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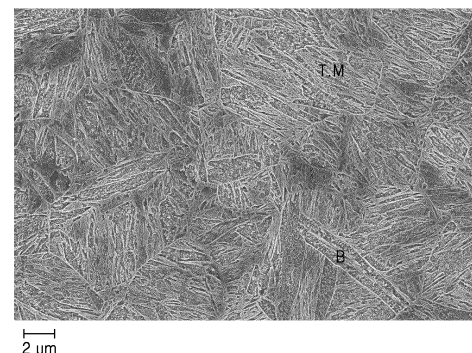
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(54) **ULTRA-HIGH STRENGTH COLD-ROLLED STEEL SHEET AND MANUFACTURING METHOD THEREFOR**

(57) Provided is an ultra-high strength cold-rolled steel sheet, including: carbon (C): 0.23% to 0.40%; silicon (Si): 0.05% to 1.0%; manganese (Mn): 0.5% to 3.0%; vanadium (V): 0.01% to 0.12%; aluminum (Al): 0.01% to 0.3%; chromium (Cr): greater than 0% and 0.5% or less; titanium (Ti): greater than 0% and 0.1% or less; phosphorus (P): greater than 0% and 0.02% or less; sulfur (S): greater than 0% and 0.01% or less; and boron (B): 0.001% to 0.005%, based on % by weight,; and a remainder being Fe and other unavoidable impurities, wherein a final microstructure includes tempered martensite having a volume fraction of 90% or more, wherein an average spacing between precipitates in the tempered martensite is 300 nm or more, an average size of the precipitates is 200 nm or less, and the number of precipitates having an average size of 40 nm or less is 25 or more based on an area of 20 μm^2 in the final microstructure.

FIG. 3



Description

[Technical Field]

[0001] The technical idea of the present invention relates to a cold-rolled steel sheet, and more particularly to an ultra-high strength cold-rolled steel sheet having excellent bendability and hydrogen embrittlement resistance and a manufacturing method thereof.

[Background Art]

[0002] Recently, various environmental and energy usage regulations have led to the demand for high-strength steel sheets for improved fuel efficiency and durability. In particular, high yield strength and tensile strength are important for making components such as front bumpers and side sills with automotive structural steel. Here, the microstructure for making a high-strength steel sheet should be composed of low-temperature structures such as martensite and bainite. This structure is prone to embrittlement fracture due to hydrogen remaining inside the steel or flowing in from the outside. This is called hydrogen embrittlement. The hydrogen embrittlement is characterized in that fracture occurs at a lower intensity than the strength at which fracture generally occurs, and becomes more sensitive as the strength increases. In addition, since materials can be destroyed by hydrogen embrittlement even under very small stresses, measures to complement this problem are being sought.

[0003] As a related document, there is Korean Patent Application No. 10-2018-0047388.

[Disclosure]

[Technical Problem]

[0004] Therefore, the present invention has been made in view of the above problems, and it is one object of the present invention to provide an ultra-high strength cold-rolled steel sheet having excellent bendability and hydrogen embrittlement resistance and a manufacturing method thereof.

[0005] It will be understood that the technical problems are only provided as examples, and the technical idea of the present disclosure is not limited thereto.

[Technical Solution]

[0006] In accordance with an aspect of the present invention, the above and other objects can be accomplished by the provision of an ultra-high strength cold-rolled steel sheet having excellent bendability and hydrogen embrittlement resistance and a manufacturing method thereof.

[0007] In accordance with another aspect of the present invention, there is provided An ultra-high strength cold-rolled steel sheet, including: carbon (C): 0.23% to 0.40%; silicon (Si): 0.05% to 1.0%; manganese (Mn): 0.5% to 3.0%; vanadium (V): 0.01% to 0.12%; aluminum (Al): 0.01% to 0.3%; chromium (Cr): greater than 0% and 0.5% or less; titanium (Ti): greater than 0% and 0.1% or less; phosphorus (P): greater than 0% and 0.02% or less; sulfur (S): greater than 0% and 0.01% or less; and boron (B): 0.001% to 0.005%, based on % by weight; and a remainder being Fe and other unavoidable impurities, wherein a final microstructure includes tempered martensite having a volume fraction of 90% or more, wherein an average spacing between precipitates in the tempered martensite is 300 nm or more, an average size of the precipitates is 200 nm or less, and the number of precipitates having an average size of 40 nm or less is 25 or more based on an area of 20 μm^2 in the final microstructure.

[0008] In accordance with an embodiment of the present invention, a surface layer of the cold-rolled steel sheet may include a soft region having a hardness less than 85% of an average hardness of a base material, wherein a ratio of a thickness of the soft region to a thickness of the base material is 0.03 to 0.10.

[0009] In accordance with an embodiment of the present invention, the cold-rolled steel sheet may have a Prior Austenite Grain Size (PAGS) of 12 μm or less.

[0010] In accordance with an embodiment of the present invention, the cold-rolled steel sheet may further include: molybdenum (Mo): 0.01% to 0.3% or niobium (Nb): 0.01% to 0.1%, based on % by weight.

[0011] In accordance with an embodiment of the present invention, a value of $[C] + [V] + [Cr] + [Mo] + [Nb]$ (where $[C]$, $[V]$, $[Cr]$, $[Mo]$ and $[Nb]$ are weight % values of carbon, vanadium, chromium, molybdenum and niobium) of the cold-rolled steel sheet may be smaller than 0.63.

[0012] In accordance with an embodiment of the present invention, the ultra-high strength cold-rolled steel sheet may have a yield strength (YP) of 1200 MPa or more, a tensile strength (TS) of 1500 MPa or more, an elongation (El) of 7.0% or more, a yield ratio of 70% or more, a bendability (R/t) of 2.5 or less and a hydrogen embrittlement elongation reduction rate

of 35% or less.

[0013] In accordance with yet another aspect of the present invention, there is provided a method of manufacturing an ultra-high strength cold-rolled steel sheet, the method including: hot-rolling steel including carbon (C): 0.23% to 0.40%; silicon (Si): 0.05% to 1.0%; manganese (Mn): 0.5% to 3.0%; vanadium (V): 0.01% to 0.12%; aluminum (Al): 0.01% to 0.3%; chromium (Cr): greater than 0% and 0.5% or less; titanium (Ti): greater than 0% and 0.1% or less; phosphorus (P): greater than 0% and 0.02% or less; sulfur (S): greater than 0% and 0.01% or less; and boron (B): 0.001% to 0.005%, based on % by weight,; and a remainder being Fe and other unavoidable impurities to provide a hot-rolled steel sheet; cold-rolling the hot-rolled steel sheet to provide a cold-rolled steel sheet; heating the cold-rolled steel sheet; annealing the heated cold-rolled steel sheet; cooling the annealed cold-rolled steel sheet; and reheating and tempering the cooled cold-rolled steel sheet, wherein, when annealing the cold-rolled steel sheet, an annealing temperature is gradually increased in a temperature range of 750°C to 950°C, without a section in which a constant temperature is maintained, until cooling the cold-rolled steel sheet.

