwhile, in a case where the distance between the plurality of regions, that is, the interval between a region having an Mn content of $1.1 \times [Mn_{ave}]$ or more and a region having an Mn content of $1.1 \times [Mn_{ave}]$ or more closest to each other is more than $10.0 \mu\text{m}$ on average, the effect of suppressing the segregation of H to the prior austenite grain boundaries cannot be sufficiently obtained, whereby the hydrogen embrittlement resistance properties decrease.

[0105] Therefore, the plurality of regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more are present (dispersed) so that the average interval between closest regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more is $10.0 \mu\text{m}$ or less.

[0106] In addition, even in a case where the regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more are dispersed as described above, it is not possible to sufficiently obtain the effect in a case where the number density of the regions is low. The number density of the regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more is set to 5.0×10^{-4} pieces/ μm^2 or more.

[0107] The identification of the regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more, the number density of the regions, and the average interval between adjacent regions are obtained by the following methods.

[0108] The dispersion state of Mn is measured using an electron probe microanalyzer (EPMA). Specifically, a sample is collected so that a cross section parallel to the rolling direction of the steel sheet serves as a measurement surface, and in a $t/4$ portion (ranging from $1/8$ to $3/8$ of the sheet thickness, in which a $1/4$ position of the sheet thickness is centered in the sheet thickness direction from the surface) of the observation section, element concentration mapping for Mn is acquired at a measurement interval of $0.1 \mu\text{m}$ with a $50 \mu\text{m} \times 50 \mu\text{m}$ region as one visual field. This operation is performed in 10 visual fields, and elemental map data for the 10 visual fields is collected as numerical data. A binarized image is made in which regions having a Mn concentration of $1.1 \times [Mn_{ave}]$ or more and regions having a Mn concentration of less than $1.1 \times [Mn_{ave}]$ are distinguished by colors. From the binarized image, a region where a region satisfying $1.1 \times [Mn_{ave}]$ or more (having the Mn content of $1.1 \times [Mn_{ave}]$ or more) extends across a plurality of pixels is regarded as one region satisfying $1.1 \times [Mn_{ave}]$ or more, and the number of regions satisfying $1.1 \times [Mn_{ave}]$ or more is obtained. By dividing the obtained number by the area of one visual field, the number density of the regions satisfying $1.1 \times [Mn_{ave}]$ or more is obtained. In addition, a value obtained by raising the value, obtained by dividing the area of one visual field by the number obtained as described above, to the $1/2$ power is defined as the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ or more.

(Mechanical Properties)

[0109] In the steel sheet according to the present embodiment, as a strength that contributes to the weight reduction of vehicle bodies of vehicles, the tensile strength (TS) is set to 1,500 MPa or more.

[0110] There is no need to limit the upper limit. However, an increase in tensile strength may cause a decrease in formability. Therefore, the tensile strength may be set to 2,500 MPa or less or 2,000 MPa or less.

(Sheet thickness)

[0111] The sheet thickness of the steel sheet according to the present embodiment is not limited, but is preferably 1.0 mm or more and 2.2 mm or less. The sheet thickness is more preferably 1.05 mm or more or 1.1 mm or more. In addition, the sheet thickness is more preferably 2.1 mm or less or 2.0 mm or less.

(Coating Layer)

[0112] The steel sheet according to the present embodiment may have a coating layer containing zinc, aluminum, magnesium, or an alloy of these metals on its one or both surfaces. The coating layer may consist of zinc, aluminum, magnesium or an alloy of these metals and impurities.

[0113] Corrosion resistance is improved by providing a coating layer on the surface. In a case where there is a concern about holes due to corrosion in a steel sheet for a vehicle, the steel sheet cannot be thinned to a certain sheet thickness or less in some cases even in a case where the high strengthening is achieved. One purpose of high strengthening of the steel sheet is to reduce the weight by making the steel sheet thinner. Accordingly, even in a case where a high strength steel sheet is developed, the site where the steel sheet is to be applied is limited in a case where the steel sheet has low corrosion resistance. As a method for solving these problems, it is considered to form a coating layer on the front and back surfaces in order to improve the corrosion resistance.

[0114] Even in a case where a coating layer is formed, the hydrogen embrittlement resistance properties of the steel sheet according to the present embodiment are not impaired.

[0115] The coating layer is, for example, a hot-dip galvanized layer, a hot-dip galvannealed layer, an electrogalvanized

layer, an aluminum plating layer, a Zn-Al alloy plating layer, an Al-Mg alloy plating layer, or a Zn-Al-Mg alloy plating layer.

[0116] In a case where the surface has a coating layer, the surface serving as a reference for the above-described t/4 portion is a surface of the base metal excluding the coating layer.

5 <Manufacturing Method>

[0117] A manufacturing method with which the above-described steel sheet according to the present embodiment can be manufactured (the steel sheet manufacturing method according to the present embodiment) will be described.

[0118] The steel sheet manufacturing method according to the present embodiment includes:

10 (I) a heating step of heating a steel piece having a predetermined chemical composition;
 (II) a hot rolling step of hot-rolling the heated steel piece to obtain a hot-rolled steel sheet;
 15 (III) a post-hot rolling cooling step in which cooling of the hot-rolled steel sheet is started within less than 1.0 second from the completion of the hot rolling step, and the steel sheet is cooled to a cooling temperature of 400°C or higher and lower than 550°C at an average cooling rate of 20 °C/sec or higher and 50 °C/sec or lower;
 (IV) a coiling step of coiling the hot-rolled steel sheet after the post-hot rolling cooling step at the coiling temperature;
 20 (V) a cold rolling step of pickling and cold-rolling the hot-rolled steel sheet after the coiling step to obtain a cold-rolled steel sheet;
 (VI) an annealing step in which the cold-rolled steel sheet after the cold rolling step is heated to an annealing temperature of 830°C or higher and lower than 900°C so that the average rate of temperature increase from room temperature to 700°C is 15 °C/sec or higher and 100 °C/sec or lower and the average rate of temperature increase from 700°C to the annealing temperature is 5 °C/sec or higher and lower than 15 °C/sec, and the heated steel sheet is held at the annealing temperature for 25 to 100 seconds to be annealed; and
 25 (VII) a post-annealing cooling step of cooling the cold-rolled steel sheet after the annealing step to 25°C to 300°C at an average cooling rate of 4 to 100 °C/sec.

[0119] Hereinafter, preferable conditions for each step will be described.

30 [Heating Step]

[0120] In the heating step, a steel piece such as a slab having a predetermined chemical composition (that is the same chemical composition as the steel sheet according to the present embodiment since the chemical composition does not substantially change in the manufacturing stage) is heated prior to the hot rolling step.

[0121] The heating temperature is not limited as long as the rolling temperature for the next step can be secured. For example, the heating temperature is 1,000°C to 1,300°C.

[0122] The steel piece to be used is preferably cast by a continuous casting method from the viewpoint of productivity, but may be manufactured by an ingot-making method or a thin slab casting method.

[0123] In a case where a steel piece obtained by continuous casting can be subjected to the hot rolling step while it maintains a sufficiently high temperature, the heating step may be omitted.

40 [Hot Rolling Step]

[0124] In the hot rolling step, the heated steel piece is hot-rolled to obtain a hot-rolled steel sheet.

[0125] The hot rolling step includes rough rolling and finish rolling. In the finish rolling, a plurality of passes of reduction is performed, and among the plurality of passes, 4 or more passes are large reduction passes with a rolling reduction of 20% or higher. The interpass time between the large reduction passes is set to 5.0 seconds or shorter. Further, the rolling start temperature is set to 950°C to 1,100°C, and the rolling finishing temperature is set to 800°C to 950°C.

(Large Reduction Passes with Rolling Reduction of 20% or Higher in Finish Rolling: 4 or More Passes)

(Interpass Time Between Large Reduction Passes: within 5.0 seconds)

[0126] The morphology of austenite grains can be controlled equiaxially and finely by controlling the rolling reduction in finish rolling, the number of times of rolling, and the interpass time. In a case where the austenite grains become equiaxed and fine, a pearlite structure is uniformly and finely formed in the subsequent post-hot rolling cooling step. The pearlite structure contains cementite, and as a result, it becomes possible to obtain a structure in which the cementite is uniformly and finely precipitated (precipitated in a dispersed manner). In a case where the number of passes (large reduction passes) with a rolling reduction of 20% or higher is less than 4, unrecrystallized austenite remains, and it is

not possible to sufficiently obtain the effect. Therefore, the rolling reduction is set to 20% or higher in 4 or more passes (4 or more passes of reduction are performed with a rolling reduction of 20% or higher). Preferably, the rolling reduction is set to 20% or higher in 5 or more passes. Meanwhile, the upper limit of the number of passes with a rolling reduction of 20% or higher is not particularly limited. However, in order to conduct more than 10 passes, it is necessary to install a large number of rolling stands, and the size of equipment and the manufacturing cost may be increased. Therefore, the number of passes (pass number) with a rolling reduction of 20% or higher may be 10 or less, 9 or less, or 7 or less.

[0127] In addition, the interpass time in finish rolling has a great influence on the recrystallization and grain growth of the austenite grains after rolling. Even in a case where the number of large reduction passes is 4 or more, the grains are likely to grow in a case where the interpass time between the large reduction passes is longer than 5.0 seconds, so the austenite grains become coarse. The interpass time is preferably 3.0 seconds or shorter or 1.0 second or shorter.

[0128] Meanwhile, it is not necessary to limit the lower limit of the interpass time. However, in a case where the interpass time between the large reduction passes is shorter than 0.2 seconds, the recrystallization of the austenite is not completed and the ratio of unrecrystallized austenite increases. Therefore, it is not possible to sufficiently obtain the effect in some cases. Therefore, the interpass time between the large reduction passes is preferably set to 0.2 seconds or longer. The interpass time may be 0.3 seconds or longer or 0.5 seconds or longer.

(Rolling Start Temperature: 950°C to 1,100°C)

(Rolling Finishing Temperature: 800°C to 950°C)

[0129] The rolling start temperature is an important factor for controlling the recrystallization of austenite. In a case where the rolling start temperature is lower than 950°C, the temperature decreases during rolling, and unrecrystallized austenite remains. Accordingly, ferrite grains are formed along the elongated unrecrystallized austenite grain boundaries, and the untransformed austenite in the grains turns into a pearlite structure. In this case, the size of the ferrite grains increases, and thus when Mn is concentrated in the pearlite structure, the average interval between the Mn-concentrated portions becomes more than 10.0 μm .

