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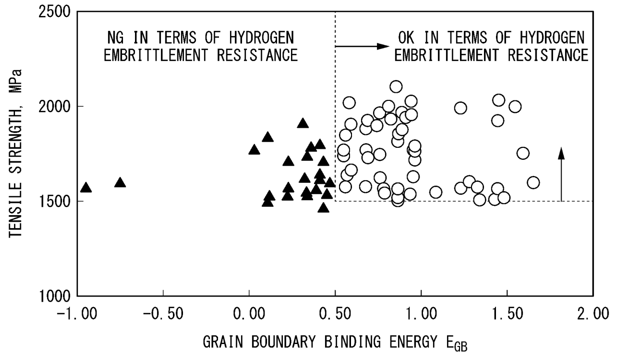
(54) STEEL SHEET

(57) What is claimed is a steel sheet having 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, when an interface where an orientation difference between adjacent martensite and tempered martensite is 15 degrees or more is defined as a prior austenite grain boundary, grain boundary binding energy E_{GB} determined by a concentration of each alloying element on the prior austenite grain boundary is 0.50 or more, and a tensile strength is 1,500 MPa or more.

FIG. 1



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Description

[Technical Field of the Invention]

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

[0002] Priority is claimed on Japanese Patent Application No. 2021-172424, filed on October 21, 2021, the content of which is incorporated herein by reference.

[Related Art]

[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 ahead of 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.

[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 entering 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.

[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).

[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.

[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, the 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.

[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, a 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.

[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 the 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 $D\gamma$ [μm] satisfy the relationship represented by $\mathrm{solB}\cdot D\gamma \geq 0.0010$, 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 $1 \times 10^6/\mathrm{mm}^2$ or more, the average dislocation density of the entire steel is 1.0×10^{15} to $2.0 \times 10^{16}/\mathrm{m}^2$, 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 binding strength of the grain boundaries. Therefore, it is considered that cracking due to hydrogen embrittlement can be suppressed in a case where the binding strength of grain boundaries can be increased. 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 required 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] Furthermore, in Patent Document 2, the steel sheet has a structure including a pearlite structure as a primary phase, in which the volume percentage of ferrite in the remainder in microstructure is 20% or less with respect to the whole structure and the lamellar pitch in the pearlite structure is 500 nm or less, and is obtained by cold-rolling a steel sheet having a Vickers hardness of HV200 or more with a rolling reduction of 60% or more (preferably 75% or more). Therefore, it is possible to easily estimate that the anisotropy is strong and the formability of the member by a cold press is low.

[0017] In addition, in Patent Document 3, in order to improve delayed fracture properties, holding for 20 minutes or longer is required at 650°C or 700°C in an atmosphere having a dew point of 15°C or higher, which also creates a problem of low productivity.

[0018] The present invention has been contrived in view of the above problems. An object of the present invention is to provide a steel sheet having excellent hydrogen embrittlement resistance properties on the premise of being a high strength steel sheet having a microstructure mainly including martensite and tempered martensite.

[Means for Solving the Problem]

[0019] As described above, the hydrogen embrittlement is considered to be cracking occurring from grain boundaries due to the segregation of hydrogen in steel to the grain boundaries and the resulting decrease in binding strength of the grain boundaries. Therefore, the present inventors have paid attention to the binding strength of the grain boundaries and conducted various studies on a method of improving the hydrogen embrittlement resistance properties.

[0020] As a result, the present inventors have found that by segregating a predetermined alloying element to grain boundaries, the binding strength of the grain boundaries is improved, entering hydrogen is less likely to segregate to the grain boundaries, and thus it is possible to suppress a decrease in binding strength of the grain boundaries due to the hydrogen even the hydrogen enters.

[0021] The present invention has been made in view of the above-described findings. The gist of the present invention is as follows.

[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: 0.80% to 2.00%; 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, when an interface where an orientation difference between adjacent martensite and tempered martensite is 15 degrees or more is defined as a prior austenite grain boundary, grain boundary binding energy E_{GB} determined by a concentration of each alloying element on the prior austenite grain boundary satisfies Expression (1), and a tensile strength is 1,500 MPa or more.

$$E_{GB} = 1 + (3 \times [Co] + 0.7 \times [Ni] + 5.5 \times [Mo] + 0.7 \times [Cr] + 2.9 \times [Ti] + 47 \times [B] + 4.3 \times [Nb] + 4.5 \times [V] + 5.2 \times [W] + 3.1 \times [Ta] + 4.3 \times [Zr] - 0.25 \times [Mn] - 0.1 \times [P] - [Cu] - 1.1 \times [Sn] - 0.6 \times [Sb] - 0.9 \times [As]) \geq 0.50 \qquad (1)$$

Here, [chemical symbol] in the expression represents the concentration of each alloying element by mass% on the prior austenite grain boundary.

[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: 0.001% 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%.

[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.

[Effects of the Invention]

[0022] According to the aspect of the present invention, it is possible to provide a steel sheet having excellent hydrogen embrittlement resistance properties.

[Brief Description of the Drawings]

[0023] FIG. 1 is a diagram showing the relationship between: hydrogen embrittlement resistance; and E_{GB} and the tensile strength of steel sheets in examples of the present invention.

[Embodiments of the Invention]

[0024] Hereinafter, a steel sheet according to an embodiment of the present invention (the steel sheet according to the present embodiment) will be described.

[0025] 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,
when an interface where an orientation difference between adjacent martensite and tempered martensite is 15 degrees or more is defined as a prior austenite grain boundary (prior γ grain boundary), grain boundary binding energy E_{GB} determined by the concentration of each alloying element on the prior austenite grain boundary is 0.50 or more, and
the tensile strength is 1,500 MPa or more.

<Chemical Composition>

[0026] First, the amount 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%". 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%

[0027] 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.

[0028] 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.

Si: 0.01% to 2.00%

[0029] 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.

[0030] Meanwhile, in a case where the Si content is more than 2.00%, the precipitation of alloy carbides is delayed in the hot-rolled structure. 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.

Mn: 0.80% to 2.00%

[0031] Mn is an effective element for increasing the strength of the steel sheet. In a case where the Mn content is less than 0.80%, the effect cannot be sufficiently obtained. Therefore, the Mn content is set to 0.80% or more. The Mn content may be 1.00% or more or 1.20% or more.

[0032] Meanwhile, in a case where the Mn content is more than 2.00%, 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 2.00% or less. The Mn content may be 1.90% or less, 1.85% or less, or 1.80% or less.

P: 0.0001% to 0.0200%

[0033] 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.

[0034] 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.

S: 0.0001 % to 0.0200%

[0035] 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, even in a case where grain boundaries are strengthened, 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.

[0036] 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.

Al: 0.001% to 1.000%

[0037] 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.

[0038] 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 even in a case where grain boundaries are strengthened, 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%

[0039] 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.

[0040] 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.

[0041] 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%

[0042] 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 severe deformation. 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.

[0043] 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.

[0044] 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, 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.

[0045] 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%

[0046] Co is an effective element for controlling the morphology of carbide and increasing the strength of the steel sheet. In addition, Co is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0047] 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%

[0048] Ni is an effective element for increasing the strength of the steel sheet. In addition, Ni is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0049] 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.

Mo: 0% to 1.000%

[0050] 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. In addition, Mo is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0051] 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.

Cr: 0% to 2.000%

[0052] Cr is an effective element for suppressing pearlitic transformation, thereby increasing the strength of steel, similar to Mn. In addition, Cr is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0053] Meanwhile, in a case where the Cr content is more than 2.000%, coarse Cr carbides may be formed in a center segregation area 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.

Ti: 0% to 0.500%

[0054] 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. In addition, Ti is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0055] 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.

B: 0% to 0.0100%

[0056] 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. In addition, B is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0057] 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.

Nb: 0% to 0.500%

[0058] 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. In addition, Nb is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0059] 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%

[0060] 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. In addition, V is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0061] 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%

[0062] Cu is an effective element for increasing 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.

[0063] 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%

[0064] W is an effective element for increasing the strength of the steel sheet. In addition, W 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. In addition, W is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0065] 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%

[0066] 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. In addition, Ta is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0067] 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%

[0068] 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.

[0069] 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%

[0070] 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.

[0071] 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%

[0072] 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.

[0073] 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%

[0074] Similar to Mg, Ca, and Y, Zr is an element capable of controlling the morphology of sulfide when contained in a small amount. In addition, Zr is an element that also contributes to an improvement in binding strength of the grain boundaries. 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.

[0075] 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%

[0076] 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.

[0077] 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%

[0078] 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.

[0079] 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%

[0080] 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.

[0081] 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%

[0082] 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.

[0083] 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%

[0084] 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.

[0085] 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.

[0086] As described above, the chemical composition of the steel sheet according to the present embodiment may contain base elements and a remainder consisting of Fe and impurities, or may contain base elements, one or more optional elements, and a remainder consisting of Fe and impurities.

[0087] 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 an average content 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.

[0088] 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)>

[0089] 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 118 to 3/8 (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.

[0090] In addition, the fraction (%) of each of the following phases is an area ratio unless otherwise specified.

Ferrite: 5.0% or less

[0091] Ferrite has an influence on the deformability of steel including martensite as a main structure. 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.

[0092] 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

[0093] The total area ratio of 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, a 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 due to an increase in non-uniformity of the microstructure caused by the formation of a structure other than the martensite and tempered martensite. 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%.

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

[0094] 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.

[0095] 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, pearlite and residual austenite are structures that deteriorate the local ductility of the steel, and are preferably as small as possible.

[0096] 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.

[0097] The area ratio of each phase in the microstructure of the steel sheet according to the present embodiment can be obtained by the following method.

(Method of Evaluating Area Ratio of Ferrite)

[0098] The area ratio of ferrite is obtained by observing 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 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 calculated in each of 8 visual fields in a 35 μm × 25 μm electron channeling contrast image by an image analysis method, and an average value thereof is defined as the area ratio of ferrite.

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

[0099] 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 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)

[0100] The area ratio of residual austenite can be calculated by measurement using X-rays. That is, a portion from 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 MoKα rays as characteristic X rays, and this is defined as the area ratio of residual austenite.

[0101] 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.

[0102] In addition, bainite is an aggregate of lath-shaped crystal grains, contains no iron-based carbide having a major axis of 20 nm or more therein or contains iron-based carbides having a major axis of 20 nm or more therein. 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°.

