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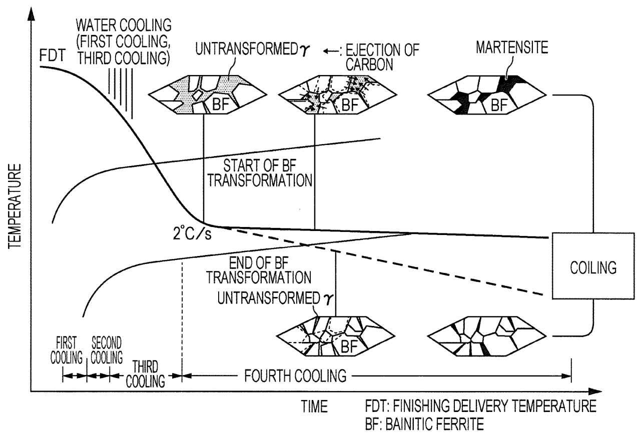
(54) **HOT-ROLLED STEEL SHEET AND METHOD FOR MANUFACTURING SAME**

(57) There is provided a high-strength hot-rolled steel sheet having high low-temperature toughness and a low yield ratio that is suitable for a steel pipe material. The hot-rolled steel sheet has a composition that contains C: 0.03% to 0.10%, Si: 0.01% to 0.50%, Mn: 1.4% to 2.2%, P: 0.025% or less, S: 0.005% or less, Al: 0.005% to 0.10%, Nb: 0.02% to 0.10%, Ti: 0.001% to 0.030%, Mo: 0.01% to 0.50%, Cr: 0.01% to 0.50%, and Ni: 0.01% to 0.50%. The composition preferably has Moeq in the range of 1.4% to 2.2%. The hot-rolled steel sheet includes an inner layer having a microstructure that contains a main phase and a second phase, the main phase being bainitic ferrite having an average grain size of 10 μm or less, the second phase having an area fraction in the range of 1.4% to 15% and containing massive martensite having an aspect ratio of less than 5.0. The hot-rolled steel sheet includes an outer layer having a microstructure that contains a tempered martensite phase or a tempered martensite phase and a tempered bainite phase.

FIG. 1



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Description

Technical Field

[0001] The present invention relates to a high-strength hot-rolled steel sheet with a low yield ratio suitable as a material for spiral steel pipes and electric-resistance-welded (ERW) pipes for use in line pipes, and a method for manufacturing the high-strength hot-rolled steel sheet with a low yield ratio. In particular, the present invention relates to maintaining a low yield ratio and high low-temperature toughness while preventing a decrease in yield strength after pipe manufacturing.

Background Art

[0002] Spiral steel pipes are manufactured by helically winding a steel sheet. Large-diameter steel pipes can be efficiently manufactured using this process. Thus, in recent years, spiral steel pipes have been widely used as line pipes for crude oil and natural gas transport. In particular, in long-distance pipelines, transport pressure is being increased to improve transportation efficiency. Furthermore, since many oil wells and gas wells are located in cold districts, long-distance pipelines often pass through cold districts. Thus, there is a demand for high-strength and high-toughness line pipes. There is also a demand for line pipes having a low yield ratio from the perspective of buckling resistance and earthquake resistance. The yield ratio of spiral steel pipes in the longitudinal direction is not significantly changed by pipe manufacturing and is substantially the same as the yield ratio of the hot-rolled steel sheet material. Thus, in order to lower the yield ratio of line pipes made of spiral steel pipes, the yield ratio of the hot-rolled steel sheet material must be lowered.

[0003] Facing such demands, for example, Patent Literature 1 describes a method for manufacturing a hot-rolled steel sheet having high low-temperature toughness, a low yield ratio, and high tensile strength for use in line pipes. In a technique described in Patent Literature 1, a hot-rolled steel sheet is manufactured by heating a steel slab to a temperature in the range of 1180°C to 1300°C, the steel slab containing, on a weight percent basis, C: 0.03% to 0.12%, Si: 0.50% or less, Mn: 1.70% or less, Al: 0.070% or less, and at least one of Nb: 0.01% to 0.05%, V: 0.01% to 0.02%, and Ti: 0.01% to 0.20%, hot-rolling the steel slab at a rough-rolling finishing temperature in the range of 950°C to 1050°C and a finishing delivery temperature in the range of 760°C to 800°C, cooling the hot-rolled sheet at a cooling rate in the range of 5°C to 20°C/s, starting air cooling at a temperature of more than 670°C, holding the temperature for 5 to 20 s, cooling the hot-rolled sheet at a cooling rate of 20°C/s or more, and coiling the hot-rolled sheet at a temperature of 500°C or less. The technique described in Patent Literature 1 can be used to manufacture a hot-rolled steel sheet having a tensile strength of 60 kg/mm^2 or more (590 MPa or more), a yield ratio of 85% or less, and high toughness represented by a fracture transition temperature of -60°C or less.

