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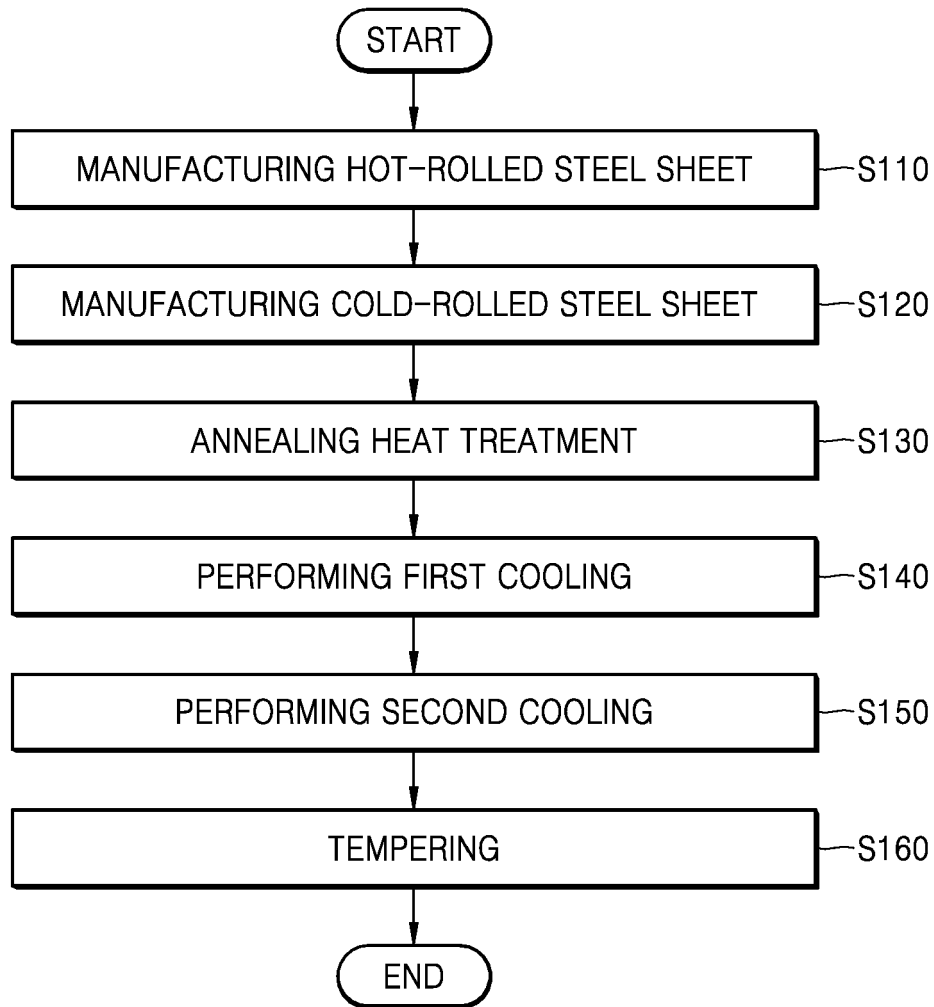
(54) **ULTRAHIGH-STRENGTH COLD ROLLED STEEL SHEET HAVING EXCELLENT HYDROGEN EMBRITTLEMENT RESISTANCE, AND MANUFACTURING METHOD THEREFOR**

(57) The present invention provides an ultra-high-strength cold-rolled steel sheet having a tensile strength of 1100 MPa or more and excellent hydrogen embrittlement resistance, and a method of manufacturing the same. According to an embodiment of the present invention, the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance comprises, in weight percent, carbon (C): 0.1% to 0.5%, silicon (Si): 0.01% to 2.0%, manganese (Mn): 0.1% to 5.0%, aluminum (Al): 0.01% to 2.0%, chromium (Cr): greater than 0% and 3.0% or less, molybde-

num (Mo): greater than 0% and 1.0% or less, nickel (Ni): greater than 0% and 0.4% or less, copper (Cu): 0.05% to 0.4%, titanium (Ti): 0.01% to 0.2%, niobium (Nb): 0.01% to 0.1%, vanadium (V): 0.01% to 1.0%, boron (B): 0.001% to 0.005%, phosphorus (P): greater than 0% and 0.02% or less, sulfur (S): greater than 0% and 0.01% or less, and the balance being iron (Fe) and unavoidable impurities, and satisfies a tensile strength (TS) of 1100 MPa or more, an elongation (EL) of 3% or more, and a non-fracture time based on the hydrogen embrittlement test method of 100 hours or more.

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FIG. 3



Description

TECHNICAL FIELD

5 **[0001]** The technical concept of the present invention relates to a steel material, and more particularly, to an ultra-high-strength cold-rolled steel sheet having excellent corrosion resistance or resistance to hydrogen embrittlement, and a method of manufacturing the same.

BACKGROUND ART

10 **[0002]** In the automotive industry, demand for crash safety of vehicle bodies has continuously increased. As the proliferation of electric vehicles has recently expanded, the number of automotive components has decreased; however, the weight of vehicles due to the introduction of batteries has increased, further expanding the demands for crash safety. Accordingly, the ultra-high strengthening of crash members such as front bumper beams, side sills, and
 15 door impact beams that contribute to crash safety is also continuously progressing. In particular, martensitic steel, which has the highest strength among cold-rolled steel sheets, has seen expanded application with the increasing use of roll-forming techniques; however, delayed fracture issues arising from its high strength exist. In particular, corrosion in hydrogen-penetrating environments is known as a fracture behavior representative of such delayed fracture. Therefore, extensive research has been conducted to enhance corrosion resistance or resistance to hydrogen embrittlement
 20 for ultra-high-strength sheet materials with a tensile strength of 1 GPa or more.

[0003] As a prior art document, there is Korean Patent Application No. 2012-0144482.

DETAILED DESCRIPTION OF THE INVENTION

25 TECHNICAL PROBLEM

[0004] The technical problem to be achieved by the technical concept of the present invention is to provide an ultra-high-strength cold-rolled steel sheet having a strength of at least 1100 MPa based on tensile strength and excellent hydrogen embrittlement resistance, and a method of manufacturing the same, by limiting the contents of elements
 30 such as copper (Cu), manganese (Mn), chromium (Cr), silicon (Si), and nickel (Ni) that affect delayed fracture caused by hydrogen embrittlement.

[0005] However, such a problem is illustrative, and the technical concept of the present invention is not limited thereto.

35 TECHNICAL SOLUTION

[0006] According to one aspect of the present invention, there is provided an ultra-high-strength cold-rolled steel sheet having a strength of at least 1100 MPa based on tensile strength and excellent hydrogen embrittlement resistance, and a method of manufacturing the same.

40 **[0007]** According to one embodiment of the present invention, the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance comprises, in weight percent, carbon (C): 0.1% to 0.5%, silicon (Si): 0.01% to 2.0%, manganese (Mn): 0.1% to 5.0%, aluminum (Al): 0.01% to 2.0%, chromium (Cr): greater than 0% and 3.0% or less, molybdenum (Mo): greater than 0% and 1.0% or less, nickel (Ni): greater than 0% and 0.4% or less, copper (Cu): 0.05% to 0.4%, titanium (Ti): 0.01% to 0.2%, niobium (Nb): 0.01% to 0.1%, vanadium (V): 0.01% to 1.0%,
 45 boron (B): 0.001% to 0.005%, phosphorus (P): greater than 0% and 0.02% or less, sulfur (S): greater than 0% and 0.01% or less, and the balance being iron (Fe) and unavoidable impurities, and satisfies a tensile strength (TS) of 1100 MPa or more, an elongation (EL) of 3% or more, and a non-fracture time of 100 hours or more based on the hydrogen embrittlement test method.

50 **[0008]** In addition, in the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance, the sum of the weight percentages of silicon and nickel, $[Si] + [Ni]$, and the sum of the weight percentages of manganese and chromium, $[Mn] + [Cr]$, may satisfy the following relational expression: $[Si] + [Ni] \leq 0.85 - 0.23 \times ([Mn] + [Cr])$.

[0009] In addition, the microstructure of the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance comprises ferrite, tempered bainite, and tempered martensite phases, wherein the area
 55 fraction of the ferrite ranges from 0% to 20%, the area fraction of the tempered bainite ranges from 5% to 20%, and the area fraction of the tempered martensite ranges from 60% to 100%, provided that the sum of the tempered bainite and the tempered martensite may satisfy a range of 80% to 100%.