<Grain Boundary Binding Energy>

[0103] Regarding cracking occurring by hydrogen embrittlement, the binding strength of grain boundaries is decreased by segregation of hydrogen in the steel to the grain boundaries, and cracking is generated from the grain boundaries of which the binding strength has been decreased. Regarding this, the binding strength of the grain boundaries is improved by segregating a predetermined alloying element to the grain boundaries. In addition, in a case where an alloying element is already segregated, it becomes difficult for the entering hydrogen to segregate to the grain boundaries, and thus it is possible to suppress a decrease in binding strength of the grain boundaries due to the hydrogen even in a case where the hydrogen enters.

[0104] The present inventors have investigated the contribution of each alloying element to improvement of the grain boundary strength, based on the consideration that in a microstructure mainly including martensite and tempered martensite, a prior austenite grain boundary that is an interface (interface between martensite and tempered martensite; martensite and martensite; or tempered martensite and tempered martensite) where an orientation difference between adjacent martensite and tempered martensite is 15 degrees or more is a main grain boundary. As a result, they have found that grain boundary binding energy E_{GB} can be expressed as Expression (1) by using the concentration of each alloying element on the grain boundary, and that the hydrogen embrittlement resistance properties are distinctly improved in a case where E_{GB} is 0.50 or more.

[0105] Therefore, in the steel sheet according to the present embodiment, when an interface where an orientation difference between adjacent martensite and tempered martensite is 15 degrees or more is defined as a prior austenite grain boundary, the grain boundary binding energy E_{GB} determined by the concentration of each alloying element on the prior austenite grain boundary satisfies Expression (1):

$$E_{GB} = 1 + (3 \times [Co] + 0.7 \times [Ni] + 5.5 \times [Mo] + 0.7 \times [Cr] + 2.9 \times [Ti] + 47 \times [B] + 4.3 \times [Nb] + 4.5 \times [V] + 5.2 \times [W] + 3.1 \times [Ta] + 4.3 \times [Zr] - 0.25 \times [Mn] - 0.1 \times [P] - [Cu] - 1.1 \times [Sn] - 0.6 \times [Sb] - 0.9 \times [As]) \geq 0.50 \qquad (1)$$

[0106] Here, [chemical symbol] in the expression represents the concentration of each alloying element by mass% on the prior austenite grain boundary.

[0107] The reason why the interface where the orientation difference is 15 degrees or more is targeted is that hydrogen tends to preferentially accumulate at the prior austenite grain boundary where the orientation difference is 15 degrees or more.

[0108] As can be seen from Expression (1), not all the alloying elements segregated to the grain boundary increase the grain boundary binding energy, and the grain boundary binding energy is increased by segregating a large amount of the alloying elements that increase the grain boundary binding energy.

[0109] Here, the interface where an orientation difference between adjacent martensite and tempered martensite is 15 degrees or more includes an interface between martensite and martensite where an orientation difference is 15 degrees or more, an interface between martensite and tempered martensite where an orientation difference is 15 degrees or more, and an interface between tempered martensite and tempered martensite where an orientation difference is 15 degrees or more.

[0110] The concentration of each alloying element on the prior austenite grain boundary is obtained by observing a t/4 portion (ranging from 118 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) in the same manner as in the above-described SEM observation using an energy dispersive X-ray spectrometer (EDS) of a transmission electron microscope (TEM). More specifically, as the transmission electron microscope (TEM), a spherical aberration corrected transmission electron microscope (Cs-corrected TEM) is used.

[0111] A flaky sample used for the TEM observation is obtained by the following method. A sample for measuring the amount of an alloying element is collected from a position ranging from 1/8 to 3/8 of the sheet thickness in a steel sheet sample, and polished up to a thickness of about 100 μm by wet polishing using emery paper.

[0112] After that, twin jet electrolytic polishing is conducted to perform electrolytic polishing up to a thickness in which the TEM observation is possible. The electrolytic polishing method is performed using a twin jet electrolytic polishing device. Since appropriate conditions for the twin jet electrolytic polishing vary depending on the base metal components of the sample, it is necessary to perform extraction for each sample. After the twin jet, the flaky sample is uniformly milled using Ar ion milling, whereby the accuracy of quantification of the element on the prior austenite grain boundary is improved.

[0113] The flaky sample obtained as described above is observed by a Cs-corrected TEM. The observation position is on the prior austenite grain boundary, and the prior austenite grain boundary is found as follows. In a bright-field image in the TEM observation, the prior austenite grain boundary, the packet boundary, and the block boundary appear as black lines when observed at a magnification of 30,000 times. The sample is inclined and rotated so that, among the black lines, a black line indicating any prior austenite grain boundary is horizontal to the incident direction of TEM electron beams. In that state, elemental analysis is performed immediately above the prior austenite grain boundary using an EDS at a magnification of 100,000 times. The elemental analysis using the integration times of EDS analysis is performed by the following method. Point analysis is performed three times immediately above the prior austenite grain boundary to quantify the alloying element concentration on the prior austenite grain boundaries. This analysis is performed on five prior austenite grain boundaries, and an average alloying element concentration is calculated. The average alloying element concentration is defined as an alloying element concentration on the prior austenite grain boundary.

(Mechanical Properties)

[0114] 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.

[0115] 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 2,000 MPa or less.

(Sheet Thickness)

[0116] The sheet thickness of the steel sheet according to the present embodiment is not limited, but is preferably 1.0 to 2.2 mm. The sheet thickness is more preferably 1.05 mm or more, and even more preferably 1.1 mm or more. In addition, the sheet thickness is more preferably 2.1 mm or less, and even more preferably 2.0 mm or less.

(Coating Layer)

[0117] 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.

[0118] 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.

[0119] 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.

[0120] 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.

[0121] 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.

<Manufacturing Method>

[0122] The steel sheet according to the present embodiment achieves its effects regardless of the manufacturing method as long as the steel sheet has the above features, and can be manufactured by a manufacturing method including the following steps (I) to (VII):

(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;
(III) a cooling step in which cooling of the hot-rolled steel sheet is started within 3.0 seconds from the completion of the hot rolling step, and the steel sheet is cooled to a coiling temperature of 550°C to 700°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 cooling step at the coiling temperature;
(V) a retaining step of retaining the hot-rolled steel sheet after the coiling step in a temperature range of 400°C to 550°C for 600 seconds or longer;
(VI) a cold rolling step of pickling and cold-rolling the hot-rolled steel sheet after the retaining step to obtain a cold-rolled steel sheet;
(VII) an annealing step of holding and annealing the cold-rolled steel sheet after the cold rolling step at an annealing temperature of 800°C or higher and lower than 900°C.

[0123] Hereinafter, preferable conditions in each step will be described.

(Heating Step)

[0124] In the heating step, a steel piece such as a slab having the same chemical composition as the steel sheet according to the present embodiment is heated prior to hot rolling.

[0125] 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.

[0126] 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.

[0127] 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.

(Hot Rolling Step)

[0128] In the hot rolling step, the heated steel piece is hot-rolled to obtain a hot-rolled steel sheet.

[0129] 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: within 5.0 seconds]

[0130] The morphology of austenite grains can be controlled equiaxially and finely by controlling the rolling reduction, the number of times of rolling, and the interpass time, in finish rolling. In a case where the austenite grains become equiaxed and fine, grain boundary diffusion of the alloying elements is promoted and precipitation of alloy carbides or nitrides at the grain boundaries is promoted. 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.

[0131] 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.

[0132] 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. In this case, 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.

(Cooling Step)

[0133] In the cooling step, cooling of the hot-rolled steel sheet after the hot rolling step is started within 3.0 seconds from the completion of the hot rolling step (the completion of the final pass in finish rolling), and the steel sheet is cooled to a coiling temperature of 550°C to 700°C at an average cooling rate of 20 °C/sec or higher and 50 °C/sec or lower.

[0134] In a case where the time from the completion of hot rolling to the start of cooling is longer than 3.0 seconds or the average cooling rate up to the coiling temperature is lower than 20 °C/sec, ferritic transformation from austenite occurs until coiling. In this case, the driving force of precipitates is reduced, and thus in the subsequent step, it becomes difficult for the precipitates to be uniformly and finely precipitated.

[0135] Meanwhile, in a case where the average cooling rate up to the coiling temperature is too high, a hard phase is likely to be formed. In this case, after that, the manufacturability significantly deteriorates and the productivity decreases.

[0136] In addition, in a case where the cooling stop temperature is lower than 550°C, the precipitation of precipitates is delayed, resulting in a deterioration in manufacturability and a decrease in productivity. In addition, it is not preferable that the cooling stop temperature be higher than 700°C, since ferritic transformation from austenite occurs, the driving force for the precipitation of carbides is reduced, and it becomes difficult for the precipitates to be uniformly and finely precipitated in the subsequent step. In addition, it is not preferable that the cooling stop temperature be higher than 700°C, since an internal oxide layer is likely to be formed on the surface of the steel sheet, and the surface is likely to be cracked or the productivity significantly deteriorates in pickling in the subsequent step.

[0137] It is not necessary to limit the lower limit of the time from the completion of hot rolling to the start of rolling, and the time may be as short as possible within the range of the equipment limitation.

(Coiling Step)

(Retaining Step)

[0138] In the coiling step, the hot-rolled steel sheet after the cooling step is coiled at the coiling temperature (cooling stop temperature). In addition, in the subsequent retaining step, the coiled hot-rolled steel sheet is held (retained) in a temperature range of 400°C to 550°C for 600 seconds or longer. Alloy carbides or nitrides are precipitated in the steel sheet by controlling the coiling and retaining conditions.

[0139] The precipitates precipitated here can be unevenly distributed at the prior austenite grain boundaries by controlling the subsequent step.

[0140] In a case where the holding temperature is too high, the precipitates coarsen and are not uniformly dispersed. In addition, in a case where the holding temperature is too low, the precipitates are refined, but it takes a lot of time until the completion of precipitation, whereby the manufacturability and the productivity decrease. In addition, in a case where the holding time is short, the alloy carbides are not sufficiently precipitated.

[0141] In order to retain the steel sheet under the above-described conditions, for example, a method such as covering or heating box covering may be performed.

(Cold Rolling Step)

[0142] In the cold rolling step, the hot-rolled steel sheet after the retaining step is recoiled, pickled, and cold-rolled to obtain a cold-rolled steel sheet.

[0143] 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 (rolling reduction) of cold rolling is not particularly limited. For example, the rolling reduction is 20% to 80%.

(Annealing Step)

[0144] In the annealing step, the cold-rolled steel sheet after the cold rolling step is held and annealed at an annealing temperature of 800°C or higher and lower than 900°C.