[0004] Patent Literature 2 describes a method for manufacturing a high-strength hot-rolled steel sheet with a low yield ratio for use in pipes. A technique described in Patent Literature 2 is a method for manufacturing a hot-rolled steel sheet that includes heating steel to a temperature in the range of 1000°C to 1300°C, the steel containing C: 0.02% to 0.12%, Si: 0.1% to 1.5%, Mn: 2.0% or less, Al: 0.01% to 0.10%, and Mo + Cr: 0.1% to 1.5%, completing hot rolling at a temperature in the range of 750°C to 950°C, cooling the hot-rolled steel sheet to a coiling temperature at a cooling rate in the range of 10°C to 50°C/s, and coiling the hot-rolled steel sheet at a temperature in the range of 480°C to 600°C. The technique described in Patent Literature 2 can be used to manufacture a hot-rolled steel sheet composed mainly of ferrite, containing martensite having an area fraction in the range of 1% to 20%, having a yield ratio of 85% or less, and having a small decrease in yield strength after pipe manufacturing, without performing rapid cooling from the austenite temperature range.

[0005] Patent Literature 3 describes a method for manufacturing an electric-resistance-welded (ERW) pipe having high low-temperature toughness and a low yield ratio. In a technique described in Patent Literature 3, an electric-resistance-welded (ERW) pipe is manufactured by hot-rolling a slab that contains, on a mass percent basis, C: 0.01% to 0.09%, Si: 0.50% or less, Mn: 2.5% or less, Al: 0.01% to 0.10%, Nb: 0.005% to 0.10%, and one or two or more of Mo: 0.5% or less, Cu: 0.5% or less, Ni: 0.5% or less, and Cr: 0.5% or less such that the Mn, Si, P, Cr, Ni, and Mo content relation Mneq satisfies 2.0 or more, cooling the hot-rolled sheet to a temperature in the range of 500°C to 650°C at a cooling rate of 5°C/s or more, coiling the hot-rolled sheet, holding the hot-rolled sheet at a temperature in this temperature range for 10 min or more, cooling the hot-rolled sheet to a temperature of less than 500°C, and forming the hot-rolled steel sheet into a electric-resistance-welded (ERW) pipe. The technique described in Patent Literature 3 can be used to manufacture an electric-resistance-welded (ERW) pipe that has a microstructure containing bainitic ferrite as a main phase, 3% or more martensite, and optionally 1% or more retained austenite, has a fracture transition temperature of -50°C or less, and has high low-temperature toughness and high plastic strain absorbing capability.

[0006] Patent Literature 4 describes a high-toughness steel plate having a low yield ratio. A technique described in Patent Literature 4 can be used to manufacture a high-toughness steel plate having a low yield ratio by heating a slab

containing C: 0.03% to 0.15%, Si: 1.0% or less, Mn: 1.0% to 2.0%, Al: 0.005% to 0.060%, Ti: 0.008% to 0.030%, N: 0.0020% to 0.010%, and O: 0.010% or less to a temperature preferably in the range of 950°C to 1300°C, hot-rolling the slab at a rolling reduction of 10% or more in the temperature range of (Ar3 transformation point + 100°C) to (Ar3 transformation point + 150°C) and at a finish-rolling temperature of 800°C to 700°C, starting accelerated cooling of the hot-rolled plate
at a temperature of (the finish-rolling temperature - 50°C) or more, water cooling the hot-rolled plate to a temperature in the range of 400°C to 150°C at an average cooling rate in the range of 5°C to 50°C/s, and then air cooling the hot-rolled plate. The hot-rolled plate has a mixed microstructure of ferrite having an average grain size in the range of 10 to 50 μm and bainite in which martensite-austenite constituent are dispersed and constitute 1% to 20% by area. The shape (rod-like or massive, as described below) of the martensite-austenite constituent is not described.