[0130] Meanwhile, in a case where the rolling start temperature is higher than 1,100°C, the temperature during the course of the rolling becomes high, and thus an alloying element that suppresses ferritic transformation is likely to be concentrated at the austenite grain boundaries. In this case, the ferritic transformation is delayed in the course of cooling after finish rolling, the ratio of the pearlite structure increases, and Mn is not sufficiently concentrated in the cementite in the pearlite structure. In this case, eventually, regions having an Mn content of $1.1 \times [\text{Mnave}]$ or more cannot be sufficiently obtained.

[0131] In addition, in a case where the rolling finishing temperature is lower than 800°C, unrecrystallized austenite remains, and as a result, the average interval between regions satisfying $1.1 \times [\text{Mnave}]$ increases.

[0132] In addition, in a case where the rolling finishing temperature is higher than 950°C, the ferritic transformation is excessively suppressed, and the interval between cementite in which Mn is concentrated increases or the number density decreases. Eventually, the average interval between the regions having an Mn content of $1.1 \times [\text{Mnave}]$ or more and the number density of the regions do not fall within the preferable ranges.

[0133] Therefore, the rolling start temperature is set to 950°C to 1,100°C, and the rolling finishing temperature is set to 800°C to 950°C.

[Post-Hot Rolling Cooling Step]

[Cooling Step]

[0134] In the post-hot rolling cooling step, cooling of the hot-rolled steel sheet obtained in the hot rolling step is started within less than 1.0 second from the completion of the hot rolling step, and the steel sheet is cooled to a cooling temperature of 400°C or higher and lower than 550°C at an average cooling rate of 20 °C/sec or higher and 50 °C/sec or lower. In addition, in the cooling step, the hot-rolled steel sheet after the post-hot rolling cooling step is coiled at the cooling temperature.

[0135] By performing these steps under predetermined conditions, the pearlite structure is finely dispersed during cooling and the cementite in the pearlite structure is also finely dispersed accordingly. In addition, Mn is concentrated in the cementite after cooling.

[0136] It is not preferable that the time from the completion of the hot rolling to the start of the cooling be 1.0 second or longer, the average cooling rate be lower than 20 °C/sec, or the cooling stop temperature (cooling temperature) be 550°C or higher, since the ferrite grains excessively grow and the interval between the pearlite structures dispersed becomes large. In this case the average interval between cementite in which Mn is concentrated increases after cooling.

[0137] Meanwhile, in a case where the average cooling rate is higher than 50 °C/sec, a hard phase such as bainite

and martensite is likely to be formed and the ratio of the pearlite structure thus decreases. Accordingly, it is not possible to sufficiently obtain the cementite in which Mn is concentrated.

[0138] In addition, in a case where the cooling stop temperature is lower than 400°C, Mn may be insufficiently concentrated in the cementite in the pearlite structure.

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[Cold Rolling Step]

[0139] In the cold rolling step, the hot-rolled steel sheet after the coiling step is recoiled, pickled, and cold-rolled to obtain a cold-rolled steel sheet.

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[0140] By performing the pickling, oxide scale on the surface of the hot-rolled steel sheet is removed, and the chemical convertibility and plating properties of the cold-rolled steel sheet can be improved. The pickling may be performed under known conditions, and may be performed once or separately performed a plurality of times. The rolling reduction of the cold rolling is not particularly limited. For example, the rolling reduction is 20% to 80%.

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[Annealing Step]

[Post-Annealing Cooling Step]

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[0141] In the annealing step, the cold-rolled steel sheet after the cold rolling step is heated to an annealing temperature of 830°C or higher and lower than 900°C so that the average rate of temperature increase from room temperature (for example, 25°C) to 700°C is 15 to 100 °C/sec and the average rate of temperature increase from 700°C to the annealing temperature is 5 °C/sec or higher and lower than 15 °C/sec, and the heated steel sheet is held at the annealing temperature for 25 to 100 seconds to be annealed. The average rate of temperature increases up to 700°C is preferably 17 °C/sec or higher, and more preferably 20 °C/sec or higher. The average rate of temperature increases from 700°C to the annealing temperature of 830°C or higher and lower than 900°C is preferably 6 °C/sec or higher and 14 °C/sec or lower, and more preferably 7 °C/sec or higher and 13 °C/sec or lower.

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[0142] After that, in the post-annealing cooling step, the cold-rolled steel sheet after the annealing step is cooled to 25°C to 300°C at an average cooling rate of 4 to 100 °C/sec.

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[0143] In these steps, while maintaining the dispersion state of Mn concentrated in the cementite, the cementite is dissolved by heating to the austenite single phase region, cooling to 300°C or lower is performed, and thus it is possible to obtain a structure mainly including martensite in which the Mn-concentrated portions are dispersed.

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[0144] In the course of temperature increase in the annealing step, in a case where the average rate of temperature increase from room temperature (for example, 25°C) to 700°C is lower than 15 °C/sec, the cementite coarsens. Since the size of the cementite is the same as that of the Mn-concentrated portion, the average interval between the regions satisfying $1.1 \times [\text{Mnave}]$ or more after annealing may increase, and the number density of the regions may decrease. Meanwhile, in order to raise the average rate of temperature increase to higher than 100 °C/sec, special equipment is required, which increases the practical cost.

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[0145] In addition, in a temperature range from 700°C to the annealing temperature (830°C or higher and lower than 900°C), the recrystallization is promoted, the grain boundaries and the density of dislocation are reduced, and thus the diffusion of Mn is suppressed. In a case where the average rate of temperature increase in this temperature range is lower than 5 °C/sec, Mn may be diffused and the dispersion state of the Mn-concentrated portions may be eliminated. Meanwhile, in a case where the average rate of temperature increase is 15 °C/sec or higher, the recrystallization may not occur, Mn may be diffused by the grain boundaries and dislocation, and the dispersion state of the Mn-concentrated portions may be eliminated.

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[0146] In a case where the annealing temperature is lower than 830°C, austenite reverse transformation may not be completed, the volume percentage of the ferrite structure may increase, and the strength may not be reached. This is because the cementite in which Mn is concentrated has high thermal stability and is thus likely to remain without being dissolved and the ferrite structure also remains accordingly. Meanwhile, in a case where the annealing temperature is 900°C or higher, Mn is diffused and the dispersion state of the Mn-concentrated portions dispersed preferably is eliminated.

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[0147] In a case where the annealing time (holding time) is shorter than 25 seconds, austenitizing may not be sufficient and a target structure may not be obtained. Meanwhile, in a case where the annealing time is longer than 100 seconds, Mn may be diffused and the dispersion state of the Mn-concentrated portions may be eliminated.

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[0148] In the post-annealing cooling step, in a case where the average cooling rate up to the cooling stop temperature is lower than 4 °C/sec, a structure such as ferrite or bainite is formed and a target structure cannot be obtained. Meanwhile, in order to raise the average cooling rate to higher than 100 °C/sec, special equipment is required, which increases the practical cost.

[0149] In a case where the cooling stop temperature is higher than 300°C, a bainite structure is formed and a target

structure cannot be obtained. Meanwhile, in order to control the cooling stop temperature to lower than 25°C, it is necessary to use a special cooling medium or the like, which creates problems in cost and productivity.

[Tempering Step]

[0150] In the steel sheet manufacturing method according to the present embodiment, a tempering step of heating the cold-rolled steel sheet after the annealing step to 50°C or higher and lower than 500°C and holding the steel sheet for 5 seconds or longer and shorter than 1,000 seconds may be further performed.

[0151] Through the tempering under the above conditions, the martensite is turned into tempered martensite, and thus the formability can be improved.

[0152] In a case where the tempering temperature (holding temperature) is lower than 50°C or the holding time is shorter than 5 seconds, the above effect cannot be obtained. Meanwhile, in a case where the tempering temperature is 500°C or higher, Mn is diffused and there is a concern that the dispersion state of the Mn-concentrated portions may be eliminated. In addition, the strength may decrease due to a decrease in dislocation density in the tempered martensite and the tensile strength may thus be decreased. In addition, in a case where the holding time is 1,000 seconds or longer, the strength decreases and the productivity decreases. The tempering may be performed in the continuous annealing equipment or performed offline in separate equipment after continuous annealing.

[0153] In the steel sheet manufacturing method according to the present embodiment, a coating layer containing zinc, aluminum, magnesium, or an alloy of these metals may be formed on the surface of the steel sheet at any point in time between the post-annealing cooling step and the tempering step.

[0154] The coating layer is preferably a coating layer containing zinc, aluminum, magnesium, or an alloy of these metals. The coating layer is, for example, a plating layer.

[0155] The coating method is not limited. However, for example, in a case where a coating layer mainly containing zinc is formed by hot-dip plating, conditions therefor are as follows: the steel sheet temperature of the cold-rolled steel sheet is adjusted to be (plating bath temperature - 40)°C to (plating bath temperature + 50)°C (heating or cooling is performed); and then the steel sheet is immersed in the plating bath at 450°C to 490°C to form a plating layer.

[0156] The reasons why the above conditions are preferable are that in a case where the steel sheet temperature in the immersion in the plating bath is lower than hot-dip galvanizing bath temperature - 40°C, the heat removed during the immersion in the plating bath may be large and a part of the molten zinc may solidify, deteriorating the appearance of the plating, and in a case where the steel sheet temperature in the immersion in the plating bath is higher than hot-dip galvanizing bath temperature + 50°C, operational problems are generated due to an increase in temperature of the plating bath.

[0157] In the formation of a plating layer mainly containing zinc, the effective Al content (the value obtained by subtracting the total Fe content from the total Al content in the plating bath) in the composition of the plating bath is preferably 0.050 to 0.250 mass%. In addition, Mg is preferably contained as necessary and the remainder preferably consists of Zn and impurities. In a case where the effective Al content in the plating bath is less than 0.050 mass%, the intrusion of Fe into the plating layer may proceed excessively, leading to a decrease in plating adhesion. Meanwhile, in a case where the effective Al content in the plating bath is more than 0.250 mass%, Al-based oxides inhibiting the movement of Fe atoms and Zn atoms may be formed at the boundary between the steel sheet and the plating layer, leading to a decrease in plating adhesion.