[0145] In the annealing step, in the course of heating to the annealing temperature that is an austenite single phase region, the precipitates act to pin the prior austenite grain boundaries in a relatively low temperature range. As a result, the precipitates are unevenly distributed on the prior austenite grain boundaries. In a case where a relatively high temperature range is reached by further heating, the precipitates become thermally unstable and dissolved. As a result, a state can be made in which the alloying elements are segregated onto the prior austenite grain boundaries.

[0146] In this state, in a case where rapid cooling is performed as in a post-annealing cooling step to be described later, it is possible to obtain a high strength steel sheet in which the austenite is transformed into martensite and the alloying elements are unevenly distributed on the prior austenite grain boundaries.

[0147] In a case where the annealing temperature is lower than 800°C, the amount of austenite formed is small and the carbides do not sufficiently dissolved. Therefore, the annealing temperature is set to 800°C or higher. The annealing temperature is preferably 830°C or higher.

[0148] Meanwhile, in a case where the annealing temperature is 900°C or higher, the grains grow and the prior austenite grain size coarsens. Therefore, the segregation of a predetermined alloying element to the grain boundaries may be suppressed and the hydrogen embrittlement resistance properties may deteriorate.

[0149] The holding time at the annealing temperature does not need to be limited. However, in a case where the holding time is shorter than 10 seconds, there is a concern that the fraction of austenite at the annealing temperature may be insufficient or the dissolving of carbides may be insufficient. Therefore, the holding time is preferably 10 seconds or longer. Meanwhile, even in a case where the holding time is long, no problems occur in the properties. However, in a case where continuous annealing is assumed, the line length of the equipment is increased. Therefore, the substantial upper limit of the holding time may be set to about 600 seconds.

[0150] The average rate of temperature increases up to the annealing temperature is preferably 2 to 35 °C/sec.

(Post-Annealing Cooling Step)

(Tempering Step)

[0151] In the post-annealing cooling step, after the annealing step, the cold-rolled steel sheet may be cooled from the annealing temperature to 25°C to 300°C at an average cooling rate of 20 to 100 °C/sec.

[0152] Due to the cooling, the steel sheet is rapidly cooled in a state in which the alloying elements segregate to the austenite grain boundaries, and the austenite is transformed into martensite. As a result, it is possible to obtain a steel sheet having a structure mainly including martensite, in which the alloy element is segregated to the prior austenite grain boundaries.

[0153] In a case where the average cooling rate is lower than 20 °C/sec, a sufficient amount of martensite is not generated. Meanwhile, in a case where the average cooling rate is higher than 100 °C/sec, equipment capacity may be insufficient and reinforcement of the equipment may be required in a case where continuous annealing is assumed. Thus, the substantial upper limit of the average cooling rate is set to 100 °C/sec.

[0154] In addition, in a case where the cooling stop temperature is higher than 300°C, untransformed austenite that has not undergone martensitic transformation is likely to undergo bainitic transformation, and the strength may decrease. Meanwhile, with a cooling stop temperature lower than 25°C, not only the effects are saturated, but also a special cooling medium or the like is required, which reduces the manufacturability or increases the cost.

[0155] The cold-rolled steel sheet after the post-annealing cooling step may be further subjected to a tempering step of heating the cold-rolled steel sheet to 50°C to 550°C and holding the steel sheet for 10 to 1,000 seconds. By performing the tempering, the alloying elements that are not segregated to the grain boundaries and are present in the grains can be segregated onto the prior austenite grain boundaries. In addition, the martensite is turned into tempered martensite, and thus the formability can be improved.

[0156] In a case where the tempering temperature (holding temperature) is lower than 50°C or the holding time is shorter than 10 seconds, the above effect cannot be obtained. Meanwhile, in a case where the tempering temperature is higher than 550°C, 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, coarse carbides may be precipitated on the prior austenite grain boundaries and deteriorate the hydrogen embrittlement resistance properties. 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.

[0157] In the above-described post-annealing cooling step, the steel sheet may be held in a temperature range of 350°C to 650°C (a second temperature range: a temperature range considered to be higher than the Ms point) for 10 to 200 seconds in the middle of cooling. In this case, the cooling rate up to the second temperature range excluding the holding and the average cooling rate from the holding temperature to 25°C to 300°C (cooling stop temperature) are each set to 20 to 100 °C/sec.

[0158] That is, in this case, after the annealing step, cooling may be performed from the annealing temperature to the second temperature range of 350°C to 650°C at the average cooling rate of 20 to 100 °C/sec, holding may be performed in the second temperature range for 10 to 200 seconds, and cooling may be performed from the second temperature range to 25°C to 300°C at the average cooling rate of 20 to 100 °C/sec.

[0159] By holding at 350°C to 650°C, the alloying elements that are not segregated to the grain boundaries and are present in the grains can be segregated onto the prior austenite grain boundaries, and the hydrogen embrittlement resistance properties can thus be improved. However, in a case where the holding temperature is lower than 350°C, bainitic transformation is likely to occur, and there is a concern that the strength may decrease. In a case where the holding time is shorter than 20 seconds, the effect of segregating the element present in the grains onto the prior austenite grain boundaries cannot be obtained. Meanwhile, in a case where the holding temperature is higher than 650°C, ferritic transformation from austenite is likely to occur, leading to a decrease in tensile strength.

[0160] In addition, in a case where the holding time is longer than 200 seconds, bainitic transformation or ferritic transformation from austenite is likely to occur. The range of the holding temperature is preferably 370°C or higher and 630°C or lower, and more preferably 390°C or higher and 610°C or lower. In addition, the range of the holding time is preferably 30 seconds or longer and 180 seconds or shorter, and more preferably 50 seconds or longer and 160 seconds or shorter.

[0161] Both the holding in the middle of the post-annealing cooling step and the tempering step further promote the segregation of the alloying elements onto the prior austenite grain boundaries. Therefore, any one step may be performed or both steps may be performed. Neither of them may be performed.

[0162] The steel sheet manufacturing method according to the present embodiment may include a coating layer forming step of forming a coating layer on the surface (one or both) of the steel sheet.

[0163] 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.

[0164] 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.

[0165] 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.

[0166] 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.

[0167] The coating layer may be formed after the post-annealing cooling step described above, during the post-annealing cooling step, or during the tempering step. That is, the formation of the coating layer may be performed as a part of the holding at 350°C to 650°C during the post-annealing cooling step or as a part of the holding at 50°C to 550°C in the tempering step.

[0168] In the formation of a plating layer mainly containing zinc as the coating layer, an alloying treatment may be further performed. Conditions for this case include, for example, holding the steel sheet with a plating layer formed thereon at 480°C to 550°C for 1 to 30 seconds.

[0169] The alloying step may also be performed during the post-annealing cooling step described above or the tempering step. That is, the formation of the coating layer may be performed as a part of the holding at 350°C to 650°C during the post-annealing cooling step or as a part of the holding at 50°C to 550°C in the tempering step.

[0170] For the purpose of improving coatability and weldability, the surface of the coating layer may be subjected to upper layer plating or various treatments such as a chromate treatment, a phosphate treatment, a lubricity improvement treatment, and a weldability improvement treatment.

[Examples]

[0171] Examples of the present invention will be shown below. The examples to be shown below are merely examples of the present invention, and the present invention is not limited thereto.

<Example 1>

[0172] Steels having chemical compositions shown in Tables 1-1 to 1-4 were melted and cast into steel pieces.

[0173] The steel piece was inserted into a furnace heated to 1,220°C, held for 60 minutes, taken out into the air, and hot-rolled to obtain a steel sheet (hot-rolled steel sheet) having a sheet thickness of 2.8 mm. In the hot rolling, finish rolling was continuously performed a total of 7 times using a rolling mill having 7 stands (so that a constant interpass time was provided), and among the passes, 4 rolling passes were performed with a rolling reduction higher than 20%. 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. The finish rolling start temperature was 1,060°C, and the finish rolling finishing temperature was 870°C.

[0174] Cooling of the hot-rolled steel sheet by water was started 2.2 seconds after completion of the hot rolling, and the steel sheet was cooled to 580°C at an average cooling rate of 38.0 °C/sec and coiled. Then, the steel sheet was put in a furnace at 530°C and held for 1,800 seconds.

[0175] 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% to obtain a cold-rolled steel sheet having a sheet thickness of 1.4 mm.

[0176] The cold-rolled steel sheet was heated to 880°C at an average rate of temperature increase of 12.0 °C/sec, held at 880°C for 120 seconds, and then cooled to 150°C at an average cooling rate of 42.0 °C/sec.

[0177] After that, the cold-rolled steel sheet was reheated to 230°C and held for 180 seconds for tempering. No plating was performed.

[0178] The chemical composition was analyzed using a sample collected from the obtained steel sheet. As a result, it was equivalent to the chemical compositions of the steels shown in Tables 1-1 to 1-4.

[0179] In addition, in the obtained cold-rolled steel sheet, area ratios of ferrite, martensite and tempered martensite, and a remainder (one or two or more of bainite, pearlite, and residual austenite) in the microstructure of a t/4 portion were obtained by the above-described methods.

[0180] The results are shown in Table 2.

[0181] In addition, the concentration of each alloying element on austenite grain boundaries was measured by the above-described method, and E_{GB} was obtained.

[0182] In addition, the tensile strength, total elongation, and hydrogen embrittlement resistance (hydrogen embrittlement resistance properties) of the obtained cold-rolled steel sheet was evaluated by the following methods.

(Method of Evaluating Tensile Properties)

[0183] AJIS 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 strip, and a tensile test was performed according to JIS Z 2241 (2011) to measure the tensile strength (TS) and the total elongation (El).

(Method of Evaluating Hydrogen Embrittlement Resistance)

[0184] The hydrogen embrittlement resistance of the steel sheet manufactured using the steel sheet manufacturing method according to the embodiment of the present invention was evaluated by the following method. Specifically, the steel sheet was sheared with a clearance of 15%, and then a U-bending test was performed at 8R. 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 in Table 2, applied stress = 1,515 MPa × 0.8 = 1,212 MPa). This is because the residual stress that is introduced during forming is considered to correspond to the tensile strength of the steel sheet.

[0185] 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 entering into the steel sheet, and the hydrogen embrittlement environment becomes severe. 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. A case where the evaluation was OK was considered a pass, and a case where the evaluation was NG was considered to be a failure.

[0186] 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 high strength and excellent hydrogen embrittlement resistance.