Citation List

Patent Literature

[0007]

PTL 1: Japanese Unexamined Patent Application Publication No. 63-227715
PTL 2: Japanese Unexamined Patent Application Publication No. 10-176239
PTL 3: Japanese Unexamined Patent Application Publication No. 2006-299413
PTL 4: Japanese Unexamined Patent Application Publication No. 2010-59472

Summary of Invention

Technical Problem

[0008] However, in the technique described in Patent Literature 1, because of the high cooling rate before and after air cooling, particularly after air cooling, the cooling rate and the cooling stop temperature must be rapidly and properly controlled. In particular, the manufacture of hot-rolled steel sheet with a large thickness needs large-scale cooling equipment. Furthermore, a hot-rolled steel sheet manufactured by using the technique described in Patent Literature 1 has a microstructure composed mainly of soft polygonal ferrite, and it is difficult to achieve the desired high strength.
[0009] The technique described in Patent Literature 2 has a problem in that a decrease in yield strength after pipe manufacturing is still observed, and it is sometimes difficult to meet the recent demand for high steel pipe strength.
[0010] The technique described in Patent Literature 3 cannot consistently meet a recent high low-temperature toughness specification for cold districts represented by a fracture transition temperature vTrs of -80°C or less.
[0011] A steel plate manufactured by using the technique described in Patent Literature 4 has low toughness represented by a fracture transition temperature vTrs as low as approximately -30°C to -41°C and cannot meet the recent demand for further improved toughness.
[0012] In recent years, there has been another demand for materials for high-strength thick-walled steel pipes in order to efficiently transport crude oil. However, there are problems of increased amounts of alloying elements due to reinforcement and necessity of rapid cooling in a process of manufacturing a hot-rolled steel sheet due to an increased thickness. Since hot-rolled steel sheets are conveyed through a water cooling zone having a limited length at a high speed before coiling, hot-rolled steel sheets having a greater thickness require stronger cooling. Thus, the steel sheets have excessively high surface hardness.
[0013] In particular, for example, in the manufacture of a hot-rolled steel sheet having a large thickness of 10 mm or more, the hot-rolled steel sheet is conveyed at a high speed in the range of 100 to 250 mpm (meter per minute) in finish rolling and is conveyed through a cooling zone at substantially the same high speed after the finish rolling. Thus, hot-rolled steel sheets having a greater thickness require cooling with a higher heat transfer coefficient. This results in hot-rolled steel sheets having excessively high surface hardness, higher hardness on the surface than in the interior thereof, and an uneven hardness distribution. Such an uneven hardness distribution can be responsible for variations in the characteristics of steel pipes. Such an uneven surface hardness distribution results from the holding of a steel sheet surface in a transition boiling temperature range (a boundary between film boiling and nucleate boiling) in the cooling process. To avoid this, it is necessary to maintain the steel sheet surface temperature at more than 500°C. In the case of steel sheets having a large thickness, however, because of an excessively low internal cooling rate, desired inner layer microstructures cannot be formed. Although the surface hardness can be made uniform by decreasing the steel sheet surface temperature below the transition boiling range, this results in a maximum cross section hardness of more than 300 points in terms of HV 0.5. Such increased hardness results in not only undesired pipe shapes after pipe manufacturing but also undesired characteristics of steel pipes and even impossibility of pipe manufacturing.

[0014] The present invention aims to solve such problems of the related art and provide a material for steel pipes, particularly a high-strength hot-rolled steel sheet that is suitable for spiral steel pipes, that can maintain its strength after spiral pipe manufacturing, and that has high low-temperature toughness and a low yield ratio, without performing complicated heat treatment or large-scale modification of equipment. In particular, it is an object of the present invention to provide a high-strength hot-rolled steel sheet having a thickness of 8 mm or more (more preferably 10 mm or more) and 50 mm or less (more preferably 25 mm or less) and having high low-temperature toughness and a low yield ratio. The term "high-strength", as used herein, refers to a yield strength of 480 MPa or more at an angle of 30 degrees with the rolling direction and a tensile strength of 600 MPa or more in the sheet width direction. The term "high low-temperature toughness", as used herein, refers to a fracture transition temperature vTrs of -80°C or less in a Charpy impact test. The term "low yield ratio", as used herein, refers to a case where a steel sheet has a continuous yielding type stress-strain curve and a yield ratio of 85% or less. The term "steel sheets" includes steel sheets and steel strips.

Solution to Problem

[0015] In order to achieve the objects, the present inventors extensively studied various factors that can affect steel pipe strength and steel pipe toughness after pipe manufacturing. As a result, the present inventors found that strength reduction due to pipe manufacturing is caused by a decrease in yield strength due to the Bauschinger effect on the inner surface side of the pipe subjected to compressive stress and by the loss of yield elongation on the outer surface side of the pipe subjected to tensile stress.