[0010] In addition, the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance

further comprises a carbide, wherein the carbide may have an average size of 100 nm or less and an aspect ratio of 5 or less.

[0011] In addition, the carbide may comprise at least one selected from the group consisting of Fe-based carbide, Ti-based carbide, Nb-based carbide, V-based carbide, and Mo-based carbide.

[0012] According to one embodiment of the present invention, the method of manufacturing the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance comprises: hot rolling a steel material comprising, in weight percent, carbon (C): 0.1% to 0.5%, silicon (Si): 0.01% to 2.0%, manganese (Mn): 0.1% to 5.0%, aluminum (Al): 0.01% to 2.0%, chromium (Cr): greater than 0% and 3.0% or less, molybdenum (Mo): greater than 0% and 1.0% or less, nickel (Ni): greater than 0% and 0.4% or less, copper (Cu): 0.05% to 0.4%, titanium (Ti): 0.01% to 0.2%, niobium (Nb): 0.01% to 0.1%, vanadium (V): 0.01% to 1.0%, boron (B): 0.001% to 0.005%, phosphorus (P): greater than 0% and 0.02% or less, sulfur (S): greater than 0% and 0.01% or less, and the balance being iron (Fe) and unavoidable impurities, to produce a hot-rolled steel sheet; cold rolling the hot-rolled steel sheet to produce a cold-rolled steel sheet; performing an annealing heat treatment by maintaining the cold-rolled steel sheet at a temperature ranging from 800°C to 950°C for 10 seconds to 600 seconds; performing first cooling of the annealing heat-treated cold-rolled steel sheet to 500°C to 700°C at a cooling rate of 0°C/sec to 50°C/sec; performing second cooling of the first-cooled cold-rolled steel sheet to 0°C to 350°C at a cooling rate of 5°C/sec or more; and a tempering step of heat-treating the second-cooled cold-rolled steel sheet at a temperature ranging from 100°C to 350°C for 10 seconds or more.

[0013] In addition, the step of producing the hot-rolled steel sheet may comprise: reheating the steel material having the alloy composition at a reheating temperature ranging from 1,150°C to 1,300°C; hot rolling the reheated steel material so as to finish at a finish rolling end temperature ranging from 800°C to 1,000°C to produce a hot-rolled steel sheet; and cooling the hot-rolled steel sheet at a cooling rate of 1 to 100°C/sec and then coiling at a coiling temperature ranging from 300°C to 700°C.

[0014] In addition, the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance manufactured by the method of manufacturing the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance satisfies a tensile strength (TS) of 1100 MPa or more, an elongation (EL) of 3% or more, and a non-fracture time of 100 hours or more based on the hydrogen embrittlement test method, and the microstructure of the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance comprises ferrite, tempered bainite, and tempered martensite phases, wherein the area fraction of the ferrite ranges from 0% to 20%, the area fraction of the tempered bainite ranges from 5% to 20%, and the area fraction of the tempered martensite ranges from 60% to 100%, provided that the sum of the tempered bainite and the tempered martensite may satisfy a range of 80% to 100%.

ADVANTAGEOUS EFFECTS

[0015] According to the technical concept of the present invention, the hydrogen embrittlement resistance of the cold-rolled steel sheet can be improved by limiting the contents of components that affect the carbon activity under a certain relational expression.

[0016] The effects of the present invention described above are set forth by way of example, and the scope of the present invention is not limited by such effects.

DESCRIPTION OF THE DRAWINGS

[0017]

Fig. 1 is a graph showing the carbon activity of components constituting an ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to an embodiment of the present invention.

Fig. 2 is a graph showing evaluation results after performing a hydrogen embrittlement test method on components constituting an ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to an embodiment of the present invention.

Fig. 3 is a process flowchart schematically illustrating a method of manufacturing an ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to an embodiment of the present invention.

MODE OF THE INVENTION

[0018] Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the accompanying drawings. The embodiments of the present invention are provided to more completely explain the

technical concept of the present invention to those skilled in the art, and the following embodiments may be modified in various other forms, and the scope of the technical concept of the present invention is not limited to the following embodiments. Rather, these embodiments are provided to make the present disclosure more faithful and complete, and to fully convey the technical concept of the present invention to those skilled in the art. In the present specification, the same reference numerals denote the same elements throughout. Furthermore, various elements and regions in the drawings are schematically illustrated. Accordingly, the technical concept of the present invention is not limited by the relative sizes or spacings depicted in the accompanying drawings.

[0019] The following approaches have been proposed to improve the corrosion resistance or hydrogen embrittlement resistance of cold-rolled steel sheets. As a method of increasing hydrogen embrittlement resistance by controlling the residual hydrogen content in steel in relation to delayed fracture caused by hydrogen, a method has been proposed in which the hydrogen content is controlled to 0.1 ppm or less during a heat treatment maintained at 350°C to 450°C in the heat treatment process after cold rolling, thereby increasing hydrogen embrittlement resistance. In addition, a method has been proposed in which the area fractions of ferrite, upper bainite, and martensite are controlled, boron, which is a grain boundary strengthening element, is added, the effective martensite grain size is controlled, and the number of Fe-based carbides is also controlled. Furthermore, a method has been proposed in which the grain size and aspect ratio of ferrite and martensite are controlled based on the cold rolling reduction ratio, thereby enhancing the hydrogen embrittlement resistance of steel sheets of 1100 MPa grade or higher. Such hydrogen embrittlement has become an important research subject not only in cold-rolled steel sheets for automotive applications but also in steel materials for pressure vessels. A method has been proposed in which, based on the increase in hydrogen embrittlement resistance resulting from the addition of copper, a microstructure is formed that reduces the fraction of banded structure in the microstructure, thereby retarding the propagation rate of cracks caused by hydrogen embrittlement. In addition, a method has been proposed in which nickel is added in an amount of 1 wt% to 4 wt% to increase hydrogen embrittlement resistance. A composition control method has been proposed in which the content ratio of nickel and copper is limited to $\text{Cu/Ni} \leq 0.6$ for heavy-gauge steel materials in the shipbuilding, offshore, construction, and civil engineering fields. A method has been proposed in which the ratio of manganese, nickel, and copper is limited to improve the stability of austenite during the manufacture of high-strength steel sheets. In this case, nickel and copper were added for the purpose of securing hardenability in steel sheets with high aluminum addition, rather than for preventing delayed fracture caused by hydrogen.

[0020] The technical concept of the present invention is to provide an ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance and a method of manufacturing the same, by controlling the alloy composition and microstructure configuration for application to ultra-high-strength automotive steel sheets having a tensile strength of at least 1100 MPa.

[0021] Hereinafter, the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to the technical concept of the present invention will be described in detail.

[0022] The ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to one embodiment of the present invention comprises, in weight percent, carbon (C): 0.1% to 0.5%, silicon (Si): 0.01% to 2.0%, manganese (Mn): 0.1% to 5.0%, aluminum (Al): 0.01% to 2.0%, chromium (Cr): greater than 0% and 3.0% or less, molybdenum (Mo): greater than 0% and 1.0% or less, nickel (Ni): greater than 0% and 0.4% or less, copper (Cu): 0.05% to 0.4%, titanium (Ti): 0.01% to 0.2%, niobium (Nb): 0.01% to 0.1%, vanadium (V): 0.01% to 1.0%, boron (B): 0.001% to 0.005%, phosphorus (P): greater than 0% and 0.02% or less, sulfur (S): greater than 0% and 0.01% or less, and the balance being iron (Fe) and unavoidable impurities.

[0023] Hereinafter, the role of each element included in the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to the present invention and the content thereof will be described as follows. In this regard, the content of each constituent element refers to weight percent based on the total weight of the steel sheet.

Carbon (C): 0.1% to 0.5%

[0024] Carbon is added to secure the strength of the steel sheet and to control the microstructure, and strength can be secured through improvement of martensite hardness. When the carbon content is less than 0.1%, it is difficult to obtain the target strength. When the carbon content exceeds 0.5%, weldability and workability may deteriorate. Therefore, it is preferable to add carbon in an amount of 0.1% to 0.5% based on the total weight of the steel sheet.