[Table 1-1]

Steel No.	Chemical Composition (mass%) Remainder: Fe and Impurities													
	C	Si	Mn	P	S	Al	N	O	Co	Ni	Mo	Cr	Ti	B
A	0.213	1.17	1.80	0.0189	0.0036	0.294	0.0059	0.0191	0.019	0.365	0.177	1.517	0.281	0.0080
B	0.241	0.80	1.20	0.0060	0.0004	0.086	0.0113	0.0021	0.200	0.493	0.869	1.873	0.060	0.0031
C	0.342	1.94	1.10	0.0156	0.0130	0.831	0.0131	0.0040				1.548	0.430	0.0058
D	0.387	0.62	1.40	0.0087	0.0103	0.961	0.0087	0.0110	0.348	0.623	0.833	1.155	0.118	0.0079
E	0.197	1.75	0.80	0.0054	0.0076	0.155	0.0099	0.0155	0.254	0.759	0.124	0.266	0.445	0.0038
F	0.282	1.21	1.50	0.0102	0.0161	0.692	0.0043	0.0012	0.053	0.574	0.053	1.688	0.197	0.0006
G	0.354	1.38	1.70	0.0030	0.0018	0.429	0.0037	0.0121	0.414	0.987	0.764	0.827	0.309	0.0023
H	0.328	1.58	1.50	0.0021	0.0139	0.395	0.0006	0.0066	0.472	0.198	0.647	0.507	0.088	0.0046
I	0.173	0.96	1.00	0.0074	0.0086	0.579	0.0161	0.0170	0.296	0.417	0.485	1.225	0.257	0.0094
J	0.376	0.28	2.00	0.0169	0.0149	0.744	0.0143	0.0085	0.311	0.905	0.458	0.952	0.379	0.0049
K	0.295	0.82	1.69	0.0138	0.0175	0.058	0.0178	0.0079		0.689	0.540	0.129	0.408	0.0013
L	0.229	0.54	1.30	0.0009	0.0049	0.520	0.0072	0.0047	0.379	0.825	0.937	0.592	0.205	0.0065
M	0.263	0.13	1.20	0.0109	0.0056	0.048	0.0025	0.0178	0.133	0.075	0.280	0.337	0.160	0.0058
N	0.285	0.32	1.70	0.0183	0.0187	0.216	0.0151	0.0144	0.231	0.230	0.222	1.827	0.469	0.0089
O	0.306	1.65	1.90	0.0128	0.0114	0.622	0.0187	0.0098	0.105	0.135	0.377	1.391	0.358	0.0017
P	$\underline{0.141}$	0.13	1.80	0.0166	0.0155	0.165	0.0043	0.0079	0.211	0.868	0.441	0.262	0.070	0.0080
Q	$\underline{0.408}$	1.19	1.40	0.0087	0.0114	0.080	0.0100	0.0151	0.435	0.614	0.251	1.006	0.322	0.0095
R	0.322	$\underline{2.06}$	1.30	0.0083	0.0157	0.074	0.0124	0.0153	0.082	0.571	0.844	0.130	0.313	0.0060
S	0.347	1.73	$\underline{0.65}$	0.0067	0.0050	0.483	0.0037	0.0075	0.288	0.334	0.508	0.266	0.200	0.0040
T	0.325	1.68	$\underline{2.12}$	0.0079	0.0021	0.585	0.0089	0.0061	0.395	0.275	0.950	0.765	0.068	0.0049
U	0.300	1.37	1.70	$\underline{0.0206}$	0.0085	0.100	0.0095	0.0083	0.466	0.324	0.337	1.262	0.142	0.0010
V	0.251	0.38	1.10	0.0036	$\underline{0.0208}$	0.930	0.0087	0.0171	0.343	0.708	0.831	1.857	0.417	0.0019
W	0.338	1.29	1.30	0.0104	0.0129	0.289	$\underline{0.0207}$	0.0151	0.403	0.637	0.108	0.365	0.087	0.0086
* The underlined value is out of the range of the present invention.														

[Table 1-2]

Steel No.	Chemical Composition (mass%) Remainder: Fe and Impurities													
	C	Si	Mn	P	S	Al	N	O	Co	Ni	Mo	Cr	Ti	B
X	0.316	1.80	1.50	0.0163	0.0055	1.034	0.0182	0.0180	0.484	0.456	0.544	0.127	0.208	0.0015
Y	0.383	0.48	0.80	0.0123	0.0114	0.552	0.0173	0.0069	0.254	0.588	0.353	1.912	0.470	0.0104
Z.	0.209	1.53	1.90	0.0011	0.0174	0.322	0.0100	0.0047	0.425	0.342	0.639	0.763	0.511	0.0085
AA	0.242	0.97	0.90	0.0027	0.0164	0.398	0.0140	0.0181	0.229	0.241	0.820	1.745	0.409	0.0035
AB	0.293	1.75	1.90	0.0148	0.0141	0.748	0.0097	0.0117	0.346	0.628	0.198	1.866	0.385	0.0008
AC	0.386	0.21	1.30	0.0016	0.0096	0.266	0.0155	0.0206	0.111	0.392	0.485	1.634	0.446	0.0065
AD	0.242	0.98	1.00	0.0077	0.0165	0.513	0.0057	0.0077	0.124	0.509	1.030	1.110	0.242	0.0095
AE	0.279	0.15	1.00	0.0162	0.0124	0.529	0.0148	0.0180	0.473	0.594	0.663	2.074	0.112	0.0081
AF	0.199	1.02	1.10	0.0185	0.0031	0.068	0.0051	0.0164	0.511	0.611	0.080	1.334	0.143	0.0073
AG	0.174	0.60	1.70	0.0147	0.0075	0.731	0.0055	0.0112	0.314	1.025	0.430	0.022	0.047	0.0036
AH	0.225	1.27	1.20	0.0162	0.0053	0.171	0.0119	0.0058	0.035	0.419	0.741	1.839	0.265	0.0079
AI	0.199	0.58	0.90	0.0131	0.0082	0.316	0.0024	0.0116	0.367	0.054	0.769	1.601	0.393	0.0065
AJ	0.290	1.43	1.50	0.0152	0.0030	0.733	0.0100	0.0041	0.065	0.756	0.764	1.439	0.103	0.0075
AK	0.233	1.66	1.90	0.0051	0.0043	0.921	0.0160	0.0127	0.193	0.907	0.469	0.839	0.470	0.0059
AL	0.187	0.71	1.80	0.0196	0.0025	0.609	0.0071	0.0137	0.208	0.817	0.269	0.109	0.128	0.0052
AM	0.298	1.83	1.40	0.0113	0.0066	0.168	0.0121	0.0017	0.146	0.451	0.872	0.597	0.462	0.0037
AN	0.255	1.60	1.60	0.0045	0.0191	0.708	0.0119	0.0169	0.280	0.802	0.416	0.763	0.120	0.0040
AO	0.234	1.13	1.30	0.0031	0.0061	0.887	0.0109	0.0139	0.178	0.091	0.613	0.418	0.194	0.0057
AP	0.223	1.06	1.50	0.0019	0.0083	0.773	0.0175	0.0099	0.239	0.662	0.314	0.952	0.271	0.0042
AQ	0.344	0.61	1.60	0.0167	0.0129	0.575	0.0081	0.0011	0.393	0.189	0.597	0.892	0.295	0.0059
AR	0.306	0.76	1.50	0.0135	0.0185	0.866	0.0173	0.0107	0.175	0.192	0.800	1.701	0.007	0.0061
AS	0.362	1.23	1.40	0.0011	0.0114	0.146	0.0140	0.0041	0.143	0.944	0.870	0.496	0.451	0.0048

* The underlined value is out of the range of the present invention.

[Table 1-3]

Steel No.	Chemical Composition (mass%) Remainder: Fe and Impurities														Remarks
	Nb	V	Cu	W	Ta	Mg	Ca	Y	Zr	La	Ce	Sn	Sb	As	
A	0.085	0.375	0.212	0.029	0.060	0.048	0.019	0.002	0.036	0.023	0.038	0.034	0.042	0.015	Development Steel
B	0.044	0.231	0.383	0.050	0.074	0.022	0.017	0.027	0.026	0.029	0.026	0.030	0.048	0.031	Development Steel
C															Development Steel
D	0.475	0.269	0.316	0.095	0.032	0.033	0.039	0.015	0.023	0.042	0.007	0.002	0.029	0.046	Development Steel
E	0.211	0.438	0.181	0.023	0.013	0.041	0.009	0.023	0.030	0.035	0.046	0.006	0.012	0.007	Development Steel
F	0.166	0.346	0.402	0.038	0.090	0.037	0.035	0.047	0.033	0.020	0.031	0.017	0.010	0.010	Development Steel
G	0.437	0.061	0.453	0.046	0.082	0.026	0.030	0.039	0.013	0.033	0.015	0.014	0.035	0.035	Development Steel
H	0.240	0.425	0.477	0.083	0.072	0.035	0.042	0.012	0.016	0.038	0.035	0.046	0.039	0.012	Development Steel
I	0.297	0.164	0.286	0.012	0.041	0.013	0.044	0.043	0.004	0.008	0.023	0.020	0.016	0.037	Development Steel
J	0.328	0.007	0.021	0.069	0.053	0.005	0.012	0.035	0.048	0.016	0.047	0.021	0.023	0.022	Development Steel
K	0.016		0.164												Development Steel
L	0.347	0.081	0.085	0.016	0.008	0.020	0.047	0.026	0.045	0.048	0.030	0.010	0.004	0.003	Development Steel
M	0.369	0.182	0.360	0.088	0.015	0.016	0.023	0.009	0.008	0.007	0.009	0.024	0.005	0.028	Development Steel
N	0.420	0.476	0.113	0.078	0.024	0.003	0.025	0.042	0.038	0.026	0.018	0.031	0.044	0.025	Development Steel
O	0.121	0.128	0.258	0.008	0.040	0.009	0.032	0.006	0.043	0.044	0.004	0.038	0.033	0.018	Development Steel
P	0.419	0.142	0.270	0.060	0.036	0.009	0.007	0.006	0.016	0.023	0.021	0.022	0.027	0.034	Comparative Steel
Q	0.456	0.321	0.303	0.096	0.094	0.027	0.016	0.036	0.009	0.041	0.005	0.008	0.020	0.022	Comparative Steel
R	0.303	0.205	0.415	0.072	0.034	0.023	0.010	0.023	0.006	0.017	0.016	0.042	0.017	0.002	Comparative Steel
S	0.101	0.392	0.094	0.021	0.018	0.018	0.048	0.013	0.023	0.015	0.021	0.033	0.017	0.030	Comparative Steel
T	0.218	0.463	0.093	0.063	0.093	0.043	0.030	0.004	0.037	0.022	0.026	0.004	0.011	0.040	Comparative Steel
U	0.447	0.114	0.265	0.073	0.061	0.030	0.043	0.026	0.003	0.035	0.013	0.025	0.038	0.032	Comparative Steel
V	0.156	0.410	0.141	0.067	0.063	0.003	0.032	0.038	0.014	0.004	0.007	0.028	0.019	0.046	Comparative Steel
W	0.347	0.028	0.044	0.097	0.014	0.020	0.016	0.032	0.033	0.012	0.033	0.015	0.037	0.006	Comparative Steel