[0014] In accordance with an embodiment of the present invention, in the annealing of the cold-rolled steel sheet, an annealing temperature (T) may satisfy a relationship of Equation 1 below dependent upon time (t):

$$\text{Annealing temperature (T)} = A \times t^2 + B \times t + C \quad (\text{where } A, B \text{ and } C \text{ constants satisfying } -0.007 < A < -0.005, 2 < B < 3, \text{ and } 500 < C < 700). \quad [\text{Equation 1}]$$

[0015] In accordance with an embodiment of the present invention, in the heating of the cold-rolled steel sheet, a heating rate may be 3°C/sec or more, and in the annealing of the cold-rolled steel sheet, a heating rate may be less than 3°C/sec.

[0016] In accordance with an embodiment of the present invention, the hot rolling may be performed under conditions of a reheating temperature (SRT) of 1180°C to 1300°C, a finish delivery temperature (FDT) of 800°C to 950°C, and a coiling temperature (CT) of 500°C to 700°C.

[0017] In accordance with an embodiment of the present invention, the cooling of the annealed cold-rolled steel sheet may include: slow-cooling the annealed cold-rolled steel sheet up to 700 to 800°C at a cooling rate of 3°C/sec to 15°C/sec; performing first rapid cooling for the slowly cooled cold-rolled steel sheet up to 300°C to 350°C at a cooling rate of 80°C/sec to 150°C/sec; and performing second rapid cooling for the cold-rolled steel sheet, which has been subjected to the first rapid cooling, up to room temperature to 300°C at a cooling rate of 30°C/sec to 90°C/sec.

[0018] In accordance with an embodiment of the present invention, the reheating and tempering of the cooled cold-rolled steel sheet may include reheating the cold-rolled steel sheet, which has been subjected to the second rapid cooling, and tempering by maintaining at 150°C to 350°C for 30 to 300 sec.

[Advantageous effects]

[0019] In accordance with the technical idea of the present invention, an ultra-high strength cold-rolled steel sheet having excellent bendability and hydrogen embrittlement resistance and a manufacturing method thereof can be implemented. Specifically, an appropriate soft (decarburized) region can be obtained by replacing an annealing holding section with a temperature rise according to a quadratic function equation, thereby achieving an ultra-high strength steel sheet that satisfies a target bendability (R/t) of 2.5 or less and that satisfies an elongation reduction rate of 35% or less upon adding hydrogen through the suppression of coarsening of the Prior Austenite Grain Size (PAGS). In addition, tempering during cooling can be suppressed through the first and second rapid cooling after the slow cooling, and homogeneous tempered martensite can be implemented through subsequent tempering. In addition, an ultra-high-strength steel sheet having a yield strength of 1200 MPa or more, a tensile strength of 1500 MPa or more, and a high yield ratio (70% or more) can be realized and, by replacing a holding section in an annealing section with a partial temperature rise, the processing time can be shortened by about 10% or more, thereby improving productivity.

[0020] The effects of the present invention are described only as examples, and the scope of the present invention is not limited by these effects.

[Description of Drawings]

[0021]

FIG. 1 is a process flowchart schematically illustrating a method of manufacturing an ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention.

FIG. 2 is a time-temperature graph illustrating annealing, cooling and tempering heat treatment processes after cold rolling in a method of manufacturing an ultra-high strength cold-rolled steel sheet according to each of comparative examples and an example of the present invention.

FIG. 3 illustrates the photograph of a representative final microstructure of the ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention.

FIG. 4 illustrates the photograph of precipitates observed in the microstructure of the ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention.

[Best Mode]

[0022] Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the accompanying drawings. Embodiments of the present disclosure are provided to more completely explain the technical idea of the present disclosure to those skilled in the art, and the following embodiments may be modified in many different forms, but the scope of the technical idea of the present disclosure is not limited to the following embodiments. Rather, the embodiments are provided to make the disclosure thorough and complete and to fully convey the technical idea of the disclosure to those skilled in the art. Like reference numerals in the specification denote like elements. Further, various elements and regions in the drawings are schematically drawn. Therefore, the technical idea of the invention is not limited by the relative size or spacing drawn in the accompanying drawings.

[0023] Hereinafter, a method of manufacturing an ultra-high strength cold-rolled steel sheet according to the technical idea of the present invention is described in detail.

[0024] FIG. 1 is a process flowchart schematically illustrating a method of manufacturing an ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention, and FIG. 2 is a time-temperature graph illustrating annealing, cooling and tempering heat treatment processes after cold rolling using a method of manufacturing an ultra-high strength cold-rolled steel sheet according to each of comparative examples and an example of the present invention.

[0025] Referring to FIG. 1, the method of manufacturing an ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention includes a step (S10) of hot-rolling steel to provide a hot-rolled steel sheet; a step (S20) of cold-rolling the hot-rolled steel sheet to provide a cold-rolled steel sheet; a step (S31) of heating the cold-rolled steel sheet; a step (S32) of annealing the heated cold-rolled steel sheet; a step (S40, S50, S60) of cooling the annealed cold-rolled steel sheet; and a step (S70) of reheating and tempering the cooled cold-rolled steel sheet.

Hot-rolling step (S10)

[0026] The ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention includes carbon (C): 0.23% to 0.40%; silicon (Si): 0.05% to 1.0%; manganese (Mn): 0.5% to 3.0%; vanadium (V): 0.01% to 0.12%; aluminum (Al): 0.01% to 0.3%; chromium (Cr): greater than 0% and 0.5% or less; titanium (Ti): greater than 0% and 0.1% or less; phosphorus (P): greater than 0% and 0.02% or less; sulfur (S): greater than 0% and 0.01% or less; and boron (B): 0.001% to 0.005%, based on % by weight,; and the remainder being Fe and other unavoidable impurities.

[0027] Hereinafter, the role and content of each component included in the ultra-high strength cold-rolled steel sheet according to the present invention are described. Here, the content of each component element means % by weight based on the total weight of the steel sheet.

Carbon (C): 0.23% to 0.40%

[0028] Carbon is added to secure the strength of steel, and the strength increases as the carbon content in a martensite structure increases. The carbon content is preferably 0.23% to 0.40%. When the carbon content is low, i.e., less than 0.23%, it is difficult to obtain the target strength. When it is greater than 0.40%, the carbon equivalent (Ceq) increases, which may be disadvantageous for weldability, bendability and hydrogen embrittlement resistance.

Silicon (Si): 0.05% to 1.0%

[0029] Silicon is a ferrite-stabilizing element that delays the formation of carbides in ferrite and has a solid solution-strengthening effect. Silicon is preferably added in an amount of 0.05% to 1.0%. If it is less than 0.05%, the effect is very small. If it exceeds 1.0%, oxides such as Mn_2SiO_4 may be formed during the manufacturing process and the carbon equivalent may be increased, which may reduce weldability. In addition, carbide precipitation may be excessively suppressed, which results in deviating from the effect of the present invention.