[Examples]

[Example 1]

[0158] Steels having chemical compositions shown in Tables 1-1 and 1-2 were melted and cast into steel pieces. The steel piece was inserted into a furnace heated to 1,200°C, subjected to a homogenization treatment for holding for 60 minutes, taken out into the air, and hot-rolled to obtain a steel sheet having a sheet thickness of 2.8 mm. In the hot rolling, a total of 7 finish rolling passes were continuously performed using a rolling mill having 7 stands (so that a constant interpass time was provided), and among the passes, 4 rolling passes with a rolling reduction higher than 20% were performed. In addition, the interpass time between each rolling pass for which a rolling reduction of 20% or higher was applied in the finish rolling and a rolling pass immediately before each rolling pass was set to 0.6 seconds. In the finish rolling, the start temperature was 1,070°C and the finishing temperature was 850°C. The steel sheet was cooled by water 0.8 seconds after completion of the finish rolling, cooled to 530°C at an average cooling rate of 29.0 °C/sec, and then coiled. However, in a case of AH-0, the steel sheet embrittled and cracked during hot rolling, and the subsequent steps were not performed.

[0159] Subsequently, oxide scale on the hot-rolled steel sheet was removed by pickling, and the steel sheet was cold-rolled with a rolling reduction of 50.0% and finished so as to have a sheet thickness of 1.4 mm.

[0160] Furthermore, the cold-rolled steel sheet was heated from room temperature to 700°C at an average rate of temperature increase of 35.0 °C/sec and was heated from 700°C to 860°C at an average rate of temperature increase of 10 °C/sec. After holding the steel sheet at 860°C for 80 seconds, the steel sheet was cooled to 190°C at an average cooling rate of 38.0 °C/sec.

5 [0161] Next, tempering was performed by reheating to 230°C and holding for 180 seconds. No plating was performed.

[0162] A microstructure of the obtained cold-rolled steel sheet was observed in the above-described manner, and the area ratio of each phase in a t/4 portion was obtained. In addition, in the t/4 portion, the number density of regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more and the average interval between closest regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more were measured.

10 [0163] The results are shown in Table 2.

[0164] In addition, the chemical compositions obtained by analyzing the samples collected from the manufactured steel sheets were the same as the chemical compositions of the steels shown in Tables 1-1 and 1-2.

[0165] In addition, tensile properties and hydrogen embrittlement resistance (hydrogen embrittlement resistance properties) of the obtained cold-rolled steel sheets were evaluated in the following manner.

15 (Method of Evaluating Tensile Properties)

[0166] A JIS No. 5 test piece was collected from a direction in which the longitudinal direction of the test piece was parallel to the orthogonal-to-rolling direction of the steel, and a tensile test was performed according to JIS Z 2241 (2011) to measure the tensile strength (TS) and the total elongation (EI).

(Method of Evaluating Hydrogen Embrittlement Resistance)

[0167] The hydrogen embrittlement resistance properties of the steel sheet manufactured using the steel sheet manufacturing method according to the embodiment of the present invention were evaluated by the following method. Specifically, the steel sheet was sheared with a clearance of 10%, and then a U-bending test was performed at 10R. A strain gauge was attached to the center of the obtained test piece, and a stress was applied by tightening both ends of the test piece with bolts. The applied stress was calculated from the monitored strain in the strain gauge. As a load stress, a stress corresponding to 80% of the tensile strength (TS) was applied (for example, in a case of A-0 in Table 2, applied stress = $2,213 \text{ MPa} \times 0.8 = 1,770 \text{ MPa}$). This is because the residual stress that is introduced during forming is considered to correspond to the tensile strength of the steel sheet.

[0168] The obtained U-bending test piece was immersed in an HCl aqueous solution having a pH of 2 at a liquid temperature of 25°C and held for 48 hours, and the presence or absence of cracking was investigated. The lower the pH of the HCl aqueous solution and the longer the immersion time, the larger the amount of hydrogen intruding into the steel sheet. Therefore, the hydrogen embrittlement environment becomes severe.

[0169] After the immersion, a case where a crack having a length longer than 1.00 mm was recognized in the U-bending test piece was evaluated NG, and a case where no crack having a length longer than 1.00 mm was recognized was evaluated OK.

[0170] A steel sheet having a tensile strength of 1,500 MPa or more and evaluated OK in terms of hydrogen embrittlement resistance was evaluated to have a high strength and excellent hydrogen embrittlement resistance.

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[Table 1-1]

Steel Type No.	Chemical Composition (mass%: Remainder being Fe and Impurities)														
	C	Si	Mn	P	S	Al	N	O	Co	Ni	Mo	Cr	Ti	B	
5	A 0.369	1.13	1.5	0.0166	0.0034	0.2285	0.0188	0.0088	0.203	0.651	0.852	0.746	0.305	0.0090	
	B 0.232	1.78	0.9	0.0180	0.0026	0.7358	0.0123	0.0078	0.457	0.469	0.695	0.066	0.0070		
	C 0.394	1.41	1.2	0.0186	0.0158	0.4723	0.0148	0.0118	0.411	0.484	0.476	0.301	0.150	0.0010	
	D 0.240	0.57	2.0	0.0105	0.0171	0.8911	0.0100	0.0191	0.374	0.699	0.347	1.502	0.098	0.0050	
	E 0.210	0.78	1.8	0.0112	0.0100	0.1596	0.0076	0.0129	0.290	0.108	0.043	0.565	0.126	0.0060	
	F 0.292	1.54	1.3	0.0088	0.0180	0.0233	0.0117	0.0136	0.331	0.369	0.426	0.976	0.244	0.0030	
	G 0.164	1.69	1.6	0.0158	0.0115	0.4352	0.0007	0.0179	0.366	0.951	0.177	0.158	0.343	0.0070	
10	H 0.175	1.90	1.0	0.0077	0.0064	0.6206	0.0041	0.0095	0.123	0.268	0.262	0.065	0.373	0.0070	
	I 0.186	0.97	1.6	0.0140	0.0006	0.8232	0.0141	0.0169	0.073	0.326	0.631	1.265	0.406	0.0080	
	J 0.279	0.11	1.1	0.0035	0.0132	0.1356	0.0169	0.0151	0.485	0.881	0.320	1.436	0.277	0.0040	
	K 0.361	0.48	0.9	0.0056	0.0069	0.3954	0.0087	0.0033	0.250	0.792		0.891	0.487	0.0020	
	L 0.310	0.32	1.3	0.0129	0.0044	0.3332	0.0018	0.0006	0.208	0.022	0.130	1.657	0.228	0.0050	
	M 0.324	0.83	1.7	0.0005	0.0135	0.9419	0.0060	0.0065	0.041	0.152	0.573	1.734	0.014	0.0010	
15	N 0.343	0.21	1.4	0.0044	0.0188	0.7161	0.0178	0.0043	0.106	0.847	0.775	1.077	0.175	0.0090	
	O 0.259	1.32	1.8	0.0021	0.0083	0.5858	0.0050	0.0022							
	P 0.144	1.13	1.9	0.0185	0.0038	0.6673	0.0181	0.0044	0.287		0.442	0.406	0.449	0.0020	
	Q 0.406	0.25	0.9	0.0099	0.0022	0.6972	0.0163	0.0103	0.159	0.690	0.907	0.817	0.033	0.0070	
	R 0.386	2.08	1.6	0.0100	0.0072	0.9315	0.0093	0.0091	0.215	0.752	0.272	0.689	0.371	0.0060	
	S 0.178	1.22	0.7	0.0143	0.0039	0.4277	0.0102	0.0109	0.300	0.614	0.554	1.886	0.042	0.0080	
	T 0.164	1.77	2.3	0.0077	0.0171	0.3058	0.0138	0.0099	0.272	0.418	0.452	0.784	0.303	0.0070	
20	U 0.230	1.10	1.6	0.0204	0.0030	0.2960	0.0189	0.0130	0.337	0.865	0.209		0.146	0.0060	
	V 0.358	0.70	1.8	0.0042	0.0205	0.3190	0.0039	0.0070	0.088	0.635		0.333	0.116	0.0060	
	W 0.260	1.26	1.7	0.0098	0.0046	1.0342	0.0015	0.0173	0.115	0.354	0.226		0.082	0.0050	
	X 0.345	0.71	1.9	0.0015	0.0177	0.6762	0.0205	0.0160	0.290	0.882	0.631	1.075	0.216	0.0070	
	Y 0.382	1.12	1.4	0.0043	0.0089	0.7820	0.0058	0.0207	0.088	0.049	0.528	0.315	0.087	0.0040	
	Z 0.341	0.57	1.4	0.0154	0.0165	0.5530	0.0035	0.0075	0.519	0.131	0.813	0.910	0.252	0.0030	
25	AA 0.207	1.54	1.2	0.0057	0.0181	0.2493	0.0030	0.0133	0.189	1.024	0.132	0.337	0.360	0.0070	
	AB 0.222	0.30	1.0	0.0127	0.0105	0.9451	0.0053	0.0058	0.236	0.730	1.022	1.535	0.346	0.0080	
	AC 0.364	1.84	1.5	0.0027	0.0076	0.2812	0.0076	0.0134	0.480	0.568	0.358	2.049	0.163	0.0070	
	AD 0.238	1.39	1.0	0.0040	0.0092	0.3185	0.0017	0.0041	0.456	0.243		0.634	0.519	0.0080	
	AE 0.216	0.60	0.9	0.0112	0.0160	0.0590	0.0052	0.0112	0.040	0.655		1.808	0.327	0.0110	
	AF 0.254	1.70	1.2	0.0017	0.0084	0.0968	0.0086	0.0085	0.238	0.969	0.786	1.675	0.273	0.0050	
	AG 0.202	1.70	1.2	0.0095	0.0135	0.4115	0.0066	0.0108		0.751	0.846	1.395	0.363	0.0040	
	AH 0.369	0.20	1.2	0.0089	0.0150	0.6881	0.0054	0.0113		0.686	0.918	0.102	0.114	0.0090	
	AI 0.285	1.82	1.3	0.0161	0.0055	0.9382	0.0097	0.0062	0.320	0.192	0.289	1.018	0.359	0.0030	
30	AJ 0.321	0.79	1.7	0.0146	0.0014	0.7968	0.0186	0.0116	0.352	0.887	0.739	0.423	0.094	0.0070	
	AK 0.388	0.59	1.9	0.0105	0.0118	0.3954	0.0085	0.0130	0.173	0.329	0.577	1.060	0.385	0.0020	
	AL 0.220	1.88	1.0	0.0062	0.0150	0.0798	0.0070	0.0038	0.396	0.174	0.331	1.541	0.132	0.0010	
	AM 0.204	0.73	1.5	0.0006	0.0109	0.8423	0.0076	0.0138	0.205	0.069	0.677	1.300	0.084	0.0080	
	AN 0.241	0.12	1.1	0.0156	0.0059	0.2451	0.0156	0.0088	0.295	0.265	0.364	1.764	0.317	0.0090	