[Table 1-4]

Steel No.	Chemical Composition (mass%) Remainder: Fe and Imparities														Remarks
	Nb	V	Cu	W	Ta	Mg	Ca	Y	Zr	La	Co	Sn	Sb	As	
X	0.104	0.284	0.142	0.067	0.086	0.003	0.039	0.047	0.024	0.019	0.025	0.030	0.028	0.042	Comparative Steel
Y	0.041	0.138	0.382	0.080	0.079	0.031	0.033	0.004	0.022	0.049	0.027	0.017	0.015	0.044	Comparative Steel
Z	0.065	0.257	0.058	0.044	0.086	0.044	0.019	0.012	0.044	0.042	0.030	0.037	0.012	0.034	Comparative Steel
AA	0.511	0.476	0.206	0.025	0.085	0.017	0.012	0.006	0.043	0.045	0.036	0.033	0.004	0.014	Comparative Steel
AB	0.473	0.512	0.125	0.049	0.022	0.038	0.036	0.004	0.021	0.009	0.019	0.010	0.034	0.048	Comparative Steel
AC	0.159	0.363	0.134	0.057	0.071	0.048	0.040	0.030	0.046	0.003	0.022	0.046	0.025	0.044	Comparative Steel
AD	0.127	0.281	0.035	0.074	0.074	0.047	0.005	0.036	0.008	0.010	0.017	0.025	0.037	0.021	Comparative Steel
AE	0.076	0.247	0.243	0.025	0.073	0.035	0.021	0.035	0.040	0.042	0.011	0.017	0.045	0.022	Comparative Steel
AF	0.251	0.199	0.424	0.011	0.043	0.025	0.005	0.022	0.026	0.032	0.047	0.032	0.025	0.042	Comparative Steel
AG	0.185	0.278	0.200	0.041	0.041	0.039	0.005	0.040	0.026	0.007	0.042	0.027	0.043	0.019	Comparative Steel
AH	0.142	0.126	0.518	0.039	0.031	0.011	0.014	0.035	0.040	0.008	0.047	0.006	0.045	0.010	Comparative Steel
AI	0.246	0.026	0.221	0.104	0.019	0.047	0.044	0.025	0.039	0.011	0.004	0.011	0.030	0.021	Comparative Steel
AJ	0.231	0.168	0.361	0.006	0.103	0.026	0.045	0.045	0.018	0.037	0.036	0.041	0.016	0.024	Comparative Steel
AK	0.293	0.388	0.423	0.068	0.069	0.039	0.027	0.043	0.036	0.045	0.043	0.052	0.027	0.038	Comparative Steel
AL	0.042	0.048	0.020	0.058	0.044	0.009	0.028	0.014	0.048	0.037	0.022	0.010	0.051	0.006	Comparative Steel
AM	0.295	0.215	0.292	0.055	0.028	0.015	0.039	0.049	0.011	0.035	0.016	0.027	0.013	0.051	Comparative Steel
AN	0.315	0.350	0.394	0.090	0.057	0.052	0.045	0.027	0.014	0.033	0.038	0.043	0.041	0.029	Comparative Steel
AC	0.437	0.117	0.438	0.059	0.065	0.027	0.051	0.018	0.030	0.029	0.009	0.007	0.021	0.005	Comparative Steel
AP	0.072	0.045	0.059	0.026	0.025	0.027	0.025	0.051	0.031	0.046	0.036	0.002	0.005	0.012	Comparative Steel
AQ	0.382	0.160	0.361	0.028	0.081	0.045	0.033	0.043	0.052	0.017	0.006	0.025	0.006	0.011	Comparative Steel
AR	0.041	0.185	0.323	0.017	0.068	0.041	0.038	0.017	0.047	0.052	0.018	0.046	0.039	0.037	Comparative Steel
AS	0.402	0.427	0.098	0.050	0.058	0.007	0.043	0.033	0.048	0.025	0.052	0.014	0.010	0.016	Comparative Steel
* The underlined value is out of the range of the present invention.															

[Table 2]

Manufacturing No.	Steel No.	Ferrite (%)	Sum of Martensite and Tempered Martensite (%)	Remainder in Microstructure	E_{GB}	Tensile Strength (MPa)	Total Elongation (%)	Hydrogen Embrittlement Resistance	Remarks
A	A	1.4	96.9	1.7	1.48	1515	9.4	OK	Invention Example
B	B	0.0	95.1	4.9	1.65	1598	7.2	OK	Invention Example
C	C	0.0	100.0	0.0	0.68	1898	8.4	OK	Invention Example
D	D	1.0	97.7	1.3	1.45	2032	8.9	OK	Invention Example
E	E	0.0	92.2	7.8	1.23	1569	8.0	OK	Invention Example
F	F	0.0	95.0	5.0	0.96	1720	7.7	OK	Invention Example
G	G	0.0	96.5	3.5	0.92	1934	7.2	OK	Invention Example
H	H	0.0	91.1	8.9	0.87	1856	8.5	OK	Invention Example
I	I	0.0	96.7	3.3	0.86	1509	9.4	OK	Invention Example
J	J	0.0	93.4	5.6	1.54	1999	6.9	OK	Invention Example
K	K	0.0	99.0	1.0	1.59	1768	8.2	OK	Invention Example
L	L	0.0	97.9	2.1	1.44	1563	8.6	OK	Invention Example
M	M	0.0	94.6	5.4	0.59	1664	8.4	OK	Invention Example
N	N	1.5	91.3	7.2	0.69	1729	9.3	OK	Invention Example
O	O	2.9	95.6	1.5	0.96	1791	7.7	OK	Invention Example
P	P	23.0	75.0	2.0	1.95	1301	7.0	NG	Comparative Example
Q	Q	0.0	98.0	2.0	0.85	2105	8.2	NG	Comparative Example
R	R	2.3	94.0	3.7	0.11	1839	7.2	NG	Comparative Example
S	S	11.5	83.0	5.5	0.69	1366	8.1	NG	Comparative Example
T	T	43.0	54.0	3.0	0.46	1848	7.0	NG	Comparative Example

(continued)

Manufacturing No.	Steel No.	Ferrite (%)	Sum of Martensite and Tempered Martensite (%)	Remainder in Microstructure	E_{GB}	Tensile Strength (MPa)	Total Elongation (%)	Hydrogen Embrittlement Resistance	Remarks
U	U	0.0	100.0	0.0	0.03	1773	7.3	NG	Comparative Example
V	V	1.8	97.5	0.7	0.95	1628	8.2	NG	Comparative Example
W	W	0.0	93.8	6.2	0.68	1886	7.6	NG	Comparative Example
X	X	1.4	95.0	3.6	0.86	1821	7.4	NG	Comparative Example
Y	Y	0.0	96.4	3.6	0.58	2020	6.8	NG	Comparative Example
Z	Z	13.0	85.1	1.9	0.32	1395	6.2	NG	Comparative Example
AA	AA	1.0	97.8	1.2	1.28	1601	8.3	NG	Comparative Example
AB	AB	2.3	94.8	2.9	1.59	1753	8.7	NG	Comparative Example
AC	AC	0.0	100.0	0.0	0.94	2029	9.2	NG	Comparative Example
AD	AD	1.8	97.0	1.2	0.47	1601	8.8	NG	Comparative Example
AE	AE	3.3	93.8	2.9	0.23	1711	8.2	NG	Comparative Example
AF	AF	1.5	95.2	3.3	0.39	1568	8.6	NG	Comparative Steel
AG	AG	0.0	99.0	1.0	0.56	1502	8.7	NG	Comparative Example
AH	AH	3.6	92.1	4.3	0.33	1551	8.3	NG	Comparative Example
AI	AI	2.3	96.8	0.9	0.43	1465	9.9	NG	Comparative Example
AJ	AJ	1.5	97.4	1.1	0.55	1744	8.3	NG	Comparative Example
AK	AK	3.5	95.8	0.7	-0.95	1575	8.1	NG	Comparative Example
AL	AL	3.9	93.6	2.5	-0.75	1598	9.0	NG	Comparative Example
AM	AM	0.0	99.0	1.0	0.95	1767	7.9	NG	Comparative Example
AN	AN	0.0	100.0	0.0	0.57	1640	8.6	NG	Comparative Example

(continued)

Manufacturing No.	Steel No.	Ferrite (%)	Sum of Martensite and Tempered Martensite (%)	Remainder in Microstructure	E_{GB}	Tensile Strength (MPa)	Total Elongation (%)	Hydrogen Embrittlement Resistance	Remarks
AO	AO	0.0	100.0	0.0	0.68	1577	9.0	NG	Comparative Example
AP	AP	1.0	98.3	0.7	0.79	1545	8.2	NG	Comparative Example
AQ	AQ	0.0	100.0	0.0	0.59	1904	7.3	NG	Comparative Example
AR	AR	2.0	98.0	0.0	0.75	1791	8.1	NG	Comparative Example
AS	AS	4.3	92.3	3.4	0.94	1957	6.5	NG	Comparative Example

[0187] Referring to Tables 1-1 to 2, in Manufacturing No. P, since the C content was low, the tensile strength was less than 1,500 MPa.

[0188] In Manufacturing No. Q, since the C content was high, the hydrogen embrittlement resistance decreased.

[0189] In Manufacturing No. R, since the Si content was high, the precipitation of alloy carbides was suppressed in the hot rolling step, the segregation of the grain boundary strengthening elements to the prior austenite grain boundaries was suppressed in the annealing step, and thus the hydrogen embrittlement resistance decreased.

[0190] In Manufacturing No. S, since the Mn content was low, the tensile strength was less than 1,500 MPa.

[0191] In Manufacturing No. T, since the Mn content was large and E_{GB} decreased, the hydrogen embrittlement resistance decreased.

[0192] In Manufacturing No. U, since the P content was high, E_{GB} decreased and the hydrogen embrittlement resistance decreased.

[0193] In Manufacturing No. V, since the S content was high, the hydrogen embrittlement resistance decreased.

[0194] In Manufacturing No. W, since the N content was high, coarse nitrides were formed and the hydrogen embrittlement resistance decreased.