Manganese (Mn): 0.5% to 3.0%

[0030] Manganese has a solid solution-strengthening effect and contributes to the improvement of strength by increasing hardenability. It is preferred to add manganese in an amount of 0.5% to 3.0%. When the amount is less than 0.5%, hardenability is not sufficient, making it difficult to secure strength. When the amount is greater than 3.0%, Formation

or segregation of inclusions such as MnS may cause processability degradation and hydrogen embrittlement resistance degradation, and reduce weldability by increasing the carbon equivalent.

Vanadium (V): 0.01% to 0.12%

[0031] Vanadium is a major element that precipitates in the form of carbide (VC) in steel, has a refinement effect of Prior Austenite Grain Size (PAGS) and contributes to improving yield strength. It is preferred to add vanadium in a content ratio of 0.01% to 0.12% based on the total weight of the ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention. When the content of vanadium is less than 0.01%, it is difficult to expect the precipitate effect. When the content of vanadium is greater than 0.12%, problems such as material deterioration, manufacturing cost increase, grain coarsening due to the formation of coarse carbonate, and an uneven structure due to excessively high recrystallization temperature occur.

Aluminum (Al): 0.01% to 0.3%

[0032] Aluminum is used as a deoxidizer and can be helpful in purifying ferrite. When the content of aluminum is less than 0.01%, the deoxidation effect may be insufficient. When the content of aluminum is greater than 0.3%, AlN may be formed during slab manufacturing, which can cause cracks during casting or hot rolling. Accordingly, it is preferred to add aluminum in a content of 0.01% to 0.3% based on the total weight of the steel sheet.

Chromium (Cr): greater than 0% and 0.5% or less

[0033] Chromium is a ferrite-stabilizing element, increases the solid solution-strengthening and hardenability of steel, and contributes to the improvement of strength by refining carbides. When the content of chromium is greater than 0.5%, weldability is hindered, thereby increasing the manufacturing cost of steel. Accordingly, it is preferred to add chromium in a content of greater than 0% and 0.5% or less based on the total weight of the steel sheet.

Titanium (Ti): greater than 0% and 0.1% or less

[0034] Titanium is a precipitate-forming element, and has the effect of precipitating TiN and TiC and refining grains. In particular, the nitrogen content inside steel can be reduced through the precipitation of TiN, and when added together with boron, the precipitation of BN can be prevented. It is preferred to add titanium in a content of greater than 0% and 0.1% or less. When the content of titanium is greater than 0.1%, it increases the manufacturing cost of steel.

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

[0035] Phosphorus is an impurity included in the manufacturing process of steel, and although it can help improve strength through solid solution strengthening, it can cause low-temperature embrittlement when included in large amounts. Accordingly, it is preferred to limit the content of phosphorus 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

[0036] Sulfur is an impurity included in a steel manufacturing process, and can form non-metallic inclusions such as FeS and MnS, thereby reducing bendability, toughness, and weldability. Accordingly, it is preferred to limit the content of sulfur to greater than 0% and 0.01% or less based on the total weight of the steel sheet.

Boron (B): 0.001% to 0.005%

[0037] Boron is a hardening element, and contributes greatly to the formation of martensite during a cooling process after annealing. It is preferred to add boron in a content of 0.001% to 0.005%. When the content is less than 0.001%, the effect is insufficient, so it is difficult to secure martensite. When the content is greater than 0.005%, the toughness of steel may be decreased.

[0038] The remaining component of the ultra-high strength cold-rolled steel sheet is iron (Fe). However, since unintended impurities from raw materials or the surrounding environment may inevitably be mixed in a normal steelmaking process, this cannot be ruled out. Since these impurities are known to anyone skilled in the art of ordinary manufacturing processes, they are not specifically mentioned in this specification.

[0039] Meanwhile, the ultra-high strength cold-rolled steel sheet according to a modified embodiment of the present

invention may additionally include at least one of elements having the following composition range in addition to the above-described alloy elements.

Molybdenum (Mo): 0.01% to 0.3%

[0040] Molybdenum plays a role in improving hydrogen embrittlement resistance, has a solution-strengthening effect and increases hardenability, thereby contributing to strength improvement. When the content of molybdenum is greater than 0.3%, it can increase the manufacturing cost of steel. Accordingly, it is preferred to add molybdenum in a content of 0.01% to 0.3% based on the total weight of the steel sheet.

Niobium (Nb): 0.01% to 0.1%

[0041] Niobium has the effect of refining Prior Austenite Grain Size (PAGS), and contributes to improving the yield strength by forming precipitates in the form of NbC. That is, Niobium is a precipitate-forming element, and improves the toughness and strength of steel through precipitation and grain refinement. It is preferred to add niobium in a content of 0.01% to 0.1%. When it is added in a content of greater than 0.1%, a low-temperature transformation structure may occur due to the delayed ferrite transformation effect during hot rolling, which may adversely affect the impact performance and increase the manufacturing cost of steel.

[0042] The ultra-high strength cold-rolled steel sheet according to the present invention having the above-described composition range may satisfy the following Relational Expression 1:

$$\text{Relational Expression 1: } [C] + [V] + [Cr] + [Mo] + [Nb] < 0.63$$

where [C], [V], [Cr], [Mo] and [Nb] are values of % by weight of carbon, vanadium, chromium, molybdenum and niobium. When Relational Expression 1 is not satisfied, precipitates may be coarsened, thereby increasing hydrogen embrittlement.

[0043] Meanwhile, steel having the above-described composition is hot-rolled, thereby providing a hot-rolled steel sheet. The hot rolling may be performed under conditions as follows: the reheating temperature (SRT): 1180°C to 1300°C, the finish delivery temperature (FDT): 800°C to 950°C, and the coiling temperature (CT): 500°C to 700°C.

[0044] The slab containing the above-described alloy components and the remainder being iron and unavoidable impurities is reheated to 1180°C to 1300°C. The slab is manufactured in the form of a semi-finished product by continuous casting of molten steel obtained through a steelmaking process. By reheating the slab, the component segregation that occurred during the casting process is homogenized and the slab is ready for hot rolling. When the Slab Reheating Temperature (SRT) is less than 1180°C, there is a problem that the segregation of the slab is not sufficiently reused. When the SRT is higher than 1300°C, the size of austenite grains increases, and the process cost may increase due to the temperature increase. The slab may be reheated for 1 to 4 hours. When the reheating time is less than 1 hour, the homogenization of segregation is insufficient. When the reheating time is longer than 4 hours, the austenite grain size increases and the process cost may increase.

[0045] The reheated slab is hot-rolled. The hot rolling is performed at a finish delivery temperature (FDT) of 800°C to 900°C. When the FDT is lower than 800°C, the rolling load increases rapidly, which reduces productivity. When the FDT is higher than 900°C, the grain size increases, which may reduce strength. After hot rolling, it is cooled to 500°C to 700°C, and then coiled. When the coiling temperature is lower than 500°C, the strength increases, and the rolling load increases during cold rolling. When the coiling temperature is higher than 700°C, defects may occur in a subsequent process due to surface oxidation.