[0016] As a result of further investigation, the present inventors found that the use of a steel sheet having a microstructure that contains fine bainitic ferrite as a main phase and hard massive martensite finely dispersed in the bainitic ferrite can suppress strength reduction after pipe manufacturing, particularly after spiral pipe manufacturing, and provide a steel pipe having a low yield ratio of 85% or less and high toughness. The present inventors found that such a microstructure can improve the work hardening ability of steel pipe materials, that is, steel sheets, sufficiently increase strength owing to work hardening on the outer surface side of the pipe during pipe manufacturing, and suppress strength reduction after pipe manufacturing, particularly after spiral pipe manufacturing. Furthermore, the present inventors found that finely dispersed massive martensite can significantly improve toughness.

[0017] The present inventors also found that the surface microstructure of steel sheets composed of a tempered martensite single phase or a mixed phase of tempered martensite and tempered bainite is effective in preventing an uneven increase in the surface hardness of the steel sheets and providing steel pipes having the desired pipe shape and uniform ductility after pipe manufacturing.

[0018] The present invention has been accomplished on the basis of these findings after further consideration. The aspects of the present invention are as follows:

(1) A hot-rolled steel sheet having a composition containing, on a mass percent basis, C: 0.03% to 0.10%, Si: 0.01% to 0.50%, Mn: 1.4% to 2.2%, P: 0.025% or less, S: 0.005% or less, Al: 0.005% to 0.10%, Nb: 0.02% to 0.10%, Ti: 0.001% to 0.030%, Mo: 0.01% to 0.50%, Cr: 0.01% to 0.50%, Ni: 0.01% to 0.50%, and a remainder of Fe and incidental impurities, wherein the hot-rolled steel sheet includes an inner layer having a microstructure that contains a main phase and a second phase, the main phase being bainitic ferrite having an average grain size of 10 μm or less, the second phase having an area fraction in the range of 1.4% to 15% and containing massive martensite having an aspect ratio of less than 5.0, and the hot-rolled steel sheet includes an outer layer having a microstructure that contains a tempered martensite phase or a tempered martensite phase and a tempered bainite phase.

(2) The hot-rolled steel sheet according to (1), wherein the composition has Moeq defined by the following formula (1) in the range of 1.4% to 2.2% by mass:

$$\text{Moeq}\ (\%) = \text{Mo} + 0.36\text{Cr} + 0.77\text{Mn} + 0.07\text{Ni} \quad (1)$$

(wherein Mn, Ni, Cr, and Mo denote the corresponding element contents (% by mass)).

(3) The hot-rolled steel sheet according to (1) or (2), further containing, on a mass percent basis, one or two or more selected from Cu: 0.50% or less, V: 0.10% or less, and B: 0.0005% or less.

(4) The hot-rolled steel sheet according to any one of (1) to (3), further containing Ca: 0.0005% to 0.0050% by mass.

(5) The hot-rolled steel sheet according to any one of (1) to (4), wherein the massive martensite has a maximum size of 5.0 μm or less and an average size in the range of 0.5 to 3.0 μm.

(6) The hot-rolled steel sheet according to any one of (1) to (5), wherein the hardness of the hot-rolled steel sheet at a depth of 0.5 mm from a surface thereof in the thickness direction is 95% or less of the maximum hardness in the thickness direction.

(7) A method for manufacturing a hot-rolled steel sheet including subjecting steel to a hot-rolling step, a cooling step, and a coiling step to form the hot-rolled steel sheet, wherein the steel contains, on a mass percent basis, C: 0.03% to 0.10%, Si: 0.01% to 0.50%, Mn: 1.4% to 2.2%, P: 0.025% or less, S: 0.005% or less, Al: 0.005% to 0.10%, Nb: 0.02% to 0.10%, Ti: 0.001% to 0.030%, Mo: 0.01% to 0.50%, Cr: 0.01% to 0.50%, Ni: 0.01% to 0.50%, and a remainder of Fe and incidental impurities, the hot-rolling step includes heating the steel to a heating temperature in the range of 1050°C to 1300°C, rough-rolling the heated steel to form a sheet bar, and finish-rolling the sheet bar such that the cumulative rolling reduction at a temperature of 930°C or less is 50% or more, thereby forming a hot-rolled steel sheet, the cooling step includes first cooling, second cooling, third cooling, and fourth cooling in this order, the first cooling being started immediately after completion of the finish rolling and including cooling the hot-rolled steel sheet to a martensitic transformation start temperature (Ms point) or less at an average cooling rate of 100°C/s or more with respect to surface temperature, the second cooling including, after completion of the first cooling, holding the hot-rolled steel sheet for 1 s or more at a surface temperature of 600°C or more, the third cooling including, after completion of the second cooling, cooling the hot-rolled steel sheet to a cooling stop temperature in the range of 600°C to 450°C at an average cooling rate in the range of 5°C to 30°C/s with respect to the temperature at half the thickness of the hot-rolled steel sheet, the fourth cooling including cooling the hot-rolled steel sheet from the cooling stop temperature of the third cooling to a coiling temperature at an average cooling rate of 2°C/s or less with respect to the temperature at half the thickness of the hot-rolled steel sheet or alternatively holding the hot-rolled steel sheet at a temperature in the range of the cooling stop temperature of the third cooling to the coiling temperature for 20 s or more, and the coiling step includes coiling the hot-rolled steel sheet at a surface temperature of 450°C or more.