[0195] In Manufacturing No. X, since the Al content was high, coarse Al oxides were formed and the hydrogen embrittlement resistance decreased.

[0196] In Manufacturing No. Y, since the B content was high, coarse B oxides were formed and the hydrogen embrittlement resistance decreased.

[0197] In Manufacturing No. Z, since the Ti content was high, coarse carbonitrides were formed and the hydrogen embrittlement resistance decreased. In addition, due to the formation of coarse carbonitrides, the amount of Ti segregated to the grain boundaries decreased and E_{GB} decreased. In addition, since the amount of C effective for increasing the strength was decreased, the tensile strength was 1,500 MPa or less.

[0198] In Manufacturing No. AA, since the Nb content was high, coarse Nb carbides were formed and the hydrogen embrittlement resistance decreased.

[0199] In Manufacturing No. AB, since the V content was high, coarse V carbides were formed and the hydrogen embrittlement resistance decreased.

[0200] In Manufacturing No. AC, since the O content was high, oxides were formed and the hydrogen embrittlement resistance decreased.

[0201] In Manufacturing No. AD, since the Mo content was high, the amount of carbonitrides precipitated increased and the hydrogen embrittlement resistance decreased. In addition, due to the formation of coarse carbonitrides, the amount of Mo segregated to the grain boundaries decreased and E_{GB} decreased.

[0202] In Manufacturing No. AE, since the Cr content was high, coarse Cr carbides were formed at the center segregation area in the steel and the hydrogen embrittlement resistance decreased. In addition, due to the formation of coarse carbonitrides, the amount of Cr segregated to the grain boundaries decreased and E_{GB} decreased.

[0203] In Manufacturing No. AF, since the Co content was high, coarse Co carbides were formed and the hydrogen embrittlement resistance decreased. In addition, due to the formation of coarse carbonitrides, the amount of Co segregated to the grain boundaries decreased and E_{GB} decreased.

[0204] In Manufacturing No. AG, since the Ni content was high, the hydrogen embrittlement resistance decreased.

[0205] In Manufacturing No. AH, since the Cu content was high, E_{GB} decreased to less than 0.50, and thus the hydrogen embrittlement resistance decreased.

[0206] In Manufacturing No. AI, since the W content was high, coarse W precipitates were formed and the hydrogen embrittlement resistance decreased. In addition, the amount of W effective for grain boundary strengthening was decreased, E_{GB} became less than 0.50, and thus the hydrogen embrittlement resistance decreased.

[0207] In Manufacturing No. AJ, since the Ta content was high, a large number of fine Ta carbides were precipitated and the hydrogen embrittlement resistance decreased.

[0208] In Manufacturing No. AK, since the Sn content was high, E_{GB} was less than 0.50 due to grain boundary embrittlement, and thus the hydrogen embrittlement resistance decreased.

[0209] In Manufacturing Nos. AL and AM, since the Sb content and the As content were high, respectively, E_{GB} was less than 0.50 due to boundary segregation and the hydrogen embrittlement resistance decreased.

[0210] In Manufacturing Nos. AN and AO, since the Mg content and the Ca content were high, respectively, the hydrogen embrittlement resistance decreased due to the formation of coarse inclusions.

[0211] In Manufacturing Nos. AP to AS, since the Y content, the Zr content, the La content, and the Ce content were high, respectively, coarse oxides were formed and the hydrogen embrittlement resistance decreased.

[0212] In contrast, in Manufacturing Nos. A to Q, by appropriately controlling the chemical compositions and structures of the steel sheets and the grain boundary strength E_{GB} at the prior austenite grain boundaries, it was possible to obtain steel sheets having a high strength and excellent hydrogen embrittlement resistance.

<Example 2>

[0213] Furthermore, in order to investigate the influences of manufacturing conditions, the steel types (Steel Nos. A to O) recognized to have excellent properties in Example 1 were targeted, and in the same equipment as in Example 1, steel pieces were inserted into a furnace heated to 1,250°C to 1,100°C, held for 60 minutes, taken out into the air, and produced into hot-rolled steel sheets having a sheet thickness of 2.3 mm under manufacturing conditions shown in Tables 3-1 and 3-2. Furthermore, cold-rolled steel sheets were obtained under conditions shown in Tables 3-1 to 3-4 following coiling. A part of the cold-rolled steel sheet was a steel sheet with a plating layer formed thereon. Here, the plating symbols GI and GA 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-dip galvanizing bath at 460°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 and by then raising the temperature of the steel sheet to 485°C. In a case where intermediate holding was performed in the second temperature range, the plating was performed as it was (without cooling to room temperature) after the intermediate holding. In a case where intermediate holding was not performed in the second temperature range, the plating was performed in the middle of cooling to 25°C to 300°C. In Tables 3-3 and 3-4, the examples in which "-" is recorded for tempering are examples not subjected to tempering. In addition, the interpass time in the tables is an interpass time between passes with a rolling reduction of 20% or higher (the interpass times were the same since the rolling was performed by a tandem rolling mill). In addition, in Tables 3-3 and 3-4, in a case where cooling to the second temperature range is performed, the holding time in the post-annealing cooling step is a holding time in the second temperature range, and in a case where the cooling stop temperature is out of the second temperature range, the holding time in the post-annealing cooling step is a holding time at a temperature near the cooling stop temperature.

[0214] In the obtained cold-rolled steel sheet (including the plated steel sheet), area ratios of ferrite, martensite and tempered martensite, and a remainder (one or two or more of bainite, pearlite, and residual austenite) in the microstructure were obtained in the same manner as in Example 1. In addition, the concentration of each alloying element on the austenite grain boundaries was measured, and E_{GB} was obtained.

[0215] In addition, the tensile strength and total elongation of the obtained cold-rolled steel sheet were evaluated by the same methods as in Example 1.

[0216] In addition, the hydrogen embrittlement resistance was evaluated by the following method.

(Method of Evaluating Hydrogen Embrittlement Resistance)

[0217] The hydrogen embrittlement resistance of the hot-dip galvanized steel sheet manufactured using the steel sheet manufacturing method according to the embodiment of the present invention was evaluated by the following method. Specifically, the steel sheet was sheared with a clearance of 15%, and then a U-bending test was performed at 8R. 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 = 1,540 MPa × 0.8 = 1,232 MPa). This is because the residual stress that is introduced during forming is considered to correspond to the tensile strength of the steel sheet.

[0218] 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 entering 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.

[0219] It is shown that the smaller the total length of the crack, the more excellent the hydrogen embrittlement resistance properties. 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 and a case where a slight crack having a crack length of 1.00 mm or shorter was recognized were evaluated OK. Among cases where the evaluation was OK, a case where no crack was recognized and a case where a crack having a crack length of 0.70 mm or shorter was formed were evaluated Ex. A case where the evaluation was OK or Ex was considered a pass, and a case where the evaluation was NG was considered a fail.

[0220] The results are shown in Table 4.

[Table 3-1]

Manufacturing No.	Steel No.	Hot Rolling Step							
		Rolling Start Temperature in Hot Rolling	Number of Passes with Rolling Reduction of 20% or Higher	Interpass Time	Rolling Finishing Temperature	Time from After Hot Rolling Step to Start of Cooling	Average Cooling Rate up to Coiling Temperature	Coiling Temperature	Retention Time at 400°C to 550°C After Hot Rolling
		°C	Number of Passes	See	°C	Sec	°C/Sec	°C	Sec
A-1	A	1081	4	4.5	884	1.9	45	635	636
B-1	B	999	4	3.4	933	2.5	47	566	831
C-1	C	1096	4	3.7	905	2.4	48	596	758
D-1	D	1004	4	1.5	842	1.2	36	698	902
E-1	E	986	4	4.2	858	1.1	37	675	974
F-1	F	1035	4	3.2	915	1.8	33	612	850
G-1	G	958	4	1.2	927	2.5	44	655	1182
H-1	H	965	4	3.2	942	2.3	31	574	1079
I-1	I	972	5	2.2	872	2.3	41	645	777
J-1	J	1028	6	2.7	808	1.1	25	585	694
K-1	K	1076	5	2.8	835	1.9	28	560	941
L-1	L	1046	4	4.6	823	1.0	39	607	1149
M-1	M	1054	5	3.1	862	2.3	21	667	1023
N-1	N	1066	6	4.1	815	1.8	26	621	668
O-1	O	1052	4	4.1	820	2.5	33	611	788
A-2	A	1016	6	4.0	899	3.6	23	680	1054
B-2	B	944	4	3.5	829	2.6	42	622	943
C-2	C	1106	5	4.1	869	2.2	44	611	1053
D-2	D	964	5	2.6	794	2.3	27	570	973
E-2	E	1017	4	3.2	954	2.9	36	680	868
F-2	F	1082	4	4.5	808	2.5	33	545	1091

(continued)

Manufacturing No.	Steel No.	Hot Rolling Step							
		Rolling Start Temperature in Hot Rolling	Number of Passes with Rolling Reduction of 20% or Higher	Interpass Time	Rolling Finishing Temperature	Time from After Hot Rolling Step to Start of Cooling	Average Cooling Rate up to Coiling Temperature	Coiling Temperature	Retention Time at 400°C to 550°C After Hot Rolling
		°C	Number of Passes	See	°C	Sec	°C/Sec	°C	Sec
G-2	G	991	4	4.5	828	1.2	28	705	1136

[Table 3-2]

Manufacturing No.	Steel No.	Hot Rolling Step							
		Rolling Start Temperature in Hot Rolling	Number of Passes with Rolling Reduction of 20% or Higher	Interpass Time	Rolling Finishing Temperature	Time from After Hot Rolling Step to Start of Cooling	Average Cooling Rate up to Coiling Temperature	Coiling Temperature	Retention Time at400°C to 550°C After Hot Rolling
		°C	Number of Passes	Sec	°C	Sec	°C/Sec	°C	Sec
H-2	H	968	6	3.5	848	1.1	19	577	1151
I-2	I	1039	6	3.7	922	1.8	44	681	803
J-2	J	1066	6	3.5	885	1.4	31	614	1166
K-2	K	1035	3	5.6	905	2.2	47	691	882
L-2	L	1070	4	4.1	819	2.4	38	664	453
M-2	M	987	4	3.2	938	2.5	34	585	513
N-2	N	1047	5	2.3	947	2.9	38	552	1220
O-2	O	999	4	2.1	851	1.5	40	661	856
A-3	A	1020	5	2.7	922	1.7	26	581	697
B-3	B	1055	5	4.6	886	1.9	33	589	906
C-3	C	1016	5	4.1	861	2.5	40	659	846
F-3	F	1092	4	3.4	867	2.7	30	608	754
G-3	G	994	5	3.3	916	2.1	21	644	999
H-3	H	1010	6	2.7	812	1.5	40	671	824
I-3	I	1058	5	2.9	914	1.9	23	600	1002
J-3	J	1074	4	4.1	847	1.1	47	602	1093
K-3	K	967	5	4.1	877	1.6	49	673	639
L-3	L	1001	4	3.6	901	1.4	37	630	628
M-3	M	1060	5	2.7	813	2.2	24	694	686
N-3	N	1083	5	2.4	835	2.5	45	573	759
O-3	O	1088	5	2.2	892	1.5	30	638	769