Cold-rolling step (S20)

[0046] The hot-rolled steel sheet is pickled to remove the surface scale layer, and cold rolling is performed. Milling is performed to remove the surface scale layer remaining after the pickling. To implement the uniform surface scale layer or completely remove the surface scale layer, milling is performed 0.3 to 1 mm from the initial thickness. If the milled thickness is less than 0.3 mm, the surface scale layer generated during hot rolling may remain, and it may be difficult to control a uniform decarburization layer during subsequent heat treatment. If milling is performed over 1mm, the waste portion increases, which may lower the recovery rate and increase the process cost. The thickness reduction ratio during cold rolling is about 40% to 70%.

Cold-rolling heat treatment (S31 to S70)

[0047] Referring to FIGS. 1 and 2, a step (S31) of heating the cold-rolled steel sheet; a step (S32) of annealing the heated cold-rolled steel sheet; a step (S40, S50, S60) of cooling the annealed cold-rolled steel sheet; and a step (S70) of reheating and tempering the cooled cold-rolled steel sheet are sequentially performed.

[0048] In the step (S31) of heating the cold-rolled steel sheet, a heating rate may be 3°C/sec or more. In the heating step (S31), the cold-rolled steel sheet can reach a temperature of A_3 to $A_3+30^\circ\text{C}$. When the heating rate in the heating step (S31) is less than 3°C/s, it takes a long time to reach the target annealing temperature, so production efficiency may decrease and the grain size may increase.

[0049] During the step (S32) of annealing the heated cold-rolled steel sheet, the annealing temperature is characterized by gradually increasing within a temperature range (ΔT) of 750°C to 950°C without a section of maintaining a constant temperature before performing the step (S40) of cooling the cold-rolled steel sheet.

[0050] The step (S32) of annealing the cold-rolled steel sheet is characterized in that the annealing temperature (T) satisfies the relationship of the following Equation 1 dependent upon time (t):

<Equation 1>

$$\text{Annealing temperature (T)} = A \times t^2 + B \times t + C$$

(where A, B and C are constants satisfying $-0.007 < A < -0.005$, $2 < B < 3$, and $500 < C < 700$)

[0051] The annealing temperature should be increased to A_3 or higher to create a single austenite phase so as to create a final structure, tempered martensite. In the present invention, the annealing temperature may vary depending on the steel type, and most thereof satisfy 750°C to 950°C. In the present invention, the following advantages can be obtained by eliminating the holding section in a general annealing section and replacing it with a temperature increase according to Equation 1.

[0052] It is possible to eliminate the disadvantage of not being able to obtain the appropriate degree of softening (decarburization) when maintained at a low temperature and the adverse effects of hydrogen embrittlement due to coarsening of Prior Austenite Grain Size (PAGS) that may occur when maintained at a high temperature, and to reduce the heat treatment time of the total annealing section by about 10%, thereby improving productivity.

[0053] Next, a step (S40) of slowly cooling the annealed cold-rolled steel sheet is performed. The step (S40) is a section of cooling a cooling rate of 3 to 15°C/sec after the annealing. For example, the annealed cold-rolled steel sheet is slowly cooled to 700 to 800°C at a cooling rate of 3°C/sec to 15°C/sec. Here, when a slow cooling-terminating temperature, i.e., a rapid cooling-starting temperature, drops below 700°C or less, ferrite transformation occurs, causing a decrease in strength and thus failing to reach the target strength.

[0054] A first rapid cooling process (S50) of the slowly cooled cold-rolled steel sheet is performed. For example, the slowly cooled cold-rolled steel sheet may be subjected to a first rapid cooling process up to a temperature of 300°C to 350°C at a cooling rate of 80°C/sec to 150°C/sec. A first rapid cooling section is a temperature section from the slow cooling-terminating temperature to the M_s transformation point or lower. In this section, it is important to suppress the transformation of ferrite and bainite through rapid cooling. In the alloy system of this embodiment, a cooling rate to suppress the transformation is about 80°C/sec or more. When the cooling rate is slower than 80°C/sec, strength may decrease due to the transformation of ferrite and bainite.

[0055] Next, the cold-rolled steel sheet that has been subjected to the first rapid cooling process is subjected to a second rapid cooling treatment step (S60). For example, the cold-rolled steel sheet that has been subjected to the first rapid cooling process may be subjected to second cooling treatment up to a temperature from room temperature to 300°C at a cooling rate of 30°C/sec to 90°C/sec. A second rapid cooling section is a temperature section from the M_s transformation point to room temperature. In this section, martensite transformation occurs. In the alloy system of this embodiment, the M_s temperature is around 350°C, and the martensite transformation starts at 300°C to 400°C. If this temperature range is maintained for a long time, tempering may occur, resulting in the formation of a tempered martensite structure with large carbides, and a decrease in strength due to the softening of the tempered martensite. In this embodiment, a cooling rate of 30°C/sec or more is required in the second cooling section to prevent this tempering. However, when the average cooling rate of the first rapid cooling section and second rapid cooling section is 70°C/sec or more, it is possible to cool without classifying the rapid cooling section.

[0056] The step (S70) of reheating and tempering the cooled cold-rolled steel sheet is performed. For example, a tempering step of reheating the cold-rolled steel sheet that has been subjected to the second cooling treatment and maintaining it at 150°C to 350°C for 30 to 300 sec. The tempering step is a section where the generated martensite is changed into tempered martensite. When tempering at a temperature of less than 150°C, it is too low to see the tempering effect, and when tempering at a temperature of greater than 300°C, the size of the carbide may become coarse, which may

cause a decrease in strength. The tempering holding time has little effect compared to the tempering temperature. However, if it is less than 30 seconds, it is difficult to obtain a stable tempering effect, and if it exceeds 5 minutes, the heat treatment efficiency may decrease, the carbide size may increase, and the strength may decrease, so it is limited to 5 minutes or less.

[0057] The ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention implemented by performing the above-described steps includes carbon (C): 0.23% to 0.40%; silicon (Si): 0.05% to 1.0%; manganese (Mn): 0.5% to 3.0%; vanadium (V): 0.01% to 0.12%; aluminum (Al): 0.01% to 0.3%; chromium (Cr): greater than 0% and 0.5% or less; titanium (Ti): greater than 0% and 0.1% or less; phosphorus (P): greater than 0% and 0.02% or less; sulfur (S): greater than 0% and 0.01% or less; and boron (B): 0.001% to 0.005%, based on % by weight, and the remainder being Fe and other unavoidable impurities.

[0058] The final microstructure contains tempered martensite with a volume fraction of 90% or more, and the remainder may be martensite and bainite. In a final microstructure of an embodiment, the volume fraction of tempered martensite may be 100%. In a final microstructure of another embodiment, the volume fraction of tempered martensite may be 90%, and the volume fraction of martensite and bainite may be 10%.