Silicon (Si): 0.01% to 2.0%

[0025] Silicon is a ferrite-stabilizing element and can suppress the growth of cementite, thereby securing hydrogen embrittlement resistance. When the silicon content is less than 0.01%, the effect of silicon addition is insufficient. When the silicon content exceeds 2.0%, ferrite may be formed in large amounts, and the target strength may not be

secured. Therefore, it is preferable to add silicon in an amount of 0.01% to 2.0% based on the total weight of the steel sheet.

Manganese (Mn): 0.1% to 5.0%

[0026] Manganese has a solid solution strengthening effect and can contribute to strength improvement by increasing hardenability. When the manganese content is less than 0.1%, hardenability is insufficient, making it difficult to secure strength, and the effect of manganese addition is insufficient. When the manganese content exceeds 5.0%, the formation of manganese bands and manganese sulfide (MnS) may deteriorate hydrogen embrittlement resistance. Therefore, it is preferable to add manganese in an amount of 0.1% to 5.0% based on the total weight of the steel sheet.

Aluminum (Al): 0.01% to 2.0%

[0027] Aluminum is used as a deoxidizer and can help purify ferrite. When the aluminum content is less than 0.01%, the effect of aluminum addition is insufficient, including an inadequate deoxidation effect. When the aluminum content exceeds 2.0%, aluminum nitride (AlN) may be formed during slab manufacturing, which can cause cracks during casting or hot rolling, and a large amount of ferrite may be formed, resulting in a decrease in strength. Therefore, it is preferable to add aluminum in an amount of 0.01% to 2.0% based on the total weight of the steel sheet.

Chromium (Cr): greater than 0% and 3.0% or less

[0028] Chromium is a ferrite-stabilizing element in steel and is a component that improves hardenability and can contribute to strength improvement by refining carbides. In addition, strength can be increased by solid solution strengthening. When the chromium content exceeds 3.0%, manufacturing costs become relatively high, and the quenching effect during cooling is large, leading to an increase in strength and a consequent relative decrease in elongation, and laser weldability may deteriorate. Therefore, it is preferable to add chromium in an amount of greater than 0% and 3.0% or less based on the total weight of the steel sheet.

Molybdenum (Mo): greater than 0% and 1.0% or less

[0029] Molybdenum has a solid solution strengthening effect and can contribute to strength improvement by increasing hardenability. In addition, hydrogen embrittlement resistance can be improved by refining Ti-based precipitates. When the molybdenum content exceeds 1.0%, the material cost may increase. Therefore, it is preferable to add molybdenum in an amount of greater than 0% and 1.0% or less based on the total weight of the steel sheet.

Nickel (Ni): greater than 0% and 0.4% or less

[0030] Nickel is a precipitate-forming element that combines with carbon (C) and nitrogen (N) to form carbides or nitrides and can improve the toughness and strength of steel through grain refinement resulting from such precipitation and the suppression of recrystallization and grain growth during rolling. In addition, it can suppress hot shortness caused by copper. When the nickel content is less than 0.02%, the effect of nickel addition is insufficient. When the nickel content exceeds 3.0%, the rolling load during rolling may increase significantly, and the manufacturing cost of the steel may increase. In particular, it is necessary to control the ratio with copper in order to prevent melting during the reheating process. Therefore, it is preferable to add nickel in an amount of greater than 0% and 0.4% or less based on the total weight of the steel sheet.

Copper (Cu): 0.05% to 0.4%

[0031] Copper is a precipitate-forming element that combines with carbon (C) and nitrogen (N) to form carbides or nitrides and can improve the toughness and strength of steel through grain refinement resulting from such precipitation and the suppression of recrystallization and grain growth during rolling. In addition, it can be added to increase hydrogen embrittlement resistance. When the copper content is less than 0.05%, the effect of copper addition is insufficient, and delayed fracture may occur. When the copper content exceeds 0.4%, as an element that induces hot shortness, cracks may occur during hot rolling, the rolling load during rolling may increase significantly, and the manufacturing cost of the steel may increase. Therefore, it is preferable to add copper in an amount of 0.05% to 0.4% based on the total weight of the steel sheet.

Titanium (Ti): 0.01% to 0.2%

[0032] Titanium is a precipitate-forming element that can provide the effects of precipitation of titanium nitride (TiN) and titanium carbide (TiC) and grain refinement. In particular, the nitrogen content within the steel can be reduced through the precipitation of TiN, and when added together with boron, the precipitation of boron nitride (BN) can be prevented, thereby maintaining boron, which is a grain boundary strengthening element, in a solid solution state. When the titanium content is less than 0.01%, BN precipitation may be induced, and the effect of titanium addition is insufficient. When the titanium content exceeds 0.2%, hydrogen embrittlement resistance may deteriorate due to coarsening of TiN precipitates, it may be difficult to secure strength due to a reduction in the solid solubility of carbon in the base material, and the manufacturing cost of the steel may increase. Therefore, it is preferable to add titanium in an amount of 0.01% to 0.2% based on the total weight of the steel sheet.

Niobium (Nb): 0.01% to 0.1%

[0033] Niobium is a precipitate-forming element that combines with carbon (C) and nitrogen (N) to form carbides or nitrides and can improve the toughness and strength of steel through grain refinement resulting from such precipitation and the suppression of recrystallization and grain growth during rolling. When the niobium content is less than 0.01%, there is no grain refinement effect, and the effect of niobium addition is insufficient. When the niobium content exceeds 0.1%, precipitates may grow and the strength-increasing effect may be absent, the rolling load during rolling may increase significantly, and the manufacturing cost of the steel may increase. Therefore, it is preferable to add niobium in an amount of 0.01% to 0.1% based on the total weight of the steel sheet.

Vanadium (V): 0.01% to 1.0%

[0034] Vanadium is a precipitate-forming element that combines with carbon (C) and nitrogen (N) to form carbides or nitrides and can improve the toughness and strength of steel through grain refinement resulting from such precipitation and the suppression of recrystallization and grain growth during rolling. When the vanadium content is less than 0.01%, there is no grain refinement effect, and the effect of vanadium addition is insufficient. When the vanadium content exceeds 1.0%, precipitates may grow and the strength-increasing effect may be absent, the rolling load during rolling may increase significantly, and the manufacturing cost of the steel may increase. Therefore, it is preferable to add vanadium in an amount of 0.01% to 1.0% based on the total weight of the steel sheet.

Boron (B): 0.001% to 0.005%

[0035] Boron is a grain boundary strengthening element and, when distributed at grain boundaries, can increase hydrogen embrittlement resistance. When the boron content is less than 0.001%, the effect of boron addition is insufficient. When the boron content exceeds 0.005%, there is a risk of grain boundary embrittlement due to the formation of boron nitride (BN). Therefore, it is preferable to add boron in an amount of 0.001% to 0.005% based on the total weight of the steel sheet.

Phosphorus (P): greater than 0% and 0.02% or less

[0036] Phosphorus is an impurity included during the steel manufacturing process, and while it can help improve strength through solid solution strengthening, when contained in large amounts, low-temperature embrittlement may occur due to grain boundary segregation, and spot weldability may deteriorate. Therefore, it is preferable to limit the phosphorus content to greater than 0% and 0.02% or less based on the total weight of the steel sheet.

Sulfur (S): greater than 0% and 0.01% or less

[0037] Sulfur is an impurity included during the steel manufacturing process, and can form non-metallic inclusions such as FeS and manganese sulfide (MnS), thereby deteriorating toughness, hydrogen embrittlement resistance, and weldability. Therefore, it is preferable to limit the sulfur content to greater than 0% and 0.01% or less based on the total weight of the steel sheet.

[0038] The remainder of the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance is iron (Fe). However, since unintended impurities from raw materials or the surrounding environment may inevitably be incorporated during a normal steelmaking process, these cannot be excluded. Since these impurities are known to anyone skilled in the art of normal manufacturing processes, all such details are not specifically mentioned in the present specification.

[0039] After martensite formation begins, carbon undergoes segregation to dislocations or interfaces, clustering and transition carbide formation, and cementite precipitation throughout all tempering processes. Therefore, carbon activity is a very important factor in the tempering process, and the factors affecting it include temperature and composition, and in particular, there are changes in the hydrogen embrittlement resistance of the final product, the cold-rolled steel sheet, depending on the content of the composition.