(8) The method for manufacturing a hot-rolled steel sheet according to (7), wherein the composition has Moeq defined by the following formula (1) in the range of 1.4% to 2.2% by mass:

$$\mathrm{Moeq}\ (\%) = \mathrm{Mo} + 0.36\mathrm{Cr} + 0.77\mathrm{Mn} + 0.07\mathrm{Ni} \quad (1)$$

(wherein Mn, Ni, Cr, and Mo denote the corresponding element contents (% by mass)).

(9) The method for manufacturing a hot-rolled steel sheet according to (7) or (8), wherein the hot-rolled steel sheet further contains, on a mass percent basis, one or two or more selected from Cu: 0.50% or less, V: 0.10% or less, and B: 0.0005% or less.

(10) The method for manufacturing a hot-rolled steel sheet according to any one of (7) to (9), wherein the hot-rolled steel sheet further contains Ca: 0.0005% to 0.0050% by mass.

Advantageous Effects of Invention

[0019] The present invention can provide a high-strength hot-rolled steel sheet having high low-temperature toughness and a low yield ratio that is particularly suitable as a material for spiral steel pipes. The hot-rolled steel sheet can maintain strength after pipe manufacturing, does not have an uneven surface hardness distribution, has low cross section hardness, has the desired pipe shape and uniform ductility in the pipe manufacturing, and has a yield strength of 480 MPa or more at an angle of 30 degrees with the rolling direction, a tensile strength of 600 MPa or more in the sheet width direction, a fracture transition temperature vTrs of -80°C or less in a Charpy impact test, and a yield ratio of 85% or less. A high-strength hot-rolled steel sheet with a low yield ratio according to the present invention can be easily manufactured at low cost without particular heat treatment. Thus, the present invention has significant industrial advantages. The present invention also has the advantage that electric-resistance-welded (ERW) pipes for use in line pipes laid using a reel barge method or line pipes that require earthquake resistance can be easily manufactured at low cost. The present invention also has the advantage that a high-strength hot-rolled steel sheet with a low yield ratio according to the present invention can be used as a material for manufacturing high-strength spiral steel pipe piles that serve as architectural members and harbor structure members having high earthquake resistance. The present invention also has the advantage that spiral steel pipes manufactured using such a hot-rolled steel sheet can be applied to high-value-added high-strength steel pipe piles because of their low yield ratios in the longitudinal direction of the pipes. Brief Description of Drawings

[0020] [Fig. 1] Fig. 1 is a schematic explanatory view illustrating the relationship between the formation of massive martensite and second cooling in cooling after hot rolling.

Description of Embodiments

[0021] The reason for limiting the composition of a hot-rolled steel sheet according to the present invention will be described below. Unless otherwise specified, the mass percentage is simply expressed in %.

C: 0.03% to 0.10%

[0022] C can precipitate as carbide and contribute to increased strength of steel sheets by precipitation hardening. C is also an element that can contribute to improved toughness of steel sheets by decreasing the crystal grain size. Furthermore, C can dissolve in steel, stabilize austenite, and promote the formation of untransformed austenite. These effects require a C content of 0.03% or more. However, a C content of more than 0.10% tends to result in the formation of coarse cementite at grain boundaries and low toughness. Thus, the C content is limited to the range of 0.03% to 0.10%, preferably 0.04% to 0.09%.

Si: 0.01% to 0.50%

[0023] Si can contribute to increased strength of steel sheets by solid-solution hardening. Si can also contribute to a low yield ratio by the formation of a hard second phase (for example, martensite). These effects require a Si content of 0.01% or more. However, a Si content of more than 0.50% results in significant formation of oxidized scale containing fayalite and a poor steel sheet appearance. Thus, the Si content is limited to the range of 0.01% to 0.50%, preferably 0.20% to 0.40%.

Mn: 1.4% to 2.2%

[0024] Mn can dissolve in steel, improve quenching hardenability, and promote the formation of martensite. Mn is also an element that can lower the bainitic ferrite transformation start temperature and contribute to improved toughness of steel sheets by decreasing the microstructure size. These effects require a Mn content of 1.4% or more. However, a Mn content of more than 2.2% results in a heat affected zone having low toughness. Thus, the Mn content is limited to the range of 1.4% to 2.2%. The Mn content preferably ranges from 1.6% to 2.0% in terms of stable formation of massive martensite.