[0059] It is characterized in that the average spacing between precipitates in the tempered martensite is 300 nm or more, the average size of the precipitate is 200 nm or less, and the number of precipitates having an average size of 40 nm or less is 25 or more based on an area of $20 \mu\text{m}^2$ in the final microstructure. When the fraction of tempered martensite in the ultra-high strength cold-rolled steel sheet base of this embodiment is A and the fraction occupied by precipitate is B, the relationship $B/A < 0.01$ is satisfied.

[0060] The Prior Austenite Grain Size (PAGS) of the ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention implemented by performing the above-described steps may be $12 \mu\text{m}$ or less. If it is coarser than this, it is difficult to confirm the effect of improving the hydrogen embrittlement characteristics by refining the grains.

[0061] To satisfy the target tensile properties and hydrogen embrittlement characteristics of the ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention, PAGS is composed of small and fine tempered martensite (90% or more) and martensite and bainite (remainder) structures.

[0062] The ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention implemented by performing the above-described steps has a soft region, which has a hardness of less than 85% of the average hardness of the base material of the cold-rolled steel sheet, in the surface layer, and a ratio of the thickness of the soft region to the thickness of the base material may be 0.03 to 0.10. The hardness of the steel sheet was measured at $30 \mu\text{m}$ intervals from the surface to the center of the plate thickness cross-section using a Vickers tester with a load of 50 g. When the hardness of the base material is Hv_M and the hardness of the soft part (decarburized part) region is Hv_S , the soft region of the steel sheet satisfying the relationship of $Hv_M/Hv_S < 0.85$ was identified.

[0063] That is, the soft region of the steel sheet surface layer is a region having less than $0.85 \times Hv_M$, and since the difference in hardness between the surface layer and the base material is small when Hv_M/Hv_S is greater than 0.85, it is difficult to have an improvement effect on the bendability characteristics, so it is set to less than 0.85. The hardness of the steel sheet base material was measured using the average of 5 points in the region of $1/4$ of the plate thickness. In the present invention, when the thickness of the base material is t_m and the thickness of the soft (decarburized) region is t_s , the relationship of $0.03 < t_s/t_m < 0.1$ is satisfied. When the thickness of the soft region is too thin (0.03 or less), it is difficult to obtain the effect of improving the bendability, and when the thickness is greater than 0.1, it is difficult to secure the target properties.

[0064] It was confirmed that the ultra-high strength cold-rolled steel sheet according to an embodiment of the present invention implemented by performing the above-described steps has properties as follows: yield strength (YP): 1200 MPa or more, tensile strength (TS): 1500 MPa or more, elongation (EI): 7.0% or more, yield ratio: 70% or more, bendability (R/t): 2.5 or less and hydrogen embrittlement elongation reduction rate: 35% or less.

Experimental examples

[0065] Hereinafter, preferred experimental examples are presented to help understand the present invention. However, the following experimental examples are only intended to help understand the present invention, and the present invention is not limited to the following experimental examples.

[0066] Table 1 shows the compositions (unit: % by weight, the remainder is iron) of steel according to the experimental examples of the present invention.

[0067] Referring to Table 1, the steel according to Example 1 satisfies the following composition ranges: carbon (C): 0.23% to 0.40%, silicon (Si): 0.05% to 1.0%, manganese (Mn): 0.5% to 3.0%, vanadium (V): 0.01% to 0.12%, aluminum (Al): 0.01% to 0.3%, chromium (Cr): greater than 0% and 0.5% or less, titanium (Ti): greater than 0% and 0.1% or less, phosphorus (P): greater than 0% and 0.02% or less, sulfur (S): greater than 0% and 0.01% or less, and boron (B): 0.001% to 0.005%, based on % by weight and the remainder being iron (Fe). However, the content of carbon in Comparative

Examples 1 and 2 was relatively low compared to Example 1 and Comparative Examples 3 and 4. Meanwhile, Comparative Examples 1 to 4 did not contain vanadium unlike Example 1.

[0068] Meanwhile, it was confirmed that the value of $[C] + [V] + [Cr] + [Mo] + [Nb]$ (where $[C]$, $[V]$, $[Cr]$, $[Mo]$ and $[Nb]$ in Example 1 are the % by weight values of carbon, vanadium, chromium, molybdenum and niobium) was smaller than 0.63, but the value of $[C] + [V] + [Cr] + [Mo] + [Nb]$ of Comparative Examples 3 and 4 was greater than 0.63 (Comparative Example 3: 0.686, Comparative Example 4: 0.631).

[0069] In the experimental examples of the present invention, Comparative Examples 1 to 4 and Example 1 were subjected to the same conditions within the ranges of the hot rolling (S10), cold rolling (S20) and post-cold rolling heat treatment (S40, S50, S60) described above. However, the annealing process (S32) of Comparative Examples 1 and 2 corresponds to the process ① shown in FIG. 2, and the annealing process (S32) of Comparative Examples 3 and 4 and Example 1 corresponds to the process ② shown in FIG. 2.

[Table 1]

	C	Si	Mn	P	S	V	Al	Cr	Mo	Nb	Ti	B
Comparative Example 1	0.233	0.182	1.18	0.02	0.0011	0	0.014	0	0	0.019	0.038	0.0014
Comparative Example 2	0.23	0.203	0.81	0.014	0.0021	0	0.024	0	0.05	0	0.043	0.0025
Comparative Example 3	0.296	0.393	1.015	0.01	0.0009	0	0.024	0.29	0.1	0	0.04	0.002
Comparative Example 4	0.301	0.391	1.02	0.01	0.0011	0	0.014	0.3	0	0.03	0.04	0.002
Example 1	0.286	0.39	1.014	0.01	0.0008	0.03	0.021	0.3	0	0	0.04	0.002

[0070] Tables 2 and 3 show the results of the property evaluation of steel according to the experimental examples of the present invention. In Table 3, the hydrogen embrittlement elongation reduction rate (%) was measured under hydrogen injection conditions of 5 mA and 1 hr.