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[Table 1-2]

Steel Type No.	Chemical Composition (mass%: Remainder being Fe and Impurities)															
	Nb	V	Cu	W	Ta	Mg	Ca	Y	Zr	La	Ce	Sn	Sb	As		
5	A	0.381	0.179	0.250	0.037	0.033	0.048	0.038	0.020	0.026	0.010	0.037	0.012	0.012	0.042	
	B	0.185	0.137	0.211	0.094	0.081	0.041	0.002	0.043	0.030	0.049	0.024	0.015	0.005	0.023	
	C	0.414	0.063	0.110		0.068	0.011	0.020	0.026		0.034	0.013	0.037	0.034	0.038	
	D	0.458	0.445	0.131	0.033		0.017	0.041	0.003	0.044	0.029	0.006	0.033	0.038	0.018	
	E	0.203	0.255	0.356	0.063	0.044	0.043	0.045	0.035	0.041	0.031	0.026	0.026	0.015	0.011	
	F	0.471	0.113	0.459	0.024	0.089	0.022	0.028	0.047	0.012	0.012	0.049	0.010	0.010	0.007	
10	G	0.245	0.227			0.068	0.098	0.002	0.025	0.017	0.010	0.046	0.030	0.042	0.018	0.004
	H	0.340	0.335			0.078	0.064	0.019	0.023	0.042	0.019	0.024	0.042	0.029	0.004	0.008
	I	0.314	0.473	0.103	0.052	0.017	0.026	0.016	0.023	0.021	0.023	0.009	0.044	0.044	0.046	
	J	0.144	0.425	0.053	0.091	0.057	0.005	0.014	0.038	0.017	0.039	0.015	0.049	0.029	0.048	
	K	0.125	0.009	0.069	0.086	0.053	0.038	0.034	0.030	0.040	0.016	0.018	0.035	0.032	0.029	
	L	0.288	0.283	0.256			0.032	0.033	0.005	0.049		0.002	0.021	0.048	0.032	
	M	0.091	0.388	0.050	0.059		0.035	0.005	0.011			0.045	0.019	0.023	0.034	
	N	0.013	0.091	0.122		0.078	0.030	0.048	0.010	0.031	0.019	0.034	0.004	0.026	0.016	
15	O															
	P	0.101	0.362	0.416	0.085	0.094	0.020	0.008	0.046	0.039		0.048	0.038	0.012	0.034	
	Q	0.347	0.050	0.218	0.081	0.068	0.037	0.014	0.042	0.007		0.010	0.009	0.043	0.022	
	R	0.209	0.132	0.222	0.024	0.060	0.011	0.007	0.017	0.029		0.033	0.011	0.033	0.004	
	S	0.395	0.467	0.050	0.063	0.035	0.020	0.021	0.005	0.022	0.030	0.008	0.009	0.017	0.007	
	T	0.435	0.273			0.032	0.049	0.045	0.039	0.045	0.025	0.015	0.038	0.034	0.003	0.018
20	U	0.359	0.269	0.032	0.092	0.008	0.040	0.031	0.012	0.013	0.032	0.038	0.018	0.004	0.017	
	V	0.109	0.102	0.035	0.074	0.082	0.026	0.048	0.039	0.047	0.013	0.037	0.021	0.033	0.016	
	W	0.144	0.421	0.062	0.091	0.018	0.041	0.038	0.026	0.004	0.010		0.034	0.048	0.026	
	X	0.119	0.314	0.064	0.058	0.092	0.011	0.010	0.011	0.029			0.022	0.021	0.011	
	Y	0.080	0.163	0.028	0.075	0.043	0.042	0.018	0.002	0.046			0.044	0.039	0.013	
	Z	0.238	0.181			0.032	0.039	0.029	0.019	0.010	0.043	0.025	0.034	0.023	0.047	
25	AA	0.339	0.016	0.120	0.084	0.078	0.049	0.029	0.036	0.041	0.011	0.024	0.041	0.045	0.047	
	AB	0.125	0.301	0.070		0.034	0.033	0.026	0.016	0.045	0.028	0.045	0.033	0.036	0.022	
	AC	0.059	0.183	0.075	0.043	0.040	0.004	0.010	0.049	0.006	0.045	0.015	0.003	0.043	0.038	
	AD	0.260	0.347	0.029	0.028	0.024	0.007	0.041	0.026	0.013	0.038	0.042	0.026	0.008	0.034	
	AE	0.046	0.081	0.057	0.059	0.067	0.004	0.017	0.003	0.017	0.036		0.033	0.046	0.043	
	AF	0.516	0.098	0.074	0.083	0.082	0.044	0.041	0.005		0.019		0.039	0.031	0.003	
	AG	0.388	0.518	0.013	0.056	0.011	0.033	0.021	0.033	0.043	0.005	0.012	0.031	0.037	0.014	
	AH	0.471	0.353	0.598		0.087	0.003	0.023	0.019	0.042	0.015	0.005	0.019	0.036	0.029	
	AI	0.037	0.046	0.041	0.103	0.053	0.013	0.035	0.035	0.016	0.046	0.045	0.030	0.005	0.041	
30	AJ	0.166	0.265			0.042		0.052	0.046	0.031	0.017	0.003	0.039	0.024	0.029	0.035
	AK	0.385	0.411			0.096		0.016	0.051	0.034	0.030	0.028	0.018	0.005	0.004	0.021
	AL	0.232	0.230	0.096	0.068	0.084	0.036	0.018	0.037	0.052	0.047	0.032	0.044	0.019	0.036	
	AM	0.291	0.159	0.021	0.061	0.071	0.026	0.018	0.012	0.004	0.025	0.040	0.051	0.023	0.040	
	AN	0.301	0.472	0.089	0.072	0.087	0.041	0.005	0.043	0.048	0.008	0.039	0.046	0.052	0.012	

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[Table 2]

No.	Steel Type	Ferrite (%)	Martensite (%)	Remainder in Microstructure (%)	Tensile Strength (MPa)	Total Elongation (%)	Average Interval Between Regions Satisfying $1.1 \times [\text{Mnave}]$ (μm)	Number Density of Regions Satisfying $1.1 \times [\text{Mnave}]$ ($\times 10^4$ pieces/ μm^2)	Hydrogen Embrittlement Resistance	Remarks
5	A-0	A	0.0	100.0	0.0	2213	7.6	8.5	5.6	OK
10	B-0	B	0.0	100.0	0.0	1742	8.2	7.5	7.3	OK
15	C-0	C	0.0	100.0	0.0	1958	9.3	5.6	7.8	OK
20	D-0	D	1.1	97.5	1.4	1553	8.2	8.2	9.4	OK
25	E-0	E	1.1	97.5	1.3	1688	7.9	9.5	6.7	OK
30	F-0	F	0.0	100.0	0.0	1840	8.3	9.7	5.9	OK
35	G-0	G	2.0	94.5	3.4	1503	9.1	8.4	8.1	OK
40	H-0	H	0.0	100.0	0.0	1590	10.1	5.8	5.8	OK
45	I-0	I	0.0	100.0	0.0	1625	7.6	5.9	7.6	OK
50	J-0	J	1.6	96.8	1.6	1759	8.3	6.7	5.8	OK
	K-0	K	1.8	97.1	1.1	1822	8.0	6.2	7.5	OK
	L-0	L	0.0	100.0	0.0	1866	7.3	8.4	9.4	OK
	M-0	M	0.0	100.0	0.0	1959	8.2	7.1	8.3	OK
	N-0	N	1.8	98.2	0.0	1869	6.3	5.9	8.8	OK
	O-0	O	1.9	97.5	0.5	1659	7.9	9.5	7.6	OK
	P-0	P	13.5	80.6	5.9	1454	11.1	8.5	6.7	OK
	Q-0	Q	2.2	95.2	2.6	2331	5.3	8.7	5.4	NG
	R-0	R	1.6	91.6	6.8	2221	4.9	8.6	6.7	NG
	S-0	S	2.5	81.0	16.5	1259	11.2	8.4	5.1	OK
	T-0	T	1.6	97.0	1.4	1539	9.2	7.6	6.9	NG
	U-0	U	0.0	100.0	0.0	1745	8.6	7.9	8.2	NG
	V-0	V	2.2	95.9	1.9	2024	7.7	8.1	5.7	NG
	W-0	W	0.0	100.0	0.0	1962	7.5	9.5	6.4	NG
	X-0	X	2.9	96.1	1.0	2013	8.5	9.2	7.4	NG
	Y-0	Y	3.1	94.2	2.7	2245	8.3	7.6	9.4	NG
	Z-0	Z	3.6	92.6	3.8	2036	8.3	5.5	6.7	NG
	AA-0	AA	0.0	95.6	4.4	1595	8.7	6.8	6.5	NG
	AB-0	AB	4.3	93.5	2.2	1652	6.3	7.8	5.6	NG
35	AC-0	AC	1.6	94.6	3.8	2038	6.8	8.8	7.2	NG
40	AD-0	AD	0.0	92.6	7.4	1594	8.9	7.4	8.2	NG
45	AE-0	AE	0.0	98.6	1.4	1526	8.5	5.6	5.7	NG
50	AF-0	AF	0.0	99.0	1.0	1899	7.3	9.2	8.2	NG
	AG-0	AG	2.6	96.2	1.2	1602	6.4	8.4	8.4	NG
	AH-0	AH	2	92	2	120	72	72	72	NG
	AI-0	AI	2.2	95.3	2.5	1823	7.6	8.6	5.7	NG
	AJ-0	AJ	4.3	92.5	3.2	1854	6.9	8.0	5.2	NG
	AK-0	AK	2.8	97.2	0.0	2069	8.3	7.6	6.7	NG
	AL-0	AL	0.0	100.0	0.0	1787	8.8	7.1	6.3	NG
	AM-0	AM	0.0	100.0	0.0	1823	7.6	6.8	5.8	NG
	AN-0	AN	0.0	100.0	0.0	1695	8.2	6.3	7.6	NG

[0171] As can be seen from Tables 1-1, 1-2, and 2, Nos. A-0 to O-0 were within the ranges of the present invention in terms of chemical composition, area ratio of the microstructure, number density of regions having an Mn content of $1.1 \times [\text{Mnave}]$ or more, and average interval between closest regions having an Mn content of $1.1 \times [\text{Mnave}]$ or more, and had an excellent tensile strength and excellent hydrogen embrittlement resistance.