P: 0.025% or less

[0025] P can dissolve in steel and contribute to increased strength of steel sheets, but lowers toughness. Thus, in the present invention, P is preferably minimized as an impurity. However, a P content of up to 0.025% is acceptable. Thus, the P content is limited to 0.025% or less, preferably 0.015% or less. Since an excessively low P content results in high refining costs, the P content is preferably approximately 0.001% or more.

S: 0.005% or less

[0026] S in steel can form coarse sulfide inclusions, such as MnS, and induce cracking of slabs. S also lowers the ductility of steel sheets. Such phenomena are noticeable at a S content of more than 0.005%. Thus, the S content is limited to 0.005% or less, preferably 0.004% or less. Although the S content may be 0%, an excessively low S content results in high refining costs. Thus, the S content is preferably approximately 0.0001% or more.

Al: 0.005% to 0.10%

[0027] Al can act as a deoxidizing agent. Al is an element that is effective in fixing N, which is responsible for strain aging. These effects require an Al content of 0.005% or more. However, an Al content of more than 0.10% results in a high oxide content of steel and low toughness of base materials and welds. When steel, such as a slab, or a steel sheet is heated in a furnace, Al tends to form a nitride surface layer, which may increase the yield ratio. Thus, the Al content is limited to the range of 0.005% to 0.10%, preferably 0.08% or less.

Nb: 0.02% to 0.10%

[0028] Nb can dissolved in steel or precipitate as carbonitride, can suppress coarsening and recrystallization of austenite grains, and allows rolling of austenite in a un-recrystallization temperature range. Nb is also an element that can form fine carbide or carbonitride precipitates and contribute to increased strength of steel sheets. During cooling after hot rolling, Nb can precipitate as carbide or carbonitride on dislocations introduced by hot rolling, act as a nucleus for $\gamma \rightarrow \alpha$ transformation, promote the formation of bainitic ferrite in grains, and contribute to the formation of fine massive untransformed austenite, which results in the formation of fine massive martensite. These effects require a Nb content of 0.02% or more. However, an excessively high Nb content of more than 0.10% may result in high deformation resistance in hot rolling, thus making hot rolling difficult. Furthermore, an excessively high Nb content of more than 0.10% results in a bainitic ferrite main phase having a high yield strength, thereby making it difficult to achieve a yield ratio of 85% or less. Thus, the Nb content is limited to the range of 0.02% to 0.10%, preferably 0.03% to 0.07%.

Ti: 0.001% to 0.030%

[0029] Ti can fix N as nitride and contribute to the prevention of cracking of slabs. Furthermore, Ti can form fine carbide precipitates and increase the strength of steel sheets. These effects require a Ti content of 0.001% or more. However, a high Ti content of more than 0.030% results in an excessively high bainitic ferrite transformation point and low toughness of steel sheets. Thus, the Ti content is limited to the range of 0.001% to 0.030%, preferably 0.005% to 0.025%.

Mo: 0.01% to 0.50%

[0030] Mo can contribute to improved quenching hardenability and promote the formation of martensite by moving C from bainitic ferrite to untransformed austenite and thereby improving the hardenability of the untransformed austenite. Furthermore, Mo is an element that can dissolve in steel and contribute to increased strength of steel sheets by solid-solution hardening. These effects require a Mo content of 0.01% or more. However, a Mo content of more than 0.50% results in the formation of an excessive amount of martensite and low toughness of steel sheets. Furthermore, a large amount of expensive Mo results in high material costs. Thus, the Mo content is limited to the range of 0.01% to 0.50%, preferably 0.10% to 0.40%.

Cr: 0.01% to 0.50%

[0031] Cr has the effects of delaying $\gamma \rightarrow \alpha$ transformation, contributing to improved quenching hardenability, and promoting the formation of martensite. These effects require a Cr content of 0.01% or more. However, a Cr content of more than 0.50% tends to result in a frequent occurrence of defects in welds. Thus, the Cr content is limited to the range of 0.01% to 0.50%, preferably 0.20% to 0.45%.

Ni: 0.01% to 0.50%

[0032] Ni can contribute to improved quenching hardenability and promote the formation of martensite. Furthermore, Ni is an element that can contribute to further improved toughness. These effects require a Ni content of 0.01% or more. However, such effects level off at a Ni content of more than 0.50% and are not expected to be proportional to the Ni content beyond this threshold. A Ni content of more than 0.50% is therefore economically disadvantageous. Thus, the Ni content is limited to the range of 0.01% to 0.50%, preferably 0.30% to 0.45%.