[Table 2]

	YS (MPa)	TS (MPa)	T.EL (%)	YR (%)	R/t
Comparative Example 1	1290	1571	6.1	82.1	0.7
Comparative Example 2	1285	1543	5.8	83.3	0.5
Comparative Example 3	1324	1749	7.2	75.7	2.2
Comparative Example 4	1339	1745	7.8	76.7	2.0
Example 1	1290	1726	8.3	74.8	2.0

[Table 3]

	Hv _s /Hv _m	t _s /t _m	Average distance of precipitate (nm)	Number of precipitates of 40 nm or less (based on 20 μm ²)	Hydrogen embrittlement elongation reduction rate (%)	PAGS (μm)
Comparative Example 1	0.63 to 0.81	0.075	320.6	20	79	13.5
Comparative Example 2	0.61 to 0.79	0.078	365.3	19	68	13.2
Comparative Example 3	0.74 to 0.83	0.049	386.8	16	72	7.40
Comparative Example 4	0.72 to 0.80	0.050	313.2	17	84	9.69
Example 1	0.72 to 0.82	0.052	499.1	54	27	8.87

[0071] Referring to Tables 2 and 3, Comparative Examples 1 and 2 has a low carbon (C) content compared to the alloy

amount of Example 1, thereby having low physical properties. In addition, the main characteristic is that the process ② shown in FIG. 2 was not applied during the annealing section, and a general heat treatment was performed as in the process ① shown in FIG. 2. As a result, the bendability was good because the difference in the hardness of the soft part was large and the thickness occupied by the soft part was large, but the processing time increased by performing general maintenance heat treatment, and as it is maintained at a relatively high temperature, the Prior Austenite Grain Size (PAGS) increased and the hydrogen embrittlement elongation reduction rate was large. Comparative Examples 3 and Comparative Example 4 showed a smaller Prior Austenite Grain Size (PAGS) than Comparative Examples 1 and 2 due to the increased content of Nb and Mo. The reason why hydrogen embrittlement was not improved even though the Prior Austenite Grain Size (PAGS) was reduced is as follows. Precipitates are generally precipitated by Mo, Nb, V, Ti, etc., but as the content of the corresponding elements increases, they are not dissolved. It was confirmed that the value of $[C] + [V] + [Cr] + [Mo] + [Nb]$ of Comparative Examples 3 and 4 exceeded 0.63 (Comparative Example 3: 0.686, Comparative Example 4: 0.631). That is, as carbides that are not dissolved in water increase during reheating, coarse precipitates are precipitated. As the precipitate becomes coarser, the average distance becomes shorter and the number of precipitates decreases, which does not contribute significantly to improving hydrogen embrittlement.

[0072] On the other hand, it was confirmed in Example 1 that relatively uniformly sized fine precipitates were evenly distributed, the conditions (yield strength (YP): 1200 MPa or more, tensile strength (TS): 1500 MPa or more, elongation (El): 7.0% or more, yield ratio: 70% or more, and bendability (R/t): 2.5 or less) proposed in the present invention were satisfied, and the hydrogen embrittlement was significantly improved (hydrogen embrittlement elongation reduction rate: 35% or less).

[0073] FIG. 3 is a photograph of a representative final microstructure of the ultra-high strength cold-rolled steel sheet according to Example 1 of the present invention, and FIG. 4 is a photograph of a precipitate observed in the microstructure of the ultra-high strength cold-rolled steel sheet according to Example 1 of the present invention.

[0074] Referring to FIGS. 3 and 4, it can be confirmed that the final microstructure of the ultra-high strength cold-rolled steel sheet according to Example 1 of the present invention includes tempered martensite having a volume fraction of 90% or more, the average spacing between precipitates inside the tempered martensite is 300 nm or more, the average size of the precipitate is 200 nm or less, and the number of precipitates having an average size of 40 nm or less is 25 or more based on an area of $20 \mu\text{m}^2$ in the final microstructure.

[0075] The technical idea of the ultra-high strength cold-rolled steel sheet according to the present invention and a manufacturing method thereof has been described above. The example of the present invention relates to a method for manufacturing ultra-high strength steel using martensite similar to the comparative examples, but has the following differences and advantages.

[0076] An appropriate soft (decarburized) region can be obtained by replacing the annealing holding section with a temperature rise according to a quadratic function equation, thereby achieving an ultra-high strength steel sheet that satisfies a target bendability (R/t) of 2.5 or less and that satisfies an elongation reduction rate of 35% or less upon adding hydrogen through the suppression of coarsening of the Prior Austenite Grain Size (PAGS). In addition, tempering during cooling can be suppressed through the first and second rapid cooling after the slow cooling, and homogeneous tempered martensite can be implemented through the subsequent tempering. In addition, an ultra-high-strength steel sheet having a yield strength of 1200 MPa or more, a tensile strength of 1500 MPa or more, and a high yield ratio (70% or more) can be realized and, by replacing the holding section in the annealing section with a partial temperature rise, the processing time can be shortened by about 10% or more, thereby improving productivity.

[0077] It will be apparent to a person skilled in the art that the technical idea of the present invention described above is not limited to the above-described embodiments and the attached drawings, and that various substitutions, modifications, and changes are possible within a scope that does not depart from the technical idea of the present invention.

Claims

1. An ultra-high strength cold-rolled steel sheet, comprising: carbon (C): 0.23% to 0.40%; silicon (Si): 0.05% to 1.0%; manganese (Mn): 0.5% to 3.0%; vanadium (V): 0.01% to 0.12%; aluminum (Al): 0.01% to 0.3%; chromium (Cr): greater than 0% and 0.5% or less; titanium (Ti): greater than 0% and 0.1% or less; phosphorus (P): greater than 0% and 0.02% or less; sulfur (S): greater than 0% and 0.01% or less; and boron (B): 0.001% to 0.005%, based on % by weight,; and a remainder being Fe and other unavoidable impurities, wherein a final microstructure comprises tempered martensite having a volume fraction of 90% or more, wherein an average spacing between precipitates in the tempered martensite is 300 nm or more, an average size of the precipitates is 200 nm or less, and the number of precipitates having an average size of 40 nm or less is 25 or more based on an area of $20 \mu\text{m}^2$ in the final microstructure.

2. The ultra-high strength cold-rolled steel sheet according to claim 1, wherein a surface layer of the cold-rolled steel

sheet comprises a soft region having a hardness less than 85% of an average hardness of a base material, wherein a ratio of a thickness of the soft region to a thickness of the base material is 0.03 to 0.10.

3. The ultra-high strength cold-rolled steel sheet according to claim 1, wherein the cold-rolled steel sheet has a Prior Austenite Grain Size (PAGS) of 12 μm or less.

4. The ultra-high strength cold-rolled steel sheet according to claim 1, further comprising: molybdenum (Mo): 0.01% to 0.3% or niobium (Nb): 0.01% to 0.1%, based on % by weight.

5. The ultra-high strength cold-rolled steel sheet according to claim 1 or 4, wherein a value of $[\text{C}] + [\text{V}] + [\text{Cr}] + [\text{Mo}] + [\text{Nb}]$ (where $[\text{C}]$, $[\text{V}]$, $[\text{Cr}]$, $[\text{Mo}]$ and $[\text{Nb}]$ are weight % values of carbon, vanadium, chromium, molybdenum and niobium) of the cold-rolled steel sheet is smaller than 0.63.

6. The ultra-high strength cold-rolled steel sheet according to claim 1, wherein the ultra-high strength cold-rolled steel sheet has a yield strength (YP) of 1200 MPa or more, a tensile strength (TS) of 1500 MPa or more, an elongation (El) of 7.0% or more, a yield ratio of 70% or more, a bendability (R/t) of 2.5 or less and a hydrogen embrittlement elongation reduction rate of 35% or less.