[0172] On the other hand, Nos. P-0 to AN-0 were outside the ranges of the present invention in terms of chemical composition, and were thus inferior in either one or more of the tensile strength and the hydrogen embrittlement resistance.

[0173] In P-0, since the C content was low, the tensile strength was less than 1,500 MPa.

[0174] In Q-0, since the C content was high, the hydrogen embrittlement resistance decreased.

[0175] In R-0, since the Si content was high, the hydrogen embrittlement resistance decreased.

[0176] In S-0, since the Mn content was low, the tensile strength was less than 1,500 MPa.

5 [0177] In T-0, since the Mn content was high, the hydrogen embrittlement resistance deteriorated.

[0178] In U-0, since the P content was high, the hydrogen embrittlement resistance decreased due to grain boundary embrittlement.

[0179] In V-0, since the S content was high, the hydrogen embrittlement resistance decreased.

10 [0180] In W-0, since the Al content was high, coarse Al oxides were formed and the hydrogen embrittlement resistance decreased.

[0181] In X-0, since the N content was high, coarse nitrides were formed and the hydrogen embrittlement resistance decreased.

15 [0182] In Y-0, since the O content was high, oxides were formed and the hydrogen embrittlement resistance decreased.

[0183] In Z-0, since the Co content was high, coarse Co carbides were precipitated and the hydrogen embrittlement resistance decreased.

20 [0184] In AA-0, since the Ni content was high, the hydrogen embrittlement resistance decreased.

[0185] In AB-0, since the Mo content was high, coarse Mo carbides crystallized and the hydrogen embrittlement resistance decreased.

[0186] In AC-0, since the Cr content was high, coarse Cr carbides were precipitated, and thus the hydrogen embrittlement resistance decreased.

25 [0187] In AD-0, since the Ti content was high, the amount of carbonitrides precipitated was large and the hydrogen embrittlement resistance decreased.

[0188] In AE-0, since the B content was high, coarse B oxides were formed in the steel and the hydrogen embrittlement resistance decreased.

30 [0189] In AF-0, since the Nb content was high, coarse Nb carbides were formed and the hydrogen embrittlement resistance decreased.

[0190] In AG-0, since the V content was high, the amount of carbonitrides precipitated was large and the hydrogen embrittlement resistance decreased.

[0191] In AH-0, since the Cu content was high, the steel sheet embrittled and cracked during hot rolling, and no further evaluation was performed.

35 [0192] In AI-0, since the W content was high, coarse W precipitates were formed and the hydrogen embrittlement resistance decreased.

[0193] In AJ-0 and AK-0, since the Mg content and the Ca content were high, coarse inclusions were formed and the hydrogen embrittlement resistance decreased.

[0194] In AL-0, since the Zr content was high, coarse Zr oxides were formed and the hydrogen embrittlement resistance decreased.

40 [0195] In AM-0 and AN-0, since the Sn content and the Sb content were high, respectively, the hydrogen embrittlement resistance decreased due to boundary segregation.

40 [Example 2]

[0196] Furthermore, in order to investigate the influences of manufacturing conditions, using the steel types A to O recognized to have excellent properties in Table 2, hot-rolled steel sheets having a sheet thickness of 2.3 mm were produced under manufacturing conditions shown in Table 3-1 in the same equipment as in Example 1, and were cold-rolled with a rolling reduction of 55% to obtain cold-rolled steel sheets. Then, the cold-rolled steel sheets were subjected to annealing and post-annealing cooling under conditions shown in Tables 3-2 to 3-3, and were tempered as necessary. In addition, some of the cold-rolled steel sheets were plated to form a galvanized layer on their surfaces. Here, the plating type symbols GI and GA in Table 3-3 represent galvanizing methods. GI indicates a steel sheet in which a galvanized layer is formed on a surface of a steel sheet by immersing the steel sheet in a hot-clip galvanizing bath at 465°C, and GA indicates a steel sheet in which an iron-zinc alloy layer is formed on a surface of a steel sheet by immersing the steel sheet in a hot-dip galvanizing bath at 465°C and by then raising the temperature of the steel sheet to 490°C. In Table 3-3, the examples in which "-" is recorded for tempering are examples not subjected to tempering.

[0197] A microstructure of the obtained cold-rolled steel sheet was observed in the same manner as in Example 1, and the area ratio of each phase in the microstructure in a t/4 portion was obtained. In addition, in the t/4 portion, the number density of regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more and the average interval between closest regions having an Mn content of $1.1 \times [Mn_{ave}]$ or more were measured.

[0198] In addition, the tensile properties of the obtained cold-rolled steel sheet were evaluated in the same manner as in Example 1.

[0199] In addition, the hydrogen embrittlement resistance (hydrogen embrittlement resistance properties) was evaluated by the following method.

(Method of Evaluating Hydrogen Embrittlement Resistance)

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[0200] The steel sheet was sheared with a clearance of 10%, and then a U-bending test was performed at 10R. A strain gauge was attached to the center of the obtained test piece, and a stress was applied by tightening both ends of the test piece with bolts. The applied stress was calculated from the monitored strain in the strain gauge. As a load stress, a stress corresponding to 80% of the tensile strength (TS) was applied (for example, in a case of A-1 in Table 4, applied stress = $2,101 \text{ MPa} \times 0.8 = 1,681 \text{ MPa}$). This is because the residual stress that is introduced during forming is considered to correspond to the tensile strength of the steel sheet.

[0201] The obtained U-bending test piece was immersed in an HCl aqueous solution having a pH of 2 at a liquid temperature of 25°C and held for 96 hours, and the presence or absence of cracking was investigated. The lower the pH of the HCl aqueous solution and the longer the immersion time, the larger the amount of hydrogen intruding into the steel sheet. Therefore, the hydrogen embrittlement environment becomes severe. After the immersion, a total length of a crack (in a case where a plurality of cracks were recognized, the sum of the individually measured values was defined as the total length) in the U-bending test piece was measured.

[0202] It is shown that the smaller the total length of the crack, the more excellent the hydrogen embrittlement resistance. In particular, a case where a crack having a crack length longer than 1.00 mm was recognized was evaluated NG, and a case where no crack was recognized or a slight crack having a crack length of 1.00 mm or shorter was recognized was evaluated OK. A case where the evaluation was OK was considered a pass, and a case where the evaluation was NG was considered a fail. In a case where the crack length is 0.50 mm or shorter, it can be determined that the hydrogen embrittlement resistance is particularly excellent.

[0203] The obtained results are shown in Table 4.

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[Table 3-1]

No.	Steel Type	Hot Rolling Start Temperature (°C)	Number of Large Reduction Passes with Rolling Reduction of 20% or Higher	Hot Rolling Step			Cooling Rate from Hot Rolling Finishing Temperature (°C/sec)	Cooling Temperature (°C)
				Interpass Time Between Large Reduction Passes (sec)	Hot Rolling Finishing Temperature (°C)	Time from Completion of Hot Rolling to Start of Cooling (sec)		
A-1	A	958	4	0.5	896	0.6	32	468
B-1	B	1011	4	0.3	827	0.8	42	488
C-1	C	1088	4	0.6	835	0.7	23	472
D-1	D	1050	4	0.6	918	0.9	21	503
E-1	E	1067	4	0.9	858	0.3	39	517
F-1	F	1006	4	0.4	850	0.4	47	511
G-1	G	1075	4	1.0	802	0.9	45	545
H-1	H	964	4	0.0	873	0.0	34	537
I-1	I	1047	4	0.4	938	0.7	37	522
J-1	J	976	4	0.8	813	0.5	26	472
K-1	K	994	4	0.3	902	0.6	26	547
L-1	L	1094	4	0.1	948	0.3	33	432
M-1	M	1023	4	0.8	920	0.1	29	414
N-1	N	982	4	0.7	864	0.4	42	529
O-1	O	1031	4	0.1	886	0.2	49	490
A-2	A	945	4	0.3	928	0.7	32	522
B-2	B	1106	4	0.4	890	0.4	27	531
C-2	C	1010	4	0.2	796	0.8	47	501
D2	D	1015	4	0.6	954	0.4	41	539
E-2	E	1075	4	5.8	941	0.9	50	519
F-2	F	1069	3	0.6	804	0.3	36	429