[Table 3-3]

Manufacturing No.	Steel No.	Cold Rolling Step	Annealing Step	Post-Annealing Cooling Step					Plating	Tempering Step	
		Rolling Reduction	Annealing Temperature	Average Cooling Rate After Annealing^{*1}	Cooling Stop Temperature	Holding Time	Average Cooling Rate After Holding	Cooling Stop Temperature		Tempering Temperature	Tempering Time
		%	°C	°C/Sec	°C	Sec	°C/Sec	°C		°C	Sec
A-1	A	61	844	52	513	128	81	203	GA	151	379
B-1	B	40	839	93	395	69	50	152	GA	122	990
C-1	C	52	859	85	-	-	-	157	None	143	159
D-1	D	57	895	79	368	51	93	217	GI	220	754
E-1	E	63	864	66	387	60	52	52	None	67	289
F-1	F	46	868	72	471	40	95	125	None	-	-
G-1	G	66	890	78	540	151	59	286	None	134	88
H-1	H	50	847	38	561	197	74	97	GA	177	42
I-1	I	55	884	30	-	-	-	113	None	102	636
J-1	J	50	875	98	493	45	43	267	GA	207	721
K-1	K	54	867	59	641	30	40	242	GA	-	-
L-1	L	61	856	52	459	56	66	28	GA	111	830
M-1	M	60	832	25	-	-	-	64	None	335	868
N-1	N	43	821	36	422	93	22	258	GA	310	543
O-1	O	55	887	45	-	-	-	203	None	223	303
A-2	A	54	822	46	623	23	26	180	None	155	267
B-2	B	54	819	65	573	89	41	141	None	257	983
C-2	C	43	881	84	396	22	30	171	None	106	147
D-2	D	41	845	79	-	-	-	221	None	243	470

(continued)

Manufacturing No.	Steel No.	Cold Rolling Step	Annealing Step	Post-Annealing Cooling Step					Plating	Tempering Step	
		Rolling Reduction	Annealing Temperature	Average Cooling Rate After Annealing[*1]	Cooling Stop Temperature	Holding Time	Average Cooling Rate After Holding	Cooling Stop Temperature		Tempering Temperature	Tempering Time
		%	°C	°C/Sec	°C	Sec	°C/Sec	°C		°C	Sec
E-2	E	45	859	38	496	29	43	133	None	91	259
F-2	F	65	832	97	459	51	44	36	None	255	644
G-2	G	55	995	47	640	36	39	182	GI	137	442

*1 An average cooling rate up to the holding temperature range, in a case where intermediate holding is performed, and
an average cooling rate up to the temperature range of 25°C to 300°C, in a case where intermediate holding is not performed

[Table 3-4]

Manufacturing No.	Steel No.	Cold Rolling Step	Annealing Step	Post-Annealing Cooling Step					Plating	Tempering Step	
		Rolling Reduction	Annealing Temperature	Average Cooling Rate After Annealing*1	Cooling Stop Temperature	Holding Time	Average Cooling Rate After Holding	Cooling Stop Temperature		Tempering Temperature	Tempering Time
		%	°C	°C/Sec	°C	Sec	°C/Sec	°C		°C	Sec
H-2	H	67	896	80	549	82	26	173	GA	295	445
I-2	I	60	867	96	369	59	56	145	GA	-	-
J-2	J	57	840	41	-	-	-	277	None	296	313
K-2	K	43	862	29	491	39	80	256	None	54	651
L-2	L	39	854	70	592	42	25	155	None	219	764
M-2	M	64	848	87	353	46	32	239	GA	284	174
N-2	N	46	833	66	520	55	36	211	GA	-	-
O-2	O	61	837	56	458	45	48	241	GA	-	-
A-3	A	56	796	42	444	68	64	290	GI	467	874
B-3	B	48	902	21	382	48	83	104	GA	440	345
C-3	c	46	827	17	631	75	76	86	GI	323	179
F-3	F	57	876	36	499	54	77	309	GI	210	703
G-3	G	42	869	52	378	21	57	247	GA	150	23
H-3	H	48	858	60	355	81	87	75	None	569	555
I-3	I	55	882	28	-	-	-	117	None	52	88
J-3	J	55	876	30	-	-	-	192	None	366	1029
K-3	K	63	891	76	346	33	96	113	GA	328	591
L-3	L	47	841	57	658	38	71	67	GA	-	-
M-3	M	69	851	90	455	202	47	201	GA	401	757

(continued)

Manufacturing No.	Steel No.	Cold Rolling Step	Annealing Step	Post-Annealing Cooling Step					Plating	Tempering Step	
		Rolling Reduction	Annealing Temperature	Average Cooling Rate After Annealing*1	Cooling Stop Temperature	Holding Time	Average Cooling Rate After Holding	Cooling Stop Temperature		Tempering Temperature	Tempering Time
		%	°C	°C/Sec	°C	Sec	°C/Sec	°C		°C	Sec
N-3	N	56	844	47	602	31	17	281	GA	-	-
O-3	O	54	885	52	621	146	94	34	GI	245	82

*1 An average cooling rate up to the holding temperature range, in a case where intermediate holding is performed, and an average cooling rate up to the temperature range of 25°C to 300°C, in a case where intermediate holding is not performed

[Table 4]

No.	Ferrite (%)	Sum of Martensite and Tempered Martensite (%)	Remainder in Microstructure (%)	E_{GB}	Tensile Strength (MPa)	Total Elongation (%)	Crack Length (mm)	Hydrogen Embrittlement Resistance	Remarks
A-1	1.4	96.9	1.7	0.93	1540	7.6	0.00	Ex	Invention Example
B-1	0.0	95.1	4.9	0.76	1622	8.4	0.12	Ex	Invention Example
C-1	0.0	100.0	0.0	0.69	1923	6.9	0.92	OK	Invention Example
D-1	1.0	97.7	1.3	1.23	1999	7.8	0.59	Ex	Invention Example
E-1	0.0	92.2	7.8	1.33	1572	7.3	0.67	Ex	Invention Example
F-1	0.0	95.0	5.0	0.96	1764	8.7	0.35	Ex	Invention Example
G-1	0.0	96.5	3.5	0.76	1965	8.7	0.11	Ex	Invention Example
H-1	0.0	91.1	8.9	0.89	1977	9.4	0.59	Ex	Invention Example
I-1	0.0	96.7	3.3	1.08	1543	8.5	0.91	OK	Invention Example
J-1	0.0	93.4	6.6	1.44	1922	7.6	0.35	Ex	Invention Example
K-1	0.0	95.7	4.3	1.34	1505	7.2	0.51	Ex	Invention Example
L-1	0.0	97.9	2.1	0.78	1566	6.2	0.00	Ex	Invention Example
M-1	0.0	94.6	5.4	0.86	1520	6.5	0.80	OK	Invention Example
N-1	1.5	91.3	7.2	0.56	1576	7.5	0.00	Ex	Invention Example
O-1	2.9	95.6	1.5	0.76	1749	8.9	0.95	OK	Invention Example
A-2	1.0	97.5	1.5	0.34	1535	8.5	1.59	NG	Comparative Example
B-2	1.0	99.0	0.0	0.41	1619	6.2	1.53	NG	Comparative Example
C-2	0.0	100.0	0.0	0.23	1576	7.5	1.25	NG	Comparative Example
D-2	0.0	100.0	0.0	0.41	1801	6.7	1.52	NG	Comparative Example
E-2	0.0	100.0	0.0	0.22	1531	6.9	1.32	NG	Comparative Example

(continued)

No.	Ferrite (%)	Sum of Martensite and Tempered Martensite (%)	Remainder in Microstructure (%)	E_{GB}	Tensile Strength (MPa)	Total Elongation (%)	Crack Length (mm)	Hydrogen Embrittlement Resistance	Remarks
F-2	1.9	98.1	0.0	0.34	1741	8.7	1.11	NG	Comparative Example
G-2	-	-	-	-	-	-	-	-	Comparative Example
H-2	3.0	95.5	1.5	0.41	1645	8.2	1.09	NG	Comparative Example
I-2	2.3	96.6	1.1	0.69	1533	6.3	0.32	Ex	Invention Example
J-2	0.0	100.0	0.0	0.68	1712	7.4	0.93	OK	Invention Example
K-2	0.0	100.0	0.0	0.11	1502	7.6	1.64	NG	Comparative Example
L-2	4.0	96.0	0.0	0.45	1544	7.5	1.23	NG	Comparative Example
M-2	0.0	96.6	3.4	0.32	1629	8.4	1.15	NG	Comparative Example
N-2	2.0	98.0	0.0	0.89	1965	8.4	0.00	Ex	Invention Example
O-2	0.0	98.6	1.4	0.81	2001	8.6	0.24	Ex	Invention Example
A-3	16.0	76.0	8.0	0.87	1345	8.1	1.25	NG	Comparative Example
B-3	1.5	97.4	1.1	0.44	1769	8.4	1.24	NG	Comparative Example
C-3	14.5	77.4	8.1	0.51	1323	8.6	1.34	NG	Comparative Example
F-3	1.4	82.1	16.5	0.53	1463	8.6	1.47	NG	Comparative Example
G-3	0.0	100.0	0.0	0.91	1945	7.1	0.55	Ex	Invention Example
H-3	2.0	98.0	0.0	0.79	1245	9.8	0.35	Ex	Comparative Example
I-3	2.3	95.6	2.1	1.43	1511	7.4	0.92	OK	Invention Example
J-3	0.0	97.7	2.3	0.81	1459	9.7	0.85	OK	Comparative Example
K-3	5.9	84.2	9.9	0.76	1134	13.5	1.25	NG	Comparative Example
L-3	3.2	85.4	11.4	0.89	1395	11.5	1.23	NG	Comparative Example

(continued)

No.	Ferrite (%)	Sum of Martensite and Tempered Martensite (%)	Remainder in Microstructure (%)	E_{GB}	Tensile Strength (MPa)	Total Elongation (%)	Crack Length (mm)	Hydrogen Embrittlement Resistance	Remarks
M-3	9.4	65.3	25.3	0.59	1232	12.7	1.11	NG	Comparative Example
N-3	2.5	78.5	19.0	0.66	1367	14.2	1.08	NG	Comparative Example
O-3	1.0	99.0	0.0	0.68	1769	8.8	0.67	Ex	Invention Example

[0221] Referring to Table 4, in Manufacturing No. A-2, the time from the completion of finish rolling to the start of cooling was long. Therefore, ferritic transformation was suppressed in the course of cooling after the finish rolling, the pearlite structure was coarsened, and thus the precipitation of alloy carbides was delayed. As a result, the alloying elements that contribute to the improvement of grain boundary strength were not segregated to the grain boundaries, and E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance decreased.