[0040] Fig. 1 is a graph showing the carbon activity of the constituent elements of the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to an embodiment of the present invention.

[0041] Referring to Fig. 1, among the elements that affect carbon activity, with respect to representative elements that remain in a solid solution state without precipitating, namely Cr, Mn, Ni, and Si, it can be confirmed that Cr and Mn decrease carbon activity, while Ni and Si are elements that increase carbon activity.

[0042] Fig. 2 is a graph showing the evaluation results after performing the hydrogen embrittlement test method on the constituent elements of the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to an embodiment of the present invention.

[0043] Hydrogen embrittlement was evaluated by the hydrogen embrittlement test method described below for conditions with a tensile strength of at least 1.1 GPa for test specimens at the end of the final heat treatment.

[0044] Referring to Fig. 2, under the assumption that the Cu content range is limited to 0.05 wt% or more and 0.40 wt% or less as described above, each axis was set according to the influence of elements on carbon activity; the X-axis represents the sum in weight percent of Mn and Cr, which decrease carbon activity, and the Y-axis represents the sum in weight percent of Si and Ni, which increase carbon activity. As a result of the hydrogen embrittlement test method evaluation, it can be seen that a certain condition is satisfied between the sum of the weight percentages of Mn and Cr and the sum of the weight percentages of Si and Ni in terms of delayed fracture performance due to hydrogen embrittlement. According to an embodiment of the present invention, it can be confirmed that the delayed fracture performance due to hydrogen embrittlement can be defined by the following relational expression: $[Si] + [Ni] \leq 0.85 - 0.23 \times ([Mn] + [Cr])$. That is, the hydrogen embrittlement effect can be confirmed for (Mn+Cr) and (Si+Ni), which have similar effects on carbon activity.

[0045] The ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance, manufactured by controlling the specific components of the alloy composition described above and their content ranges and through the manufacturing method described below, can satisfy, for example, tensile strength (TS): at least 1100 MPa, elongation (EL): at least 3%, and non-fracture time based on the hydrogen embrittlement test method: at least 100 hours.

[0046] The microstructure of the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance may comprise ferrite, tempered bainite, and tempered martensite phases. The area fraction of the ferrite may range from 0% to 20%, the area fraction of the tempered bainite may range from 5% to 20%, and the area fraction of the tempered martensite may range from 60% to 100%, provided that the sum of the tempered bainite and tempered martensite may satisfy a range of 80% to 100%. The area fraction refers to the area ratio derived by analyzing microstructure photographs through an image analyzer. In addition, the area fractions of the microstructure described above are based on the results of analysis at a point one-quarter of the way through the thickness direction of the steel sheet using a scanning electron microscope in a direction perpendicular to the rolling direction.

[0047] Carbides need to be present in order to suppress delayed fracture caused by hydrogen embrittlement. Such carbides can serve to trap and immobilize hydrogen that has diffused into and penetrated the steel sheet, thereby preventing the hydrogen from moving freely within the interior of the steel sheet. However, if the size of the carbides is too large, embrittlement caused by hydrogen accumulated at the interface may occur, and therefore it is preferable that the size of the carbides be limited.

[0048] Accordingly, the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance may further comprise carbides. The carbides may have an average size (particle diameter) of, for example, 100 nm or less, for example, in the range of 1 nm to 100 nm. The carbides may have an aspect ratio of, for example, 5 or less, for example, in the range of 1 to 5. Here, the aspect ratio refers to the ratio of the major axis length to the minor axis length of the carbide. When the average size of the carbides exceeds 100 nm, it can be considered that martensite has been excessively tempered or that retained austenite has been formed due to insufficient stabilization.

[0049] The carbides may include both cementite and transition carbides, or may include carbides in which Fe is not present, and may include, for example, at least one of Fe-based carbide, Ti-based carbide, Nb-based carbide, V-based carbide, and Mo-based carbide. Specifically, the carbides may include, for example, at least one of Fe_3C , ϵ -carbide ($Fe_{2.5}C$), η -carbide (Fe_2C), (Fe, substitutional element) $_{2-3}C$, and (Ti, Nb, V, Mo)(C, N).

Hydrogen Embrittlement Test Method

[0050] In the present invention, the hydrogen embrittlement test method for quantitatively measuring delayed fracture due to hydrogen embrittlement of the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrit-

tlement resistance is as follows.

[0051] The cold-rolled steel sheet is cut using shearing, laser, water jet, milling, wire (EDM), or the like to prepare specimens having a length of 100 mm to 300 mm and a width of 10 mm to 50 mm. At this time, the longitudinal direction of the specimen is fabricated to be at 0 degrees or 90 degrees with respect to the rolling direction of the material.

[0052] Subsequently, stresses of 60%, 70%, 80%, 90%, and 100% of the yield strength are applied to the specimen using a 2-point or 4-point bending method. At this time, the applied stress must be varied according to the yield strength of each cold-rolled steel sheet. Under the stress application conditions, fracture must not occur under three or more conditions, including the 100% stress condition specimen.

[0053] The stress-applied specimen is immersed in a hydrochloric acid (HCl) solution having a concentration of 0.01 N to 0.2 N, preferably a 0.1 N hydrochloric acid solution. Since hydrogen is injected into the interior of the specimen by such immersion, this can be referred to as an accelerated test for delayed fracture caused by hydrogen. The immersed test specimen is maintained for at least 100 hours. At this time, fracture must not occur under even one of the above stress conditions.

[0054] Hereinafter, a method of manufacturing the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to the present invention will be described with reference to the accompanying drawings.

Method of Manufacturing Ultra-High-Strength Cold-Rolled Steel Sheet Having Excellent Hydrogen Embrittlement Resistance

[0055] Fig. 3 is a process flowchart schematically illustrating a method of manufacturing the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to an embodiment of the present invention and relates to a method of manufacturing an uncoated cold-rolled steel sheet.

[0056] Referring to Fig. 3, the method of manufacturing the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance according to an embodiment of the present invention comprises a hot-rolled steel sheet manufacturing step (S110), a cold-rolled steel sheet manufacturing step (S120), an annealing heat treatment step (S130), a first cooling step (S140), a second cooling step (S150), and a tempering step (S160).

Hot-Rolled Steel Sheet Manufacturing Step (S110)

[0057] In the hot-rolled steel sheet manufacturing step (S110), a steel material is prepared comprising, in weight percent, carbon (C): 0.1% to 0.5%, silicon (Si): 0.01% to 2.0%, manganese (Mn): 0.1% to 5.0%, aluminum (Al): 0.01% to 2.0%, chromium (Cr): greater than 0% and 3.0% or less, molybdenum (Mo): greater than 0% and 1.0% or less, nickel (Ni): greater than 0% and 0.4% or less, copper (Cu): 0.05% to 0.4%, titanium (Ti): 0.01% to 0.2%, niobium (Nb): 0.01% to 0.1%, vanadium (V): 0.01% to 1.0%, boron (B): 0.001% to 0.005%, phosphorus (P): greater than 0% and 0.02% or less, sulfur (S): greater than 0% and 0.01% or less, and the balance being iron (Fe) and unavoidable impurities.

[0058] In the manufacturing method according to the present invention, the semi-finished product subject to the hot rolling process may be, for example, a slab. A slab in a semi-finished state can be obtained by obtaining molten steel of a predetermined composition through a steelmaking process and then through a continuous casting process.

[0059] The steel material described above, for example a slab plate, is reheated at a reheating temperature (Slab Reheating Temperature, SRT) of 1,150°C to 1,300°C for 1 hour to 5 hours. Through such reheating, a complete single-phase austenite transformation occurs, and re-dissolution of segregated components during casting and re-dissolution of precipitates may occur, whereby the steel material is homogenized and becomes capable of hot rolling. When the reheating temperature is less than 1,150°C, the components segregated during casting may not be sufficiently re-dissolved and may not be uniformly distributed. When the reheating temperature exceeds 1,300°C, austenite grains may coarsen, which can cause a decrease in yield strength. In addition, as the reheating temperature increases, there are problems of increased manufacturing costs and decreased productivity due to heating costs and additional time required to adjust the hot rolling temperature. When the reheating time is less than 1 hour, the reduction of segregation bands may be insufficient, and when it exceeds 5 hours, the grain size increases and process costs may rise.

[0060] The reason for limiting the reheating temperature range is explained as follows.