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No.	Steel Type	Hot Rolling Step					Coiling Rate from Hot Rolling Finishing Temperature (°C/sec)	Coiling Temperature (°C)
		Hot Rolling Start Temperature (°C)	Number of Large Reduction Passes with Rolling Reduction of 20% or Higher	Interpass Time Between Large Reduction Passes (sec)	Hot Rolling Finishing Temperature (°C)	Time from Completion of Hot Rolling to Start of Cooling (sec)		
G-2	G	981	4	0.4	933	0.8	27	546
H-2	H	998	4	0.5	866	4.2	24	419
I-2	I	1005	4	0.8	836	0.4	19	543
J-2	J	963	4	0.2	850	0.7	51	544
K-2	K	974	4	0.5	843	0.2	28	387
L-2	L	1045	4	0.6	826	0.1	24	654
M-2	M	1086	4	0.9	853	0.5	22	540
N-2	N	1019	4	0.7	826	0.5	41	420
O-2	O	1058	4	0.7	873	0.6	38	478
A-3	A	1070	4	0.1	919	0.9	38	423
B-3	B	987	4	0.1	819	0.3	32	465
C-3	C	1029	4	0.9	900	0.2	29	498
D-3	D	961	4	0.8	846	0.5	34	476
E-3	E	1066	4	0.2	946	0.7	43	532
F-3	F	989	4	0.8	881	0.6	39	513
G-3	G	1031	4	0.5	836	0.2	35	505
H-3	H	975	4	0.3	922	0.7	25	476
I-3	I	960	4	0.0	912	0.9	45	530
J-3	J	1085	4	0.4	890	0.3	45	455
K-3	K	1091	4	0.9	880	0.9	22	487
N-3	N	1019	4	0.7	826	0.5	41	420

(continued)

No.	Steel Type	Hot Rolling Start Temperature (°C)	Number of Large Reduction Passes with Rolling Reduction of 20% or Higher	Hot Rolling Step			Cooling Rate from Hot Rolling Finishing Temperature (°C/sec)	Coiling Temperature (°C)
				Interpass Time Between Large Reduction Passes (sec)	Hot Rolling Finishing Temperature (°C)	Time from Completion of Hot Rolling to Start of Cooling (sec)		
N-4	N	1019	4	0.7	826	0.5	41	420
N-5	N	1019	4	0.7	826	0.5	41	420

[Table 3-2]

No.	Steel Type	Annealing Step			
		Average Rate of Temperature Increase from Room Temperature to 700°C (°C/sec)	Average Rate of Temperature Increase from 700°C to Annealing Temperature (°C/sec)	Annealing Temperature (Highest Heating Temperature) (°C)	Holding Time (sec)
A-1	A	30	8	868	57
B-1	B	22	5	880	32
C-1	C	77	10	890	62
D-1	D	74	12	891	40
E-1	E	65	7	881	43
F-1	F	20	11	837	88
G-1	G	91	11	858	66
H-1	H	41	7	833	82
I-1	I	33	14	843	30
J-1	J	58	13	849	92
K-1	K	86	14	866	74
L-1	L	50	9	856	97
M-1	M	97	6	896	78
N-1	N	47	13	848	54
O-1	O	71	10	875	49
A-2	A	76	11	853	79
B-2	B	61	12	846	62
C-2	C	42	14	858	34
D-2	D	54	8	837	49
E-2	E	85	8	832	87
F-2	F	96	13	848	40
G-2	G	67	7	840	44
H-2	H	17	12	852	83
I-2	I	66	7	878	81
J-2	J	22	6	839	98
K-2	K	99	13	884	74
L-2	L	84	13	895	56
M-2	M	13	14	865	50
N-2	N	35	11	884	67
O-2	O	73	3	878	94
A-3	A	33	19	868	35
B-3	B	89	9	805	70
C-3	C	45	8	902	28
D-3	D	53	6	874	15

(continued)

No.	Steel Type	Annealing Step			
		Average Rate of Temperature Increase from Room Temperature to 700°C (°C/sec)	Average Rate of Temperature Increase from 700°C to Annealing Temperature (°C/sec)	Annealing Temperature (Highest Heating Temperature) (°C)	Holding Time (sec)
E-3	E	28	9	866	103
F-3	F	37	7	858	61
G-3	G	22	13	888	94
H-3	H	48	10	850	38
I-3	I	72	12	889	74
J-3	J	33	12	899	46
K-3	K	54	5	871	77
N-3	N	10	11	884	67
N-O	N	35	18	884	67
N-5	N	35	4	884	67

[Table 3-3]

No.	Steel Type	Post-Annealing Cooling		Tempering Step		Plating Step	Remarks
		Average Cooling Rate from Annealing Temperature to Cooling Stop Temperature (°C/sec)	Cooling Stop Temperature (°C)	Holding Temperature (°C)	Holding Time (sec)		
A-1	A	21	69	188	177	GA	Invention Example
B-1	B	72	164	-	-	None	Invention Example
C-1	C	76	28	-	-	None	Invention Example
D-1	D	8	221	58	447	GA	Invention Example
E-1	E	25	279	106	704	GA	Invention Example
F-1	F	88	253	-	-	None	Invention Example
G-1	G	98	125	-	-	None	Invention Example
H-1	H	66	141	255	749	None	Invention Example
I-1	I	48	186	213	964	None	Invention Example
J-1	J	22	232	168	511	GA	Invention Example

(continued)

No.	Steel Type	Post-Annealing Cooling		Tempering Step		Plating Step	Remarks	
		Average Cooling Rate from Annealing Temperature to Cooling Stop Temperature (°C/sec)	Cooling Stop Temperature (°C)	Holding Temperature (°C)	Holding Time (sec)			
5	K-1	K	54	53	-	-	None	Invention Example
10	L-1	L	83	194	-	-	GA	Invention Example
15	M-1	M	59	83	306	33	GA	Invention Example
20	N-1	N	42	105	-	-	None	Invention Example
25	O-1	O	16	287	-	-	GA	Invention Example
30	A-2	A	14	211	464	653	GA	Comparative Example
35	B-2	B	18	104	475	468	GA	Comparative Example
40	C-2	C	93	200	263	583	None	Comparative Example
45	D-2	D	75	275	243	90	None	Comparative Example
50	E-2	E	65	163	120	708	GI	Comparative Example
55	F-2	F	26	170	391	864	None	Comparative Example
	G-2	G	14	44	385	127	GI	Invention Example
	H-2	H	17	131	219	918	GI	Comparative Example
	I-2	I	12	189	454	784	GA	Comparative Example
	J-2	J	76	241	200	273	None	Comparative Example
	K-2	K	78	59	392	705	None	Comparative Example
	L-2	L	40	165	90	62	None	Comparative Example
	M-2	M	91	281	283	803	None	Comparative Example
	N-2	N	34	295	93	406	None	Invention Example

(continued)

No.	Steel Type	Post-Annealing Cooling		Tempering Step		Plating Step	Remarks
		Average Cooling Rate from Annealing Temperature to Cooling Stop Temperature (°C/sec)	Cooling Stop Temperature (°C)	Holding Temperature (°C)	Holding Time (sec)		
O-2	O	20	256	78	175	GI	Comparative Example
A-3	A	83	53	180	298	None	Comparative Example
B-3	B	48	204	143	223	None	Comparative Example
C-3	C	85	121	319	395	None	Comparative Example
D-3	D	46	153	432	292	None	Comparative Example
E-3	E	61	79	351	24	None	Comparative Example
F-3	F	1	238	301	856	GA	Comparative Example
G-3	G	26	134	180	951	GI	Invention Example
H-3	H	33	94	54	601	GI	Invention Example
I-3	I	25	224	517	372	GA	Comparative Example
J-3	J	35	151	103	505	None	Invention Example
K-3	K	54	331	235	69	None	Comparative Example
N-3	N	34	295	93	406	None	Comparative Example
N-4	N	34	295	93	406	None	Comparative Example
N-5	N	34	295	93	406	None	Comparative Example

[Table 4]

No.	Ferrite (area%)	Martensite (area%)	Remainder in Microstructure (area%)	Tensile Strength (MPa)	Total Elongation (%)	Average Interval Between Regions Satisfying 1.1 × [Mnave] (μm)	Number Density of Regions Satisfying 1.1 × [Mnave] (×10 ⁻⁴ pieces/μm ²)	Crack Length (mm)	Hydrogen Embrittlement Resistance	Remarks
A-1	0.0	1000	0.0	2101	7.6	8.5	6.7	0.11	OK	Invention Example
H-1	0.0	1000	0.0	1598	8.2	7.5	5.8	0.45	OK	Invention Example
C-1	0.0	1000	0.0	2302	9.3	5.6	9.5	0.00	OK	Invention Example
D-1	1.5	97.5	1.0	1853	8.2	8.2	6.7	0.12	OK	Invention Example
E-1	1.1	97.6	1.3	1605	7.9	9.5	8.8	0.21	OK	Invention Example
F-1	1.8	97.0	1.2	1906	8.3	9.7	7.2	0.11	OK	Invention Example
G-1	2.0	94.6	3.4	1503	9.1	8.4	5.8	0.14	OK	Invention Example
H-1	3.4	96.6	0.0	1535	10.1	5.8	9.5	0.10	OK	Invention Example
I-1	2.2	97.8	0.0	1625	7.6	5.9	10.5	0.20	OK	Invention Example
J-1	0.0	1000	0.0	1722	8.3	6.7	5.6	0.00	OK	Invention Example
K-1	0.0	100.0	0.0	2104	8.0	6.2	7.5	0.38	OK	Invention Example
L-1	0.0	1000	0.0	1973	7.3	8.4	7.7	0.00	OK	Invention Example
M-1	0.0	1000	0.0	1659	8.2	7.1	5.9	0.48	OK	Invention Example

(continued)

No.	Ferrite (area%)	Martensite (area%)	Remainder in Microstructure (area%)	Tensile Strength (MPa)	Total Elongation (%)	Average Interval Between Regions Satisfying $1.1 \times [M_{ave}]$ (μm)	Number Density of Regions Satisfying $1.1 \times [M_{ave}] \times 10^{-4}$ pieces/ μm^2)	Crack Length (mm)	Hydrogen Embrittlement Resistance	Remarks
N-1	1.8	98.2	0.0	1998	6.3	5.9	6.2	0.12	OK	Invention Example
G-1	1.9	97.6	0.5	1768	7.9	9.5	8.2	0.20	OK	Invention Example
A-2	0.0	1000	0.0	1655	11.1	<u>13.4</u>	8.9	1.51	NG	Comparative Example
B-2	2.2	97.0	0.8	1578	5.3	9.3	<u>4.3</u>	2.11	NG	Comparative Example
C-2	1.5	96.0	2.4	1678	4.9	12.4	8.9	1.23	NG	Comparative Example
D-2	0.0	1000	0.0	1589	11.2	8.5	<u>2.2</u>	1.35	NG	Comparative Example
E-2	1.5	97.5	0.9	1601	9.2	<u>18.8</u>	6.7	1.54	NG	Comparative Example
F-2	0.0	100.0	0.0	1555	8.6	<u>11.5</u>	5.2	1.23	NG	Comparative Example
G-2	0.0	1000	0.0	1554	7.7	8.1	5.8	0.21	OK	Invention Example
H-2	0.0	1000	0.0	1577	7.5	<u>13.4</u>	9.7	1.58	NG	Comparative Example
I-2	1.1	98.3	0.6	1576	8.5	<u>11.2</u>	9.3	1.22	NG	Comparative Example
J-2	3.1	96.6	0.3	1767	8.3	7.9	<u>4.1</u>	1.13	NG	Comparative Example
K-2	0.0	1000	0.0	1590	7.5	8.2	<u>3.9</u>	1.15	NG	Comparative Example