[0222] In Manufacturing No. B-2, since the rolling start temperature was low in the hot rolling, unrecrystallized austenite remained, the precipitation of alloy carbides was delayed, and E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance decreased.

[0223] In Manufacturing No. C-2, since the rolling start temperature was high in the hot rolling, crystal grains of recrystallized austenite coarsened, the precipitation of alloy carbides was delayed, and E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance decreased.

[0224] In Manufacturing No. D-2, since the rolling finishing temperature was low, unrecrystallized austenite remained, the precipitation of alloy carbides was delayed, and E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance decreased.

[0225] In Manufacturing No. E-2, since the rolling finishing temperature was high, crystal grains of recrystallized austenite coarsened, the precipitation of alloy carbides was delayed, and E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance decreased.

[0226] In Manufacturing No. F-2, since the coiling temperature was low, the diffusion of the alloying elements was delayed, the precipitation of alloy carbides was suppressed, and E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance decreased.

[0227] In Manufacturing No. G-2, since the coiling temperature was high, an internal oxide layer was formed on the surface layer of the hot-rolled steel sheet, and the surface of the steel sheet was cracked in the subsequent treatment. Therefore, structure analysis and evaluation of mechanical properties were not performed.

[0228] In Manufacturing No. H-2, since the average cooling rate up to the coiling temperature was low, ferritic and pearlitic transformation occurred, the precipitation of alloy carbides was suppressed, and E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance decreased.

[0229] In Manufacturing No. K-2, since the interpass time between passes with a rolling reduction of 20% or higher in the finish rolling was long, the precipitation of alloy carbides was delayed in the hot rolling step. As a result, E_{GB} was less than 0.50 and the hydrogen embrittlement resistance decreased.

[0230] In Manufacturing No. L-2, the holding temperature after the hot rolling step was low, the retention time at 400°C to 550°C was shorter than 600 seconds, and thus the precipitation of alloy carbides was not sufficient. Therefore, E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance deteriorated.

[0231] In Manufacturing No. M-2, the holding temperature after the hot rolling step was high and the retention time at 400°C to 550°C was shorter than 600 seconds. Therefore, the precipitation of alloy carbides was not sufficient, and thus E_{GB} was less than 0.50. As a result, the hydrogen embrittlement resistance decreased.

[0232] In Manufacturing No. A-3, since the annealing temperature was low, ferritic transformation proceeded during holding and the tensile strength was less than 1,500 MPa.

[0233] In Manufacturing No. B-3, since the annealing temperature was high, the concentration of the alloying element segregated to the grain boundaries decreased. As a result, E_{GB} was less than 0.50 and the hydrogen embrittlement resistance decreased.

[0234] In Manufacturing No. C-3, since the average cooling rate from the annealing temperature was low, ferritic transformation occurred in the course of cooling and the tensile strength did not reach 1,500 MPa.

[0235] In Manufacturing No. F-3, since the cooling stop temperature was high, bainitic transformation occurred and the tensile strength did not reach 1,500 MPa.

[0236] In Manufacturing No. H-3, since the tempering temperature was high, martensite was softened and the tensile strength did not reach 1,500 MPa.

[0237] In Manufacturing No. J-3, since the tempering time was long, martensite was excessively softened and the tensile strength did not reach 1,500 MPa.

[0238] In Manufacturing No. K-3, since the cooling stop temperature and the intermediate holding temperature in the post-annealing cooling step were low (out of the second temperature range), bainitic transformation occurred and the tensile strength did not reach 1,500 MPa.

[0239] In Manufacturing No. L-3, since the cooling stop temperature and the intermediate holding temperature in the post-annealing cooling step were high (out of the second temperature range), ferritic transformation and pearlitic transformation occurred, and the tensile strength did not reach 1,500 MPa.

[0240] In Manufacturing No. M-3, since the holding time at the second cooling stop temperature was long, bainitic transformation occurred during holding and the tensile strength did not reach 1,500 MPa.

[0241] In Manufacturing No. N-3, since the cooling rate from the second cooling stop temperature was slow, ferritic transformation and bainitic transformation occurred in the course of cooling, and the tensile strength did not reach 1,500 MPa.

[0242] In contrast, in all of the examples according to the present invention, by appropriately controlling the hot rolling, coiling, annealing, and the like, it was possible to obtain steel sheets having a high strength and excellent hydrogen embrittlement resistance.

[0243] FIG. 1 is a diagram showing the relationship of hydrogen embrittlement resistance with E_{GB} and the tensile strength of the steel sheets in Examples 1 and 2. In FIG. 1, the symbol ▲ indicates an example in which the target hydrogen embrittlement resistance was not achieved, and the symbol ○ indicates an example in which the target hydrogen embrittlement resistance was achieved. As shown in FIG. 1, in a case where E_{GB} is 0.50 or more, it is possible to obtain excellent hydrogen embrittlement resistance even for a high strength material of 1,500 MPa or more.

[Industrial Applicability]

[0244] According to the present invention, it is possible to provide a high strength steel sheet having 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: 0.80% to 2.00%;
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,

when an interface where an orientation difference between adjacent martensite and tempered martensite is 15 degrees or more is defined as a prior austenite grain boundary, grain boundary binding energy E_{GB} determined by a concentration of each alloying element on the prior austenite grain boundary satisfies Expression (1), and a tensile strength is 1,500 MPa or more,

$$\begin{aligned}E_{GB} = 1 + (3 \times [Co] + 0.7 \times [Ni] + 5.5 \times [Mo] + 0.7 \times [Cr] + 2.9 \times [Ti] + 47 \times [B] +\\ 4.3 \times [Nb] + 4.5 \times [V] + 5.2 \times [W] + 3.1 \times [Ta] + 4.3 \times [Zr] - 0.25 \times [Mn] - 0.1 \times [P]\\ - [Cu] - 1.1 \times [Sn] - 0.6 \times [Sb] - 0.9 \times [As]) \geq 0.50\end{aligned} \quad (1),$$

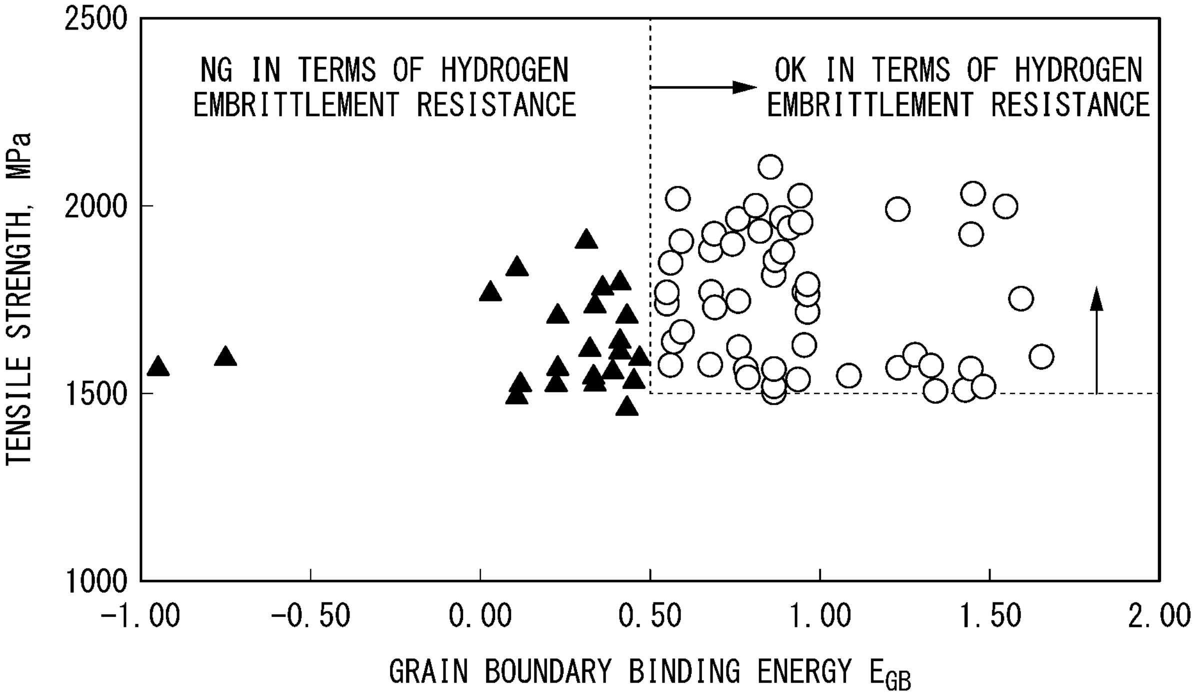
here, [chemical symbol] in the expression represents the concentration of each alloying element by mass% on the prior austenite grain boundary.

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%,
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: 0.001% 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%.

3. The steel sheet according to claim 1 or 2,
wherein a coating layer containing zinc, aluminum, magnesium, or an alloy of these metals is provided on a surface.

FIG. 1


NG IN TERMS OF HYDROGEN EMBRITTLEMENT RESISTANCE
OK IN TERMS OF HYDROGEN EMBRITTLEMENT RESISTANCE
TENSILE STRENGTH, MPa
2500
2000
1500
1000
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00
GRAIN BOUNDARY BINDING ENERGY E_{GB}

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/039380

A. CLASSIFICATION OF SUBJECT MATTER

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00-38/60; C21D9/46; C21D8/02

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2020/203158 A1 (NIPPON STEEL CORPORATION) 08 October 2020 (2020-10-08)	1-3
A	WO 2020/129402 A1 (JFE STEEL CORPORATION) 25 June 2020 (2020-06-25)	1-3
A	WO 2021/045168 A1 (NIPPON STEEL CORPORATION) 11 March 2021 (2021-03-11)	1-3

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

* Special categories of cited documents:
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **15 December 2022**	Date of mailing of the international search report **27 December 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/039380

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