[0061] The melting point of copper is 1084.6°C, which is lower than that of iron. When copper is present in the slab, it can migrate to the surface. If the surface temperature of the slab or bar is higher than the melting point of copper, the copper that has migrated to the surface may melt and penetrate along the grain boundaries of the steel material, causing hot shortness, which involves a decrease in ductility and the occurrence of cracks. One method to prevent such hot shortness is to add nickel to form a complete solid solution of copper and nickel, thereby suppressing the melting of copper. Therefore, in order to prevent liquid copper from penetrating into the steel sheet during reheating,

the temperature of the Cu-Ni solid solution needs to be at least 1150°C or higher. In addition, in order to suppress the cost increase due to nickel addition, the upper limit of the melting point of the Cu-Ni solid solution was set to 1300°C or lower. The melting point of the Cu-Ni solid solution can be calculated using the ThermoCalc program.

[0062] Subsequently, the reheated steel material is first subjected to hot rolling after heating for shape adjustment.

The hot rolling may be performed continuously by width rolling, rough rolling, and finish rolling. By the hot rolling step, the steel material can form a hot-rolled steel material. The hot-rolled steel material may be a hot-rolled steel sheet.

[0063] The rough rolling is a step of rolling the slab to produce a bar and may be performed in the range of from the reheating end temperature (1,150°C to 1,300°C) to 1000°C.

[0064] The finish rolling may be completed at a finish rolling end temperature (FRT) of 800°C to 1,000°C. When the finish rolling end temperature is less than 800°C, the rolling load may increase sharply, resulting in decreased productivity. When the finish rolling end temperature exceeds 1,000°C, grains may coarsen, resulting in a decrease in the strength of the final steel material.

[0065] Subsequently, the hot-rolled steel material is cooled to a predetermined coiling temperature. The cooling may be performed by either air cooling or water cooling, and may be cooled at a cooling rate of, for example, 1°C/s to 100°C/s. A faster cooling rate may be advantageous for reducing the average grain size. The cooling is preferably performed to a coiling temperature ranging from, for example, 400°C to 700°C, for example, to 500°C to 650°C.

[0066] Subsequently, the hot-rolled steel sheet is coiled at a coiling temperature (CT) of, for example, 300°C to 700°C, for example, at 500°C to 650°C. When the coiling temperature is less than 300°C, the shape of the coiled hot-rolled coil may become non-uniform, and the strength may increase, resulting in an increased rolling load during cold rolling. When the coiling temperature exceeds 700°C, a non-uniform microstructure may be generated due to the difference in cooling rate between the center and edge portions of the steel sheet, and defects may occur in subsequent processes due to surface oxidation and the like. The coiled steel material may be cooled to room temperature.

Cold-Rolled Steel Sheet Manufacturing Step (S120)

[0067] In the cold-rolled steel sheet manufacturing step (S120), the hot-rolled steel sheet is used to adjust the thickness of the final produced steel sheet. The coiled hot-rolled steel sheet is subjected to a pickling treatment in which it is cleaned with acid. Subsequently, the pickled hot-rolled steel sheet is cold-rolled at a cold reduction ratio of, for example, at least 35%, for example, 35% to 70%, to form a cold-rolled steel sheet. A higher reduction ratio can increase hydrogen embrittlement resistance through the grain refinement effect. When the cold reduction ratio is less than 35%, it is difficult to obtain a uniform microstructure, and since the number of nucleation sites for recrystallization during annealing is small, grains may grow excessively during the annealing heat treatment described below, resulting in a sharp decrease in strength. When the cold reduction ratio exceeds 70%, the number of nucleation sites becomes excessively large, and the grains formed by the annealing heat treatment may be too fine, resulting in decreased ductility and deteriorated formability.

Annealing Heat Treatment Step (S130)

[0068] In the annealing heat treatment step (S130), the cold-rolled steel sheet may be heat-treated in a continuous annealing furnace having a conventional slow cooling section.

[0069] The annealing heat treatment is performed by heating at a heating rate of, for example, at least 1°C/s, for example, 1°C/s to 10°C/s, to a temperature ranging from, for example, Ac3-50°C or higher, for example, 800°C to 950°C, and then maintaining for, for example, 10 seconds to 600 seconds. When the annealing heat treatment temperature is less than 800°C or the holding time is less than 10 seconds, it is difficult to form sufficient austenite, and the ferrite fraction may increase, resulting in a decrease in strength. When the annealing heat treatment temperature exceeds 950°C or the holding time exceeds 600 seconds, the size of austenite grains may coarsen or productivity may decrease excessively.

[0070] The Ac3 temperature can be calculated by the following formula:

$$Ac3 = 910 - 203 \times [C]^{0.5} - 30[Mn] + 44.7[Si] + 31.5[Mo] - 15.2[Ni]$$

where [C] is the carbon content (wt%) in the steel material, [Mn] is the manganese content (wt%) in the steel material, [Si] is the silicon content (wt%) in the steel material, [Mo] is the molybdenum content (wt%) in the steel material, and [Ni] is the nickel content (wt%) in the steel material.

First Cooling Step (S140)

[0071] In the first cooling step (S140), the annealing heat-treated cold-rolled steel sheet is subjected to first cooling at a cooling rate of, for example, 0°C/s to 50°C/s, to, for example, 500°C to 700°C. The cooling may be performed by air cooling or water cooling. The first cooling may be referred to as a slow cooling step.

Second Cooling Step (S150)

[0072] In the second cooling step (S150), the first-cooled cold-rolled steel sheet is subjected to second cooling at a cooling rate of at least 5°C/s, for example, 5°C/s to 30°C/s, to, for example, below the martensite transformation finish temperature (M_f), for example, in the range of room temperature (0°C to 40°C) to 350°C. During the second cooling, additional ferrite transformation must be suppressed.

Tempering Step (S160)

[0073] In the tempering step (S160), the second-cooled cold-rolled steel sheet is heated at a heating rate of at most 100°C/s and heat-treated at, for example, a temperature ranging from 100°C to 350°C for a holding time of, for example, at least 10 seconds.

[0074] By this tempering heat treatment, the formation and growth of transition carbides and the growth of cementite may proceed. The tempering heat treatment may be maintained for a long time at a low temperature, for example, 200°C or lower, but at a high temperature, for example, a temperature exceeding 200°C, the growth of cementite must be suppressed by maintaining for a relatively short time in order to control the decrease in hydrogen embrittlement resistance.

[0075] A cold-rolled steel sheet can be formed by performing the steps described above. The method can also be applied to steel sheets that are electroplated using uncoated steel materials.

Experimental Examples

[0076] Hereinafter, preferred experimental examples are presented to aid in understanding the present invention. However, the following experimental examples are only intended to aid in understanding the present invention, and the present invention is not limited by the following experimental examples. Content not described herein can be sufficiently inferred technically by those skilled in the art, and therefore the description thereof will be omitted.

[0077] Steels having the compositions (unit: wt%) shown in Tables 1 and 2 below were prepared, and cold-rolled steel sheets according to Examples and Comparative Examples were prepared through predetermined hot rolling, cold rolling, and heat treatment processes. In Tables 1 and 2, the balance consists of iron (Fe) and impurities inevitably contained in the steelmaking process and the like. The unit of content of each component is weight percent. At this time, the Examples and Comparative Examples listed in Tables 1 and 2 are all limited to steel grades in which Cu is added in a content of 0.05 to 0.40 wt%.