(continued)

No.	Ferrite (area%)	Martensite (area%)	Remainder in Microstructure (area%)	Tensile Strength (MPa)	Total Elongation (%)	Average Interval Between Regions Satisfying $1.1 \times [M_{ave}]$ (μm)	Number Density of Regions Satisfying $1.1 \times [M_{ave}] \times 10^{-4}$ pieces/ μm^2)	Crack Length (mm)	Hydrogen Embrittlement Resistance	Remarks
L-2	0.0	98.5	1.5	1967	8.7	<u>20.5</u>	11.1	2.14	NG	Comparative Example
M-2	3.4	92.5	4.1	1707	6.3	<u>14.5</u>	7.8	1.69	NG	Comparative Example
N-2	1.8	95.6	2.6	2073	6.8	8.8	9.4	0.05	OK	Invention Example
O-2	0.0	96.5	3.5	1878	8.9	7.5	<u>4.6</u>	1.54	NG	Comparative Example
A-3	0.0	98.6	1.4	2208	8.5	8.5	<u>4.3</u>	1.63	NG	Comparative Example
B-3	<u>14.0</u>	<u>86.0</u>	0.0	<u>1368</u>	7.3	9.2	8.7	1.23	NG	Comparative Example
C-3	2.6	96.2	1.2	1688	6.4	6.5	<u>4.8</u>	1.22	NG	Comparative Example
D-3	<u>11.6</u>	<u>88.4</u>	0.0	<u>1434</u>	5.5	6.6	6.1	1.84	NG	Comparative Example
E-3	2.2	90.3	2.5	1554	7.6	7.9	<u>4.4</u>	1.96	NG	Comparative Example
F-3	<u>5.6</u>	<u>80.1</u>	<u>14.3</u>	<u>1469</u>	6.9	8.9	9.5	0.48	OK	Comparative Example
G-3	2.8	97.2	0.0	1521	8.3	7.6	6.7	0.26	OK	Invention Example
H-3	0.0	98.7	1.3	1533	8.8	7.1	8.5	0.23	OK	Invention Example
I-3	0.0	96.7	3.3	<u>1359</u>	7.6	6.8	5.7	0.84	OK	Comparative Example

(continued)

No.	Ferrite (area %)	Martensite (area %)	Remainder in Microstructure (area %)	Tensile Strength (MPa)	Total Elongation (%)	Average Interval Between Regions Satisfying $1.1 \times$ [Mnave] (μm)	Number Density of Regions Satisfying $1.1 \times [Mnave] (\times 10^{-4}$ pieces/μm ²)	Crack Length (mm)	Hydrogen Brittlement Resistance	Remarks
J-3	0.0	1000	0.0	1656	8.2	6.3	5.5	0.12	OK	Invention Example
K-3	0.0	<u>83.5</u>	<u>16.5</u>	<u>1398</u>	8.2	6.3	6.7	0.39	OK	Comparative Example
N-3	0.5	97.0	2.5	1958	7.2	<u>14.2</u>	<u>4.2</u>	1.35	NG	Comparative Example
N-4	1.0	98.0	1.0	1922	7.6	7.8	<u>4.5</u>	1.85	NG	Comparative Example
N-5	0.9	96.0	3.1	1890	8.1	<u>11.3</u>	<u>3.9</u>	1.52	NG	Comparative Example

[0204] As can be seen from Tables 3-1, 3-2, 3-3, and 4, in all of the examples according to the present invention, it was possible to obtain a steel sheet having a high strength and excellent hydrogen embrittlement resistance particularly by appropriately controlling the conditions of hot rolling, coiling, annealing, and post-annealing cooling.

5 [0205] On the other hand, in A-2, since the hot rolling start temperature was low, the temperature decreased during rolling and a large amount of unrecrystallized austenite remained. As a result, the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased and the hydrogen embrittlement resistance deteriorated.

[0206] In B-2, since the hot rolling start temperature was high, an alloying element segregated to austenite grain boundaries during rolling and ferritic transformation was delayed. As a result, the number density of regions satisfying $1.1 \times [Mn_{ave}]$ decreased and the hydrogen embrittlement resistance deteriorated.

10 [0207] In C-2, since the hot rolling finishing temperature was low, unrecrystallized austenite was formed. As a result, the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased and the hydrogen embrittlement resistance deteriorated.

[0208] In D-2, since the hot rolling finishing temperature was high, ferritic transformation was excessively suppressed. As a result, the number density of regions satisfying $1.1 \times [Mn_{ave}]$ decreased and the hydrogen embrittlement resistance deteriorated.

15 [0209] In E-2, since the interpass time was long in hot rolling, a large amount of unrecrystallized austenite remained. As a result, the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased and the hydrogen embrittlement resistance deteriorated.

[0210] In F-2, the number of passes with a rolling reduction of 20% or higher was small. As a result, the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased and the hydrogen embrittlement resistance deteriorated.

[0211] In H-2, since a time from after the finish rolling to the start of cooling was long, ferritic transformation occurred excessively. Thus, the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased and the hydrogen embrittlement resistance deteriorated.

20 [0212] In I-2, since the cooling rate after the completion of the hot rolling was low, ferritic transformation occurred excessively. Thus, the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased and the hydrogen embrittlement resistance deteriorated.

[0213] In J-2, since the cooling rate after completion of the finish rolling was high, a large number of bainite and martensite structures were formed. As a result, the number density of regions satisfying $1.1 \times [Mn_{ave}]$ decreased and the hydrogen embrittlement resistance deteriorated.

30 [0214] In K-2, since the coiling temperature was low, bainite and martensite structures were formed. As a result, the number density of regions satisfying $1.1 \times [Mn_{ave}]$ decreased and the hydrogen embrittlement resistance deteriorated.

[0215] In L-2, since the coiling temperature was high, the ratio of the ferrite structure increased. As a result, the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased and the hydrogen embrittlement resistance deteriorated.

35 [0216] In M-2 and N-3, since the average rate of temperature increase up to 700°C was low, cementite coarsened in the course of temperature increase, and the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased. Moreover, in N-3, the number density of the regions satisfying $1.1 \times [Mn_{ave}]$ decreased. As a result, the hydrogen embrittlement resistance deteriorated.

40 [0217] In O-2 and N-4, since the rate of temperature increase up to the highest heating temperature (annealing temperature) in the annealing step was low, the diffusion of Mn occurred. Thus, the number density of regions satisfying $1.1 \times [Mn_{ave}]$ decreased and the hydrogen embrittlement resistance deteriorated.

[0218] In A-3 and N-5, since the rate of temperature increase up to the highest heating temperature in the annealing step was high, the recrystallization was not completed and Mn-concentrated portions were eliminated by dislocation and grain boundaries. As a result, the number density of regions satisfying $1.1 \times [Mn_{ave}]$ decreased. In addition, in N-5, the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ increased. As a result, the hydrogen embrittlement resistance decreased.

45 [0219] In B-3, since the highest heating temperature in the annealing step was low, the ratio of the ferrite structure exceeded 5%, and as a result, the hydrogen embrittlement resistance deteriorated. In addition, since the ratio of the ferrite structure was high, the tensile strength was lower than 1,500 MPa and the hydrogen embrittlement resistance also deteriorated.

50 [0220] In C-3, since the highest heating temperature in the annealing step was too high, Mn-concentrated portions were eliminated, and as a result, regions satisfying $1.1 \times [Mn_{ave}]$ were reduced and the hydrogen embrittlement resistance decreased.

[0221] In D-3, since the holding time at the highest heating temperature in the annealing step was short, the ratio of the martensite structure was lower than 90% and the tensile strength was lower than 1,500 MPa.

55 [0222] In E-3, since the holding time at the highest heating temperature in the annealing step was long, Mn was diffused and the dispersion state of Mn-concentrated portions was eliminated. Thus, regions satisfying $1.1 \times [Mn_{ave}]$ were reduced and the hydrogen embrittlement resistance decreased.

[0223] In F-3, since the cooling rate from the highest heating temperature in the annealing step was too low, ferritic

transformation and bainitic transformation occurred, and as a result, the tensile strength was lower than 1,500 MPa.

[0224] In 1-3, since the tempering temperature was high, the dislocation density in the martensite structure decreased, and as a result, the tensile strength was lower than 1,500 MPa.

[0225] In K-3, since the cooling stop temperature was too high, bainitic transformation occurred, and as a result, the tensile strength was lower than 1,500 MPa.

[0226] FIG. 1 is a graph showing influences of the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ and the number density of regions satisfying $1.1 \times [Mn_{ave}]$ on the hydrogen embrittlement resistance of the steel sheets of Examples 1 and 2. In the drawing, the symbol O is a steel sheet having excellent hydrogen embrittlement resistance, and the symbol X is an example in which the hydrogen embrittlement resistance is inferior. As is clear from FIG. 1, it is found that a steel sheet having excellent hydrogen embrittlement resistance can be obtained by controlling the average interval between regions satisfying $1.1 \times [Mn_{ave}]$ to 10.0 μm or less and controlling the number density of regions satisfying $1.1 \times [Mn_{ave}]$ to 5.0×10^{-4} pieces/ μm^2 or more.

[Industrial Applicability]

[0227] According to the present invention, it is possible to provide a steel sheet having a high strength and excellent hydrogen embrittlement resistance properties. When applied as a steel sheet for a vehicle, the steel sheet contributes to the weight reduction of a vehicle body, thereby improving fuel efficiency.