7. A method of manufacturing an ultra-high strength cold-rolled steel sheet, the method comprising:

hot-rolling steel comprising carbon (C): 0.23% to 0.40%; silicon (Si): 0.05% to 1.0%; manganese (Mn): 0.5% to 3.0%; vanadium (V): 0.01% to 0.12%; aluminum (Al): 0.01% to 0.3%; chromium (Cr): greater than 0% and 0.5% or less; titanium (Ti): greater than 0% and 0.1% or less; phosphorus (P): greater than 0% and 0.02% or less; sulfur (S): greater than 0% and 0.01% or less; and boron (B): 0.001% to 0.005%, based on % by weight,; and a remainder being Fe and other unavoidable impurities to provide a hot-rolled steel sheet;
cold-rolling the hot-rolled steel sheet to provide a cold-rolled steel sheet;
heating the cold-rolled steel sheet;
annealing the heated cold-rolled steel sheet;
cooling the annealed cold-rolled steel sheet; and
reheating and tempering the cooled cold-rolled steel sheet,
wherein, when annealing the cold-rolled steel sheet, an annealing temperature is gradually increased in a temperature range of 750°C to 950°C, without a section in which a constant temperature is maintained, until cooling the cold-rolled steel sheet.

8. The method according to claim 7, wherein, in the annealing of the cold-rolled steel sheet, an annealing temperature (T) satisfies a relationship of Equation 1 below dependent upon time (t):

[Equation 1]

$$\text{Annealing temperature (T)} = A \times t^2 + B \times t + C$$

(where A, B and C constants satisfying $-0.007 < A < -0.005$, $2 < B < 3$, and $500 < C < 700$).

9. The method according to claim 7, wherein, in the heating of the cold-rolled steel sheet, a heating rate is 3°C/sec or more, and
in the annealing of the cold-rolled steel sheet, a heating rate is less than 3°C/sec.

10. The method according to claim 7, wherein the hot rolling is performed under conditions of a reheating temperature (SRT) of 1180°C to 1300°C, a finish delivery temperature (FDT) of 800°C to 950°C, and a coiling temperature (CT) of 500°C to 700°C.

11. The method according to claim 7, wherein the cooling of the annealed cold-rolled steel sheet comprises:

slow-cooling the annealed cold-rolled steel sheet up to 700 to 800°C at a cooling rate of 3°C/sec to 15°C/sec;
performing first rapid cooling for the slowly cooled cold-rolled steel sheet up to 300°C to 350°C at a cooling rate of 80°C/sec to 150°C/sec; and

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performing second rapid cooling for the cold-rolled steel sheet, which has been subjected to the first rapid cooling, up to room temperature to 300°C at a cooling rate of 30°C/sec to 90°C/sec.

- 5 **12.** The method according to claim 7, wherein the reheating and tempering of the cooled cold-rolled steel sheet comprises reheating the cold-rolled steel sheet, which has been subjected to the second rapid cooling, and tempering by maintaining at 150°C to 350°C for 30 to 300 sec.