[0033] These components are base components. In the present invention, the amounts of these components are preferably adjusted in the ranges described above such that Moeq defined by the following formula (1) ranges from 1.4% to 2.2%:

$$\text{Moeq (\%)} = \text{Mo} + 0.36\text{Cr} + 0.77\text{Mn} + 0.07\text{Ni} \quad (1)$$

(wherein Mn, Ni, Cr, and Mo denote the corresponding element contents (% by mass)).

[0034] Moeq is an indicator of the quenching hardenability of untransformed austenite that remains in a steel sheet after the cooling step. Moeq of less than 1.4% results in insufficient quenching hardenability of untransformed austenite, which results in transformation of untransformed austenite into pearlite or the like during the subsequent coiling step. Moeq of more than 2.2% results in the formation of an excessive amount of martensite and low toughness. Thus, Moeq is preferably limited to the range of 1.4% to 2.2%. Moeq of 1.5% or more results in a low yield ratio and further improved ductility. Thus, Moeq is more preferably 1.5% or more.

[0035] In addition to the components described above, if necessary, a hot-rolled steel sheet according to the present invention may contain one or two or more selected from Cu: 0.50% or less, V: 0.10% or less, and B: 0.0005% or less, and/or Ca: 0.0005% to 0.0050%.

[0036] One or two or more selected from Cu: 0.50% or less, V: 0.10% or less, and B: 0.0005% or less

[0037] Cu, V, and B are elements that can contribute to reinforcement of steel sheets and can be used as required.

[0038] V and Cu can contribute to reinforcement of steel sheets by solid-solution hardening or precipitation hardening. B can segregate at grain boundaries and contribute to reinforcement of steel sheets due to improved quenching hardenability. In order to produce these effects, Cu: 0.01% or more, V: 0.01% or more, and/or B: 0.0001% or more are preferred. However, steel sheets having a V content of more than 0.10% have low weldability. Steel sheets having a B content of more than 0.0005% have low toughness. Steel sheets having a Cu content of more than 0.50% have poor hot workability. Thus, when steel sheets contain these elements, Cu: 0.50% or less, V: 0.10% or less, and/or B: 0.0005% or less are preferred.

Ca: 0.0005% to 0.0050%

[0039] Ca is an element that can contribute to morphology control of sulfide by which coarse sulfide becomes spherical sulfide. Steel sheets can contain Ca, if necessary. In order to produce these effects, Ca: 0.0005% or more is preferred. However, steel sheets having a Ca content of more than 0.0050% have low cleanliness. Thus, when steel sheets contain Ca, Ca: 0.0005% to 0.0050% is preferred.

[0040] The remainder other than the components described above is Fe and incidental impurities. The incidental impurities may be N: 0.005% or less, O: 0.005% or less, Mg: 0.003% or less, and/or Sn: 0.005% or less.

[0041] The reason for limiting the microstructure of a high-strength hot-rolled steel sheet with a low yield ratio according to the present invention will be described below.

[0042] A high-strength hot-rolled steel sheet with a low yield ratio according to the present invention has a composition as described above and has different microstructures on an outer surface layer (hereinafter also referred to simply as an outer layer) in the thickness direction and on an inner surface layer (hereinafter also referred to simply as an inner layer) in the thickness direction. Steel pipes formed of a steel sheet having such different microstructures at different positions in the thickness direction can have a low yield ratio and uniform ductility. The term "an outer surface layer (outer layer) in the thickness direction", as used herein, refers to a region having a depth of less than 1.5 mm from the front and back sides of a steel sheet in the thickness direction. The term "an inner surface layer (inner layer) in the thickness direction", as used herein, refers to a region having a depth of 1.5 mm or more from the front and back sides of a steel sheet in the thickness direction.

[0043] The outer surface layer (outer layer) in the thickness direction has a single-phase microstructure composed of a tempered martensite phase or a mixed microstructure composed of a tempered martensite phase and a tempered bainite phase. Such a microstructure allows the steel sheet to have low hardness on the outer surface thereof in the thickness direction and be provided with high uniform ductility. Since pipe forming is a bending deformation, processing strain in the thickness direction increases with distance from the center of the steel sheet in the thickness direction and increases with the thickness of the steel sheet. Thus, it is important to control the outer layer microstructure.