Claims

1. A steel sheet comprising, as a chemical composition, by mass%:

C: 0.150% to 0.400%;
 Si: 0.01% to 2.00%;
 Mn: 0.8% to 2.0%;
 P: 0.0001% to 0.0200%;
 S: 0.0001% to 0.0200%;
 Al: 0.001% to 1.000%;
 N: 0.0001% to 0.0200%;
 O: 0.0001% to 0.0200%;
 Co: 0% to 0.500%;
 Ni: 0% to 1.000%;
 Mo: 0% to 1.000%;
 Cr: 0% to 2.000%;
 Ti: 0% to 0.500%;
 B: 0% to 0.0100%;
 Nb: 0% to 0.500%;
 V: 0% to 0.500%;
 Cu: 0% to 0.500%;
 W: 0% to 0.100%;
 Ta: 0% to 0.100%;
 Mg: 0% to 0.050%;
 Ca: 0% to 0.050%;
 Y: 0% to 0.050%;
 Zr: 0% to 0.050%;
 La: 0% to 0.050%;
 Ce: 0% to 0.050%;
 Sn: 0% to 0.050%;
 Sb: 0% to 0.050%;
 As: 0% to 0.050%; and
 a remainder: Fe and impurities,
 wherein a microstructure includes, by area ratio,

ferrite: 5.0% or less,
 martensite and tempered martensite: more than 90.0% in total, and
 a remainder: one or two or more of bainite, pearlite, and residual austenite,

in a cross section in a sheet thickness direction, regions having an Mn content of $1.1 \times [\text{Mnave}]$ or more, where the $[\text{Mnave}]$ is an average Mn content throughout the sheet thickness direction,

5 have a number density of 5.0×10^{-4} pieces/ μm^2 or more and
are present so that an average interval between closest regions having an Mn content of $1.1 \times [\text{Mnave}]$ or
more is $10.0 \mu\text{m}$ or less, and

a tensile strength is 1,500 MPa or more.

10 2. The steel sheet according to claim 1,

wherein the chemical composition comprises one or two or more selected from the group consisting of
Co: 0.01% to 0.500%,
Ni: 0.01% to 1.000%,
15 Mo: 0.01% to 1.000%,
Cr: 0.001% to 2.000%,
Ti: 0.001% to 0.500%,
B: 0.0001% to 0.0100%,
Nb: 0.001% to 0.500%,
20 V: 0.001% to 0.500%,
Cu: 0.001% to 0.500%,
W: 0.001% to 0.100%,
Ta: 0.001% to 0.100%,
25 Mg: 0.0001% to 0.050%,
Ca: 0.001% to 0.050%,
Y: 0.001% to 0.050%,
Zr: 0.001% to 0.050%,
La: 0.001% to 0.050%,
30 Ce: 0.001% to 0.050%,
Sn: 0.001% to 0.050%,
Sb: 0.001% to 0.050%, and
As: 0.001% to 0.050%.

3. The steel sheet according to claim 1 or 2,

35 wherein a coating layer containing zinc, aluminum, magnesium, or an alloy of these metals is provided on a surface.

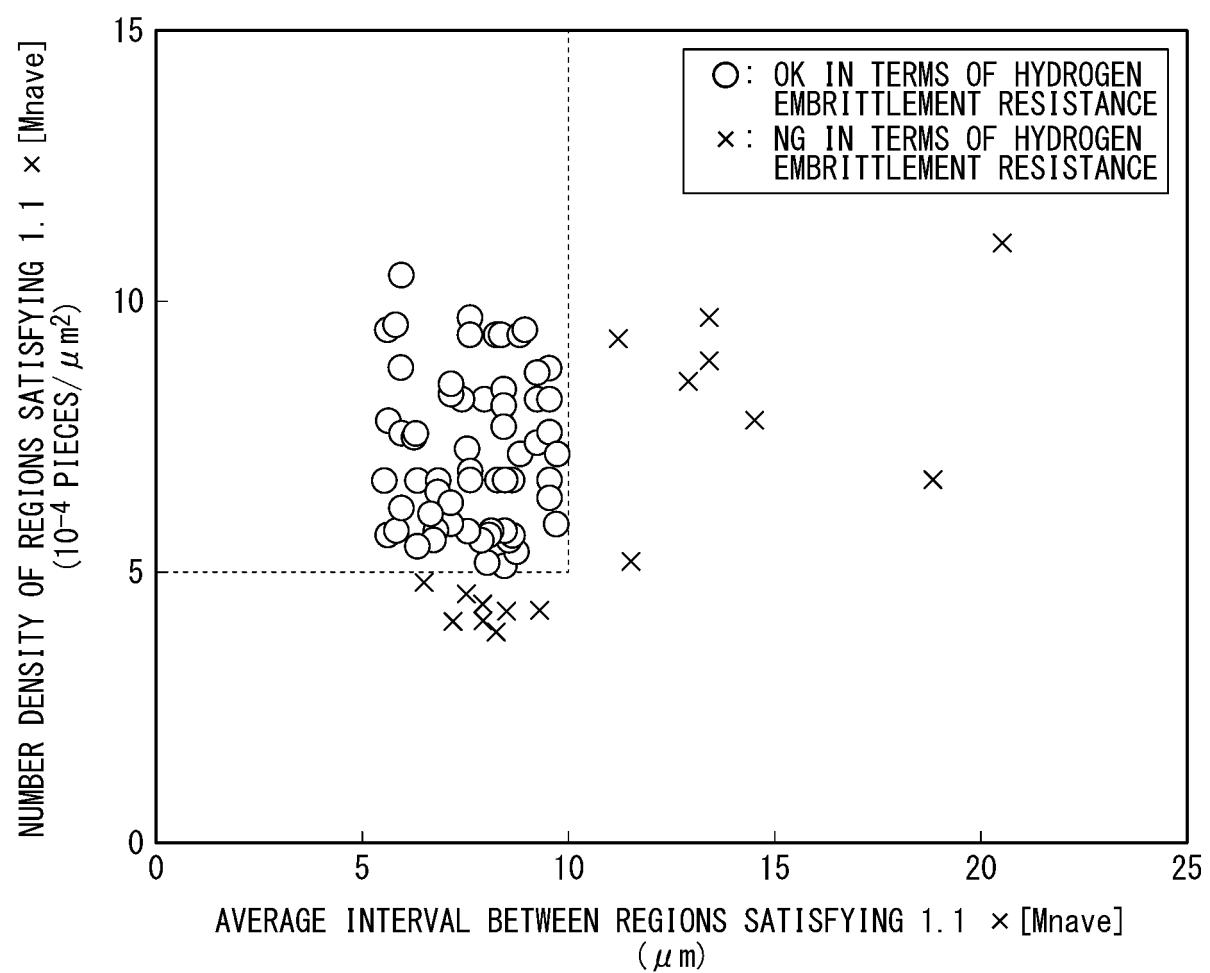
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FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/039377

5	A. CLASSIFICATION OF SUBJECT MATTER <i>C22C 38/00</i> (2006.01)i; <i>C22C 38/60</i> (2006.01)i; <i>C21D 9/46</i> (2006.01)n FI: C22C38/00 301U; C22C38/00 301T; C22C38/60; C21D9/46 F; C21D9/46 J According to International Patent Classification (IPC) or to both national classification and IPC													
10	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C22C38/00-38/60; C21D9/46; C21D8/02													
15	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													
20	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)													
25	C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding: 2px;">Category*</th> <th style="text-align: left; padding: 2px;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="text-align: left; padding: 2px;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 2px;">A</td> <td style="text-align: center; padding: 2px;">WO 2020/203158 A1 (NIPPON STEEL CORP.) 08 October 2020 (2020-10-08)</td> <td style="text-align: center; padding: 2px;">1-3</td> </tr> <tr> <td style="text-align: center; padding: 2px;">A</td> <td style="text-align: center; padding: 2px;">WO 2020/129402 A1 (JFE STEEL CORP.) 25 June 2020 (2020-06-25)</td> <td style="text-align: center; padding: 2px;">1-3</td> </tr> <tr> <td style="text-align: center; padding: 2px;">A</td> <td style="text-align: center; padding: 2px;">WO 2021/045168 A1 (NIPPON STEEL CORP.) 11 March 2021 (2021-03-11)</td> <td style="text-align: center; padding: 2px;">1-3</td> </tr> </tbody> </table>		Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	WO 2020/203158 A1 (NIPPON STEEL CORP.) 08 October 2020 (2020-10-08)	1-3	A	WO 2020/129402 A1 (JFE STEEL CORP.) 25 June 2020 (2020-06-25)	1-3	A	WO 2021/045168 A1 (NIPPON STEEL CORP.) 11 March 2021 (2021-03-11)	1-3
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A	WO 2020/203158 A1 (NIPPON STEEL CORP.) 08 October 2020 (2020-10-08)	1-3												
A	WO 2020/129402 A1 (JFE STEEL CORP.) 25 June 2020 (2020-06-25)	1-3												
A	WO 2021/045168 A1 (NIPPON STEEL CORP.) 11 March 2021 (2021-03-11)	1-3												
30														
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40	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.													
45	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family													
50	Date of the actual completion of the international search 15 December 2022 Date of mailing of the international search report 27 December 2022													
55	Name and mailing address of the ISA/JP Japan Patent Office (ISA/JP) 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915 Japan Telephone No.													

INTERNATIONAL SEARCH REPORT Information on patent family members							International application No. PCT/JP2022/039377
5	Patent document cited in search report		Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
10	WO	2020/203158	A1	08 October 2020	US	2022/0282351	A1
					EP	3950975	A1
					CN	112969804	A
					KR	10-2021-0091790	A
15	WO	2020/129402	A1	25 June 2020	US	2022/0056549	A1
					EP	3875615	A1
					CN	113195755	A
					KR	10-2021-0092279	A
20	WO	2021/045168	A1	11 March 2021	US	2022/0275493	A1
					EP	4026922	A1
					CN	114286870	A
					KR	10-2022-0038466	A
25							
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35							
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2021172425 A [0002]
- JP 2006207019 A [0012]
- JP 2010138489 A [0012]
- JP 2011179030 A [0012]
- JP 2010215958 A [0012]
- JP 2016153524 A [0012]
- JP 2016050343 A [0012]