[Table 1]

Classification	C	Si	Mn	Cr	Mo	Ni	Cu
Example 1	0.244	0.107	1.919	0.415	0.210	0.099	0.093
Example 2	0.239	0.100	1.830	0.408	0.208	0.149	0.139
Example 3	0.249	0.101	1.855	0.396	0.208	0.197	0.193
Example 4	0.259	0.102	1.892	0.499	0.207	0.053	0.120
Example 5	0.259	0.102	1.892	0.499	0.207	0.053	0.120
Example 6	0.243	0.103	1.468	0.602	0.206	0.106	0.102
Example 7	0.243	0.103	1.468	0.602	0.206	0.106	0.102
Example 8	0.260	0.300	1.490	0.012	0.207	0.106	0.133
Example 9	0.249	0.074	0.995	0.000	0.102	0.105	0.095
Example 10	0.249	0.074	0.995	0.000	0.102	0.105	0.095
Example 11	0.249	0.074	0.995	0.000	0.102	0.105	0.095
Example 12	0.230	0.040	1.976	1.102	0.399	0.061	0.200

(continued)

Classification	C	Si	Mn	Cr	Mo	Ni	Cu
Example 13	0.361	0.005	0.456	0.214	0.233	0.289	0.301
Comparative Example 1	0.273	0.122	1.952	0.899	0.207	0.103	0.097
Comparative Example 2	0.273	0.122	1.952	0.899	0.207	0.103	0.097
Comparative Example 3	0.263	0.592	1.482	0.409	0.208	0.115	0.088
Comparative Example 4	0.302	0.403	3.013	0.602	0.008	0.100	0.211
Comparative Example 5	0.300	0.811	2.987	0.002	0.202	0.021	0.202
Comparative Example 6	0.401	0.611	0.387	0.001	0.401	0.206	0.183
Comparative Example 7	0.285	0.412	1.012	0.146	0.000	0.199	0.088

[Table 2]

Classification	Ti	Nb	V	B	Si+Ni	Mn+ Cr	0.85 - 0.23X([Mn] +[Cr])	Relati onal Expre ssion Satisf ied
Example 1	0.038	0.001	0.001	0.0026	0.206	2.334	0.313	OK
Example 2	0.031	0.003	0.000	0.0020	0.249	2.238	0.335	OK
Example 3	0.030	0.003	0.000	0.0022	0.298	2.251	0.332	OK
Example 4	0.048	0.003	0.001	0.0025	0.155	2.390	0.300	OK
Example 5	0.028	0.020	0.001	0.0024	0.209	2.070	0.374	OK
Example 6	0.028	0.020	0.001	0.0024	0.209	2.070	0.374	OK
Example 7	0.029	0.05	0.062	0.0024	0.405	1.502	0.504	OK
Example 8	0.029	0.000	0.000	0.0025	0.179	0.995	0.621	OK
Example 9	0.029	0.000	0.000	0.0025	0.179	0.995	0.621	OK
Example 10	0.039	0.000	0.000	0.0015	0.101	3.078	0.142	OK
Example 11	0.033	0.031	0.031	0.0025	0.294	0.670	0.696	OK
Example 12	0.039	0.000	0.000	0.0015	0.101	3.078	0.142	OK
Example 13	0.033	0.031	0.031	0.0025	0.294	0.670	0.696	OK
Comparative Example 1	0.031	0.003	0.001	0.0026	0.225	2.851	0.194	NG
Comparative Example 2	0.031	0.003	0.001	0.0026	0.225	2.851	0.194	NG
Comparative Example 3	0.031	0.021	0.010	0.0027	0.707	1.891	0.415	NG
Comparative Example 4	0.031	0.005	0.002	0.0022	0.503	3.615	0.019	NG
Comparative Example 5	0.045	0.001	0.001	0.0035	0.832	2.989	0.163	NG
Comparative Example 6	0.022	0.000	0.000	0.0045	0.817	0.388	0.761	NG
Comparative Example 7	0.027	0.000	0.000	0.0021	0.611	1.158	0.584	NG

[0078] Referring to Tables 1 and 2, the Examples satisfied the compositional range of the present invention and the relational expression $[Si]+[Ni] \leq 0.85 - 0.23 \times ([Mn]+[Cr])$. In contrast, the Comparative Examples differ in that they do not satisfy the relational expression among the compositional ranges.

[0079] Table 3 shows the manufacturing process condition values for the ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance of the Comparative Examples and Examples, and the results of measuring the fracture time based on the hydrogen embrittlement test method.

[Table 3]

Classification	Annealing Heat Treatment Temperature (°C)	Second Cooling End Temperature (°C)	Tempering Temperature (°C)	Tempering Time (sec)	Fracture Time Based on Hydrogen Embrittlement Test Method (hr) [Applied Stress, MPa]
Example 1	840	200	150	21,600	Non-fracture (100%)
Example 2	840	200	150	21,600	Non-fracture (100%)
Example 3	840	220	150	21,600	Non-fracture (100%)
Example 4	840	220	150	21,600	Non-fracture [100%]
Example 5	840	220	150	43,200	Non-fracture [100%]
Example 6	840	220	150	43,200	Non-fracture [100%]
Example 7	840	220	180	21,600	Non-fracture [100%]
Example 8	840	220	150	43,200	Non-fracture [100%]
Example 9	830	150	230	240	Non-fracture [100%]
Example 10	830	170	250	120	Non-fracture [100%]
Example 11	830	190	250	120	Non-fracture [100%]
Example 12	840	220	150	21,600	Non-fracture [100%]
Example 13	820	170	240	120	Non-fracture [100%]
Comparative Example 1	840	200	180	21,600	48 [70~100%]
Comparative Example 2	840	200	150	64,800	48 [70~100%]
Comparative Example 3	840	220	150	43,200	72 [100%]
Comparative Example 4	810	220	150	21,600	12 [60~100%]
Comparative Example 5	810	220	150	21,600	24 [60~100%]
Comparative Example 6	820	170	240	120	72 [90, 100%]
Comparative Example 7	840	170	240	120	48 [70~100%]

[0080] In the manufacturing processes of the Examples and Comparative Examples, conditions other than those listed in Table 3, for example, the hot rolling and cold rolling process conditions, were all manufactured identically so as to satisfy the process conditions of the present invention.

[0081] Referring to Table 3, the Examples and Comparative Examples satisfied the process conditions of the present invention with respect to the annealing heat treatment temperature, the second cooling end temperature, the tempering temperature, and the tempering time.

[0082] However, referring to Table 3, the Examples did not exhibit fracture under conditions in which a load of 300% of the yield strength was applied for 100 hours or more. Accordingly, it can be seen that the Examples have excellent resistance to hydrogen embrittlement. In contrast, the Comparative Examples exhibited fracture in less than 100 hours under conditions in which a load of 60% to 100% of the yield strength was applied. This demonstrates that the Comparative Examples are susceptible to hydrogen embrittlement as a result of not satisfying the compositional range of the present invention and the relational expression $[Si] + [Ni] \leq 0.85 - 0.23 \times ([Mn] + [Cr])$.

[0083] When the tempering is performed at a relatively high temperature, the growth of carbides in the longitudinal direction becomes very active, and thus the yield strength and tensile strength of the steel material may decrease; furthermore, since the carbides may act as fracture initiation sites upon hydrogen penetration, the steel may become susceptible to hydrogen embrittlement. In contrast, when the tempering is performed at a relatively low temperature, heat treatment control over the growth of the carbides is more readily achievable, thereby facilitating the securing of the desired strength and suppressing fracture due to hydrogen embrittlement.

[0084] It will be apparent to those skilled in the art to which the technical concept of the present invention pertains that the technical concept of the present invention described above is not limited to the foregoing embodiments and the accompanying drawings, and that various substitutions, modifications, and alterations are possible without departing from the technical concept of the present invention.

Claims

1. An ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance, comprising, in weight percent: from 0.1% to 0.5% of carbon (C); from 0.01% to 2.0% of silicon (Si); from 0.1% to 5.0% of manganese (Mn); from 0.01% to 2.0% of aluminum (Al); greater than 0% and 3.0% or less of chromium (Cr); greater than 0% and 1.0% or less of molybdenum (Mo); greater than 0% and 0.4% or less of nickel (Ni); from 0.05% to 0.4% of copper (Cu); from 0.01% to 0.2% of titanium (Ti); from 0.01% to 0.1% of niobium (Nb); from 0.01% to 1.0% of vanadium (V); from 0.001% to 0.005% of boron (B); greater than 0% and 0.02% or less of phosphorus (P); greater than 0% and 0.01% or less of sulfur (S); and the balance being iron (Fe) and unavoidable impurities, wherein the cold-rolled steel sheet has a tensile strength (TS) of at least 1100 MPa, an elongation (EL) of at least 3%, and a non-fracture time of at least 100 hours based on a hydrogen embrittlement test method.