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FIG. 1

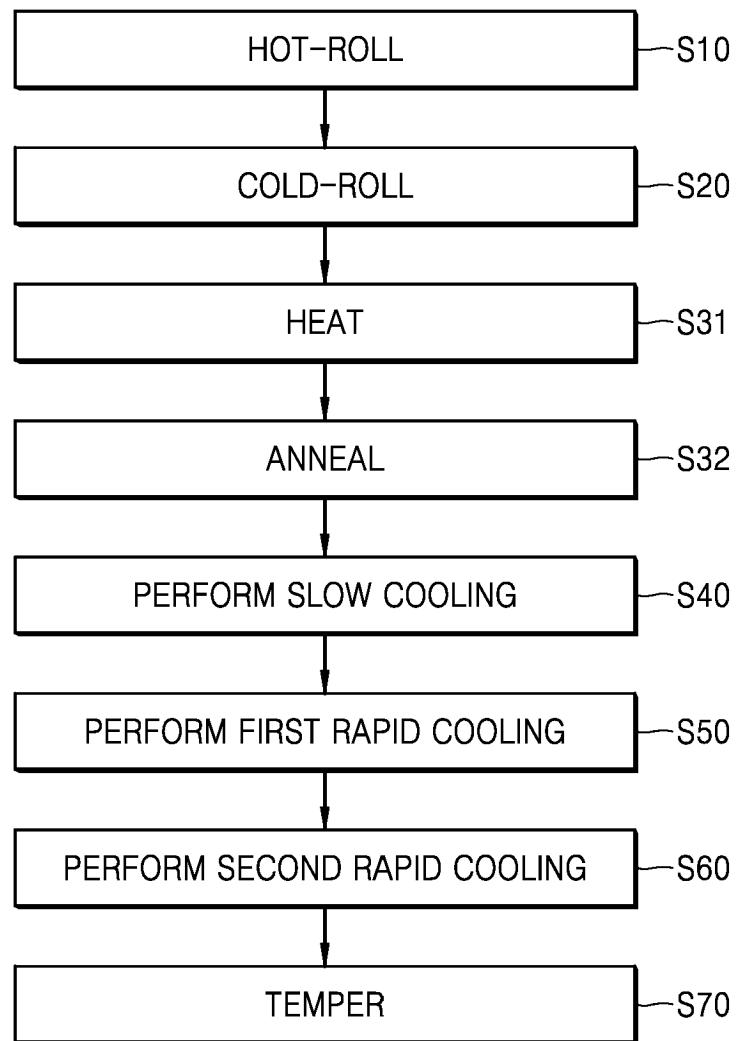


FIG. 2

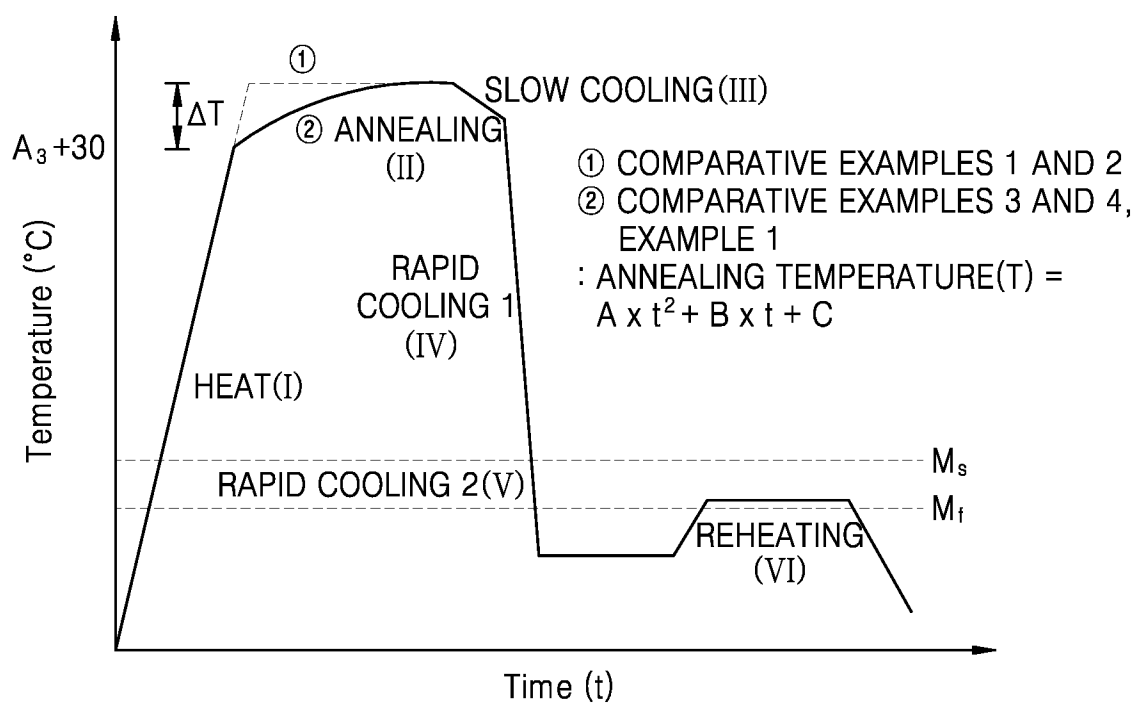
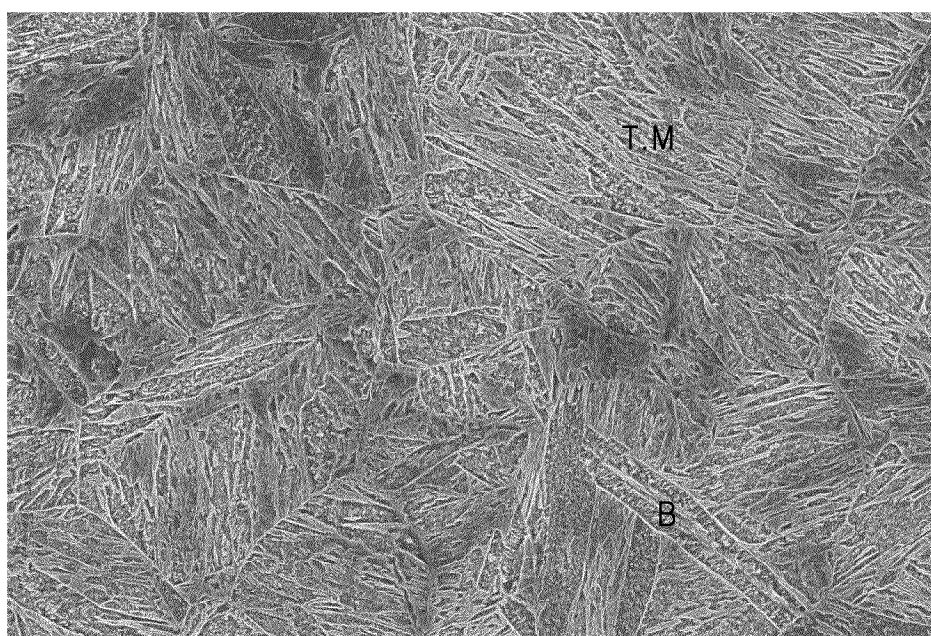
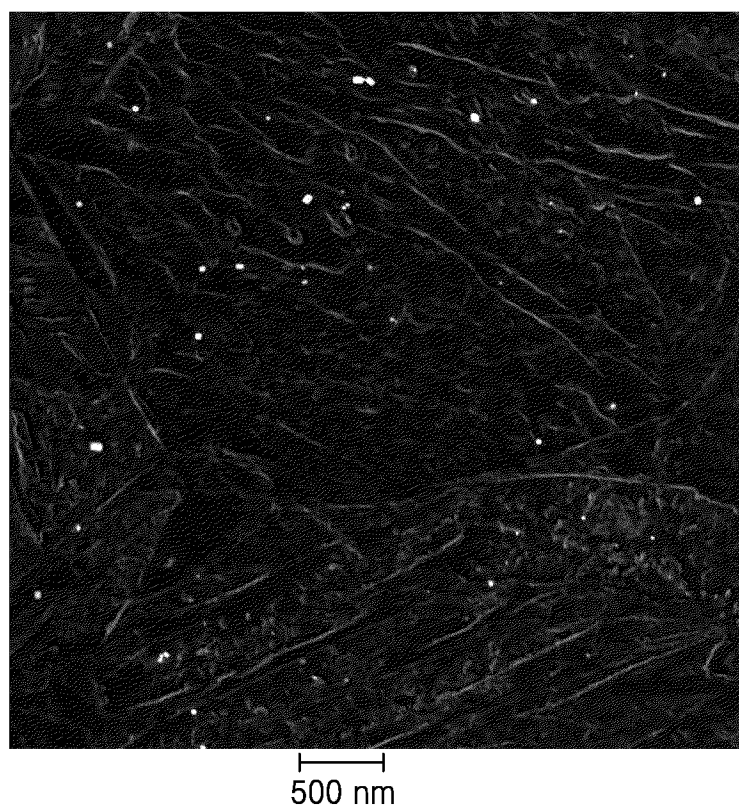


FIG. 3



2 μm

FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/019639

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/38(2006.01)i; C22C 38/24(2006.01)i; C22C 38/28(2006.01)i; C22C 38/32(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 38/38(2006.01); C21D 8/02(2006.01); C22C 38/00(2006.01); C22C 38/02(2006.01); C22C 38/04(2006.01);
C22C 38/06(2006.01); C22C 38/14(2006.01); C22C 38/32(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: 냉연강판(cold rolled steel plate), 열연(hot rolling), 냉연(cold rolling), 승온(temperature rising), 소둔(annealing), 서냉(slow cooling), 급냉(quenching), 템퍼링(tempering), 수소취성(hydrogen embrittlement)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X A	KR 10-2020-0118445 A (TATA STEEL NEDERLAND TECHNOLOGY B.V.) 15 October 2020 (2020-10-15) See paragraphs [0053], [0080] and [0091]-[0092]; claim 1; and figure 4.	7-10 1-6,11-12
A	KR 10-2009-0122346 A (CORUS STAAL B.V.) 27 November 2009 (2009-11-27) See paragraphs [0066]-[0071]; claim 10; and figure 2.	1-12
A	WO 2014-019964 A1 (TATA STEEL NEDERLAND TECHNOLOGY BV) 06 February 2014 (2014-02-06) See claim 1; and figure 1.	1-12
A	KR 10-2403767 B1 (HYUNDAI STEEL COMPANY) 30 May 2022 (2022-05-30) See paragraphs [0058]-[0099]; and figure 1.	1-12



Further documents are listed in the continuation of Box C.



See patent family annex.

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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

30 August 2023

Date of mailing of the international search report

30 August 2023

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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