2. The ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance of claim 1, wherein a sum $[Si]+[Ni]$ of the weight percentages of the silicon and the nickel, and a sum $[Mn]+[Cr]$ of the weight percentages of the manganese and the chromium satisfy the following relational expression:

$$[Si]+[Ni] \leq 0.85 - 0.23 \times ([Mn]+[Cr])$$

3. The ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance of claim 1, wherein a microstructure of the ultra-high-strength cold-rolled steel sheet comprises ferrite, tempered bainite, and tempered martensite phases,

wherein an area fraction of the ferrite ranges from 0% to 20%, an area fraction of the tempered bainite ranges from 5% to 20%, and an area fraction of the tempered martensite ranges from 60% to 100%, and wherein a sum of the tempered bainite and the tempered martensite satisfies a range of from 80% to 100%.

4. The ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance of claim 1, wherein the cold-rolled steel sheet further comprises a carbide, wherein the carbide has an average size of no greater than 100 nm and an aspect ratio of no greater than 5.

5. The ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance of claim 4, wherein the carbide comprises at least one selected from the group consisting of Fe-based carbide, Ti-based carbide, Nb-based carbide, V-based carbide, and Mo-based carbide.

6. A method of producing an ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance, the method comprising:

hot rolling a steel material comprising, in weight percent, from 0.1% to 0.5% of carbon (C), from 0.01% to 2.0% of silicon (Si), from 0.1% to 5.0% of manganese (Mn), from 0.01% to 2.0% of aluminum (Al), greater than 0% and 3.0% or less of chromium (Cr), greater than 0% and 1.0% or less of molybdenum (Mo), greater than 0% and 0.4% or less of nickel (Ni), from 0.05% to 0.4% of copper (Cu), from 0.01% to 0.2% of titanium (Ti), from 0.01% to 0.1% of niobium (Nb), from 0.01% to 1.0% of vanadium (V), from 0.001% to 0.005% of boron (B), greater than 0% and 0.02% or less of phosphorus (P), greater than 0% and 0.01% or less of sulfur (S), and the balance being iron (Fe) and unavoidable impurities, to produce a hot-rolled steel sheet;
cold rolling the hot-rolled steel sheet to produce a cold-rolled steel sheet;
performing an annealing heat treatment by maintaining the cold-rolled steel sheet at a temperature ranging from 800°C to 950°C for a duration of from 10 seconds to 600 seconds;
performing a first cooling of the annealing heat-treated cold-rolled steel sheet to a temperature ranging from 500°C to 700°C at a cooling rate of from 0°C/s to 50°C/s;
performing a second cooling of the first-cooled cold-rolled steel sheet to a temperature ranging from 0°C to 350°C at a cooling rate of at least 5°C/s; and
performing a tempering step of heat-treating the second-cooled cold-rolled steel sheet at a temperature ranging from 100°C to 350°C for a duration of at least 10 seconds.

7. The method of producing an ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance of claim 6, wherein the producing of the hot-rolled steel sheet comprises:

reheating the steel material having the alloy composition at a reheating temperature ranging from 1,150°C to 1,300°C;

hot rolling the reheated steel material such that hot rolling is completed at a finish rolling end temperature ranging from 800°C to 1,000°C, to produce a hot-rolled steel sheet; and

cooling the hot-rolled steel sheet at a cooling rate of from 1°C/s to 100°C/s and then coiling the hot-rolled steel sheet at a coiling temperature ranging from 300°C to 700°C.

8. The method of producing an ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance of claim 6, wherein the ultra-high-strength cold-rolled steel sheet produced by the method of producing an ultra-high-strength cold-rolled steel sheet having excellent hydrogen embrittlement resistance has a tensile strength (TS) of at least 1100 MPa, an elongation (EL) of at least 3%, and a non-fracture time of at least 100 hours based on a hydrogen embrittlement test method, and wherein a microstructure of the ultra-high-strength cold-rolled steel sheet comprises ferrite, tempered bainite, and tempered martensite phases, an area fraction of the ferrite ranges from 0% to 20%, an area fraction of the tempered bainite ranges from 5% to 20%, and an area fraction of the tempered martensite ranges from 60% to 100%, and a sum of the tempered bainite and the tempered martensite satisfies a range of from 80% to 100%.

FIG. 1

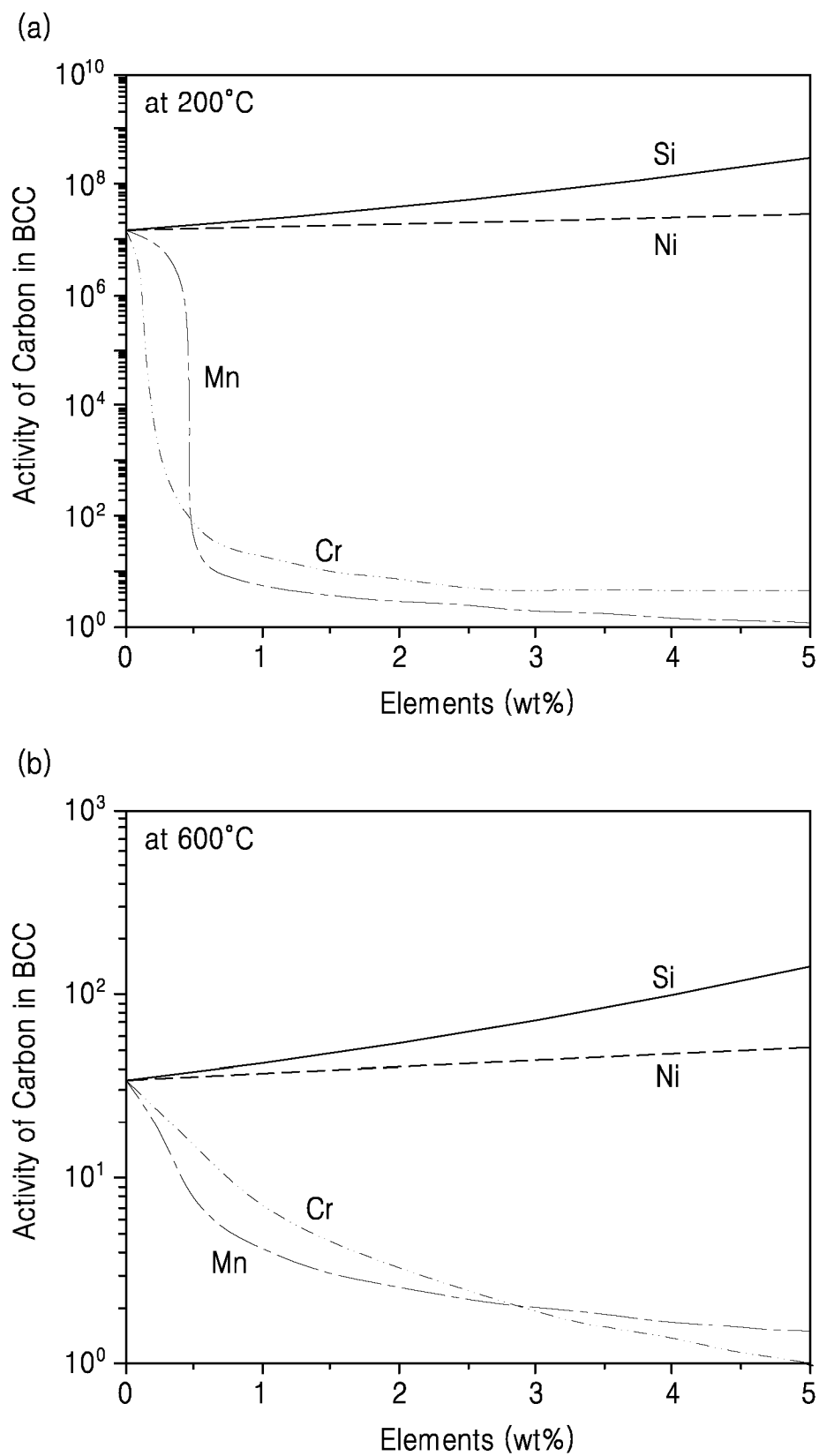


FIG. 2

< HYDROGEN EMBRITTLEMENT EVALUATION RESULT BASED ON
Mn, Cr, Si, Ni (0.05~0.40Cu) >

HYDROGEN EMBRITTLEMENT EVALUATION RESULT : OK (○), NG (□)

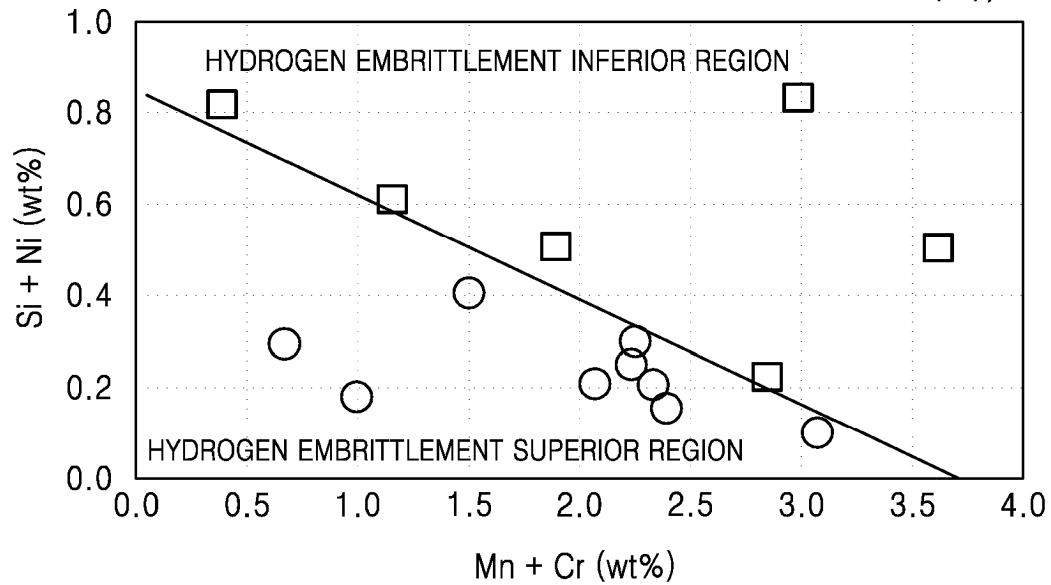
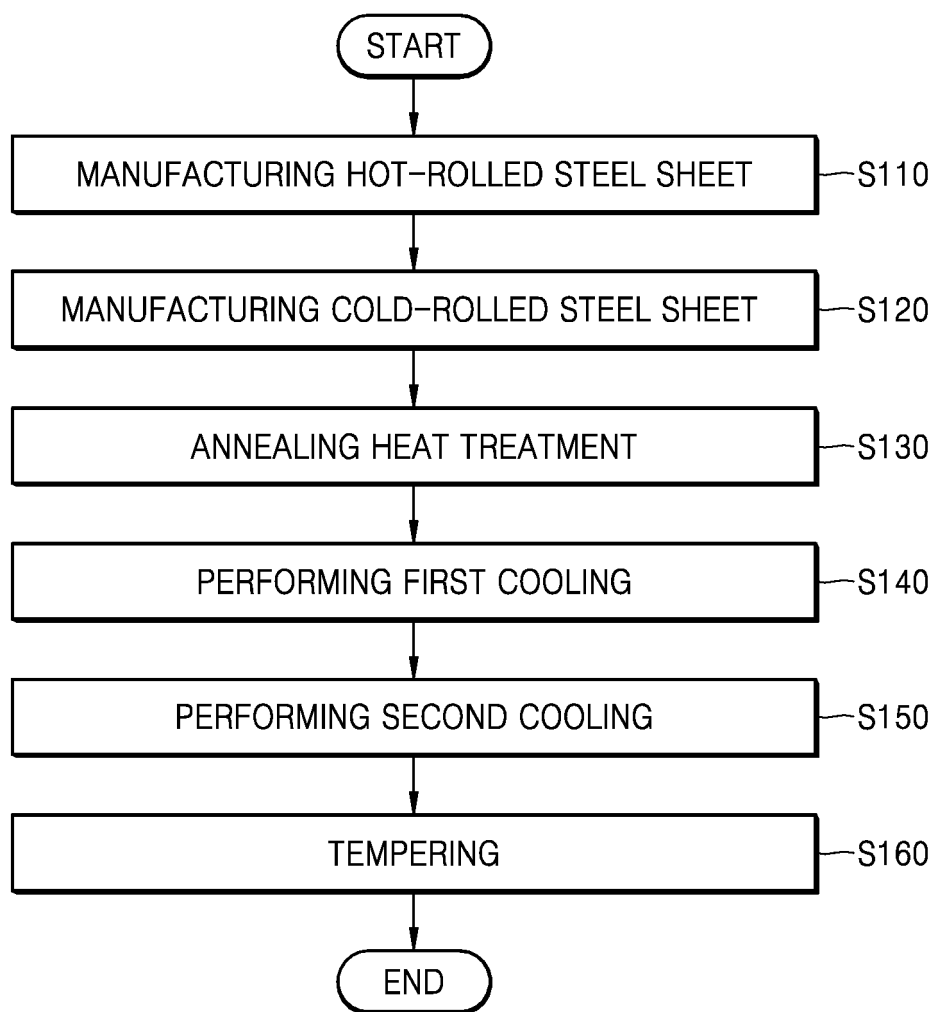


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2024/095727

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/58(2006.01)i; C22C 38/44(2006.01)i; C22C 38/42(2006.01)i; C22C 38/50(2006.01)i; C22C 38/48(2006.01)i;
C22C 38/46(2006.01)i; C22C 38/54(2006.01)i; C21D 8/02(2006.01)i; C21D 9/46(2006.01)i

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)

C22C 38/58(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/00(2006.01); C22C 38/02(2006.01);
C22C 38/38(2006.01)

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

Korean utility models and applications for utility models: IPC as above

Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 어닐링(annealing), 템퍼링(tempering), 구리(Cu), 망간(Mn), 크롬(Cr), 수소취성
(hydrogen embrittlement)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015-151428 A1 (JFE STEEL CORPORATION) 08 October 2015 (2015-10-08) See paragraphs [0016]-[0023], [0038] and [0052] and tables 1-3.	1-8
A	KR 10-2020-0036759 A (POSCO) 07 April 2020 (2020-04-07) See claims 1-12 and tables 1-4.	1-8
A	KR 10-2018-0016518 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORPORATION) 14 February 2018 (2018-02-14) See claim 8 and tables 1-13.	1-8
A	KR 10-2013-0027793 A (HYUNDAI HYSCO CO., LTD.) 18 March 2013 (2013-03-18) See claims 1-5, tables 1-2 and figure 1.	1-8
A	KR 10-2022-0086233 A (POSCO) 23 June 2022 (2022-06-23) See claims 1-6 and tables 1-3.	1-8

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

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INTERNATIONAL SEARCH REPORT Information on patent family members

International application No.

PCT/KR2024/095727

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Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2015-151428 A1	08 October 2015	CN 106133173 A	16 November 2016
		CN 106133173 B	19 January 2018
		EP 3128026 A1	08 February 2017
		EP 3128026 B1	06 March 2019
		JP 5896085 B1	30 March 2016
		JP WO2015-151428 A1	13 April 2017
		US 10329636 B2	25 June 2019
		US 2017-0022582 A1	26 January 2017
KR 10-2020-0036759 A	07 April 2020	CN 112752862 A	04 May 2021
		CN 112752862 B	06 May 2022
		EP 3859041 A1	04 August 2021
		JP 2022-501510 A	06 January 2022
		JP 7410936 B2	10 January 2024
		KR 10-2276741 B1	13 July 2021
		US 11753693 B2	12 September 2023
		US 2022-0033926 A1	03 February 2022
		US 2023-0340633 A1	26 October 2023
		WO 2020-067752 A1	02 April 2020
KR 10-2018-0016518 A	14 February 2018	BR 112017025389 A2	07 August 2018
		CN 107636184 A	26 January 2018
		CN 114990431 A	02 September 2022
		EP 3309273 A1	18 April 2018
		EP 3309273 B1	26 May 2021
		JP 6187710 B2	30 August 2017
		JP WO2016-199922 A1	22 June 2017
		KR 10-2081361 B1	25 February 2020
		MX 2017015286 A	19 February 2018
		TW 201713778 A	16 April 2017
		TW I602927 B	21 October 2017
		US 10745775 B2	18 August 2020
		US 2018-0298462 A1	18 October 2018
		WO 2016-199922 A1	15 December 2016
KR 10-2013-0027793 A	18 March 2013	None	
KR 10-2022-0086233 A	23 June 2022	KR 10-2023-0082600 A	08 June 2023
		KR 10-2023-0082601 A	08 June 2023
		KR 10-2645525 B1	11 March 2024

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- KR 20120144482 [0003]