[0044] An uneven cooling history of a hot-rolled steel sheet, for example, cooling of a hot-rolled steel sheet through a transition boiling region results in a local increase in hardness and uneven hardness. These problems can be avoided when the outer layer has a single-phase microstructure composed of a tempered martensite phase or a mixed microstructure composed of a tempered martensite phase and a tempered bainite phase. The mixture ratio of the tempered martensite phase to the tempered bainite phase of the mixed microstructure is not particularly limited. From the perspective of temper softening treatment, the area fraction of the tempered martensite phase preferably ranges from 60% to 100%, and the area fraction of the tempered bainite phase preferably ranges from 0% to 40%. The microstructure can be formed under certain manufacturing conditions, in particular, at a cumulative rolling reduction of 50% or more at a temperature of 930°C or less in finish rolling, and by sequentially performing a first cooling, second cooling, third cooling, and fourth cooling in a cooling step after the completion of the finish rolling. The first cooling includes cooling the hot-rolled steel sheet to a martensitic transformation start temperature (Ms point) or less at an average cooling rate of 100°C/s or more with respect to surface temperature. The second cooling includes, after the completion of the first cooling, holding the hot-rolled steel sheet for 1 s or more at a surface temperature of 600°C or more. The third cooling includes, after the completion of the second cooling, cooling the hot-rolled steel sheet to a cooling stop temperature in the range of 600°C to 450°C at an average cooling rate in the range of 5°C to 30°C/s with respect to the temperature at half the thickness of the hot-rolled steel sheet. The fourth cooling includes cooling the hot-rolled steel sheet from the cooling stop temperature of the third cooling to a coiling temperature at an average cooling rate of 2°C/s or less with respect to the temperature at half the thickness of the hot-rolled steel sheet or alternatively holding the hot-rolled steel sheet at a temperature in the range of the cooling stop temperature of the third cooling to the coiling temperature for 20 s or more. The microstructure and area fraction can be identified and calculated by observing and measuring using the methods described below in the examples.

[0045] The hardness of a steel sheet at a depth of 0.5 mm from a surface thereof in the thickness direction is preferably 95% or less of the maximum hardness in the thickness direction. The fact that the hardness of a hot-rolled steel sheet at a depth of 0.5 mm from a surface thereof in the thickness direction is not equal to the maximum hardness in the thickness direction is important in ensuring the workability of the hot-rolled steel sheet and the desired pipe shape after pipe manufacturing. The maximum hardness in the thickness direction preferably corresponds to a Vickers hardness HV 0.5 of 165 points or more and 300 points or less, more preferably 280 points or less. This hardness can be achieved under certain manufacturing conditions, in particular, by performing a first cooling and a second cooling in a cooling step after the completion of finish rolling, the first cooling including cooling the hot-rolled steel sheet to a martensitic transformation start temperature (Ms point) or less at an average cooling rate of 100°C/s or more with respect to surface temperature, the second cooling including, after the completion of the first cooling, holding the hot-rolled steel sheet for 1 s or more at a surface temperature of 600°C or more. The hardness can be measured using the method described below in the examples.

[0046] The inner surface layer (inner layer) in the thickness direction has a microstructure composed of a main phase and a second phase. The main phase is a bainitic ferrite phase. The second phase is formed of massive martensite having an aspect ratio of less than 5.0 dispersed in the main phase. The main phase herein refers to a phase having an occupied area of 50% by area or more. The bainitic ferrite preferably has an area fraction of 85% or more, more preferably 88.3% or more. The bainitic ferrite main phase has a substructure having a high dislocation density and contains needle-shaped ferrite and acicular ferrite. The bainitic ferrite does not include polygonal ferrite having a very low dislocation density or semi(quasi)-polygonal ferrite including a substructure, such as fine subgrains. In order to achieve the desired high strength, the bainitic ferrite main phase must contain fine carbonitride precipitates. The bainitic ferrite main phase has an average grain size of 10 μm or less. An average grain size of more than 10 μm results in insufficient work hardening ability in a region having a low strain of less than 5% and a decrease in yield strength due to bending in spiral pipe manufacturing. The desired low-temperature toughness can be achieved by decreasing the average grain size of the main phase even when the steel sheet contains much martensite.

[0047] The second phase in the inner layer has an area fraction in the range of 1.4% to 15% and is formed of massive martensite having an aspect ratio of less than 5.0. Massive martensite in the present invention is martensite formed from untransformed austenite at prior γ grain boundaries or within prior γ grains in a cooling process after rolling. In the present invention, such massive martensite is dispersed at prior γ grain boundaries or between bainitic ferrite grains of the main phase. Martensite is harder than the main phase, can introduce a large number of mobile dislocations into bainitic ferrite during processing, and allows yield behavior of a continuous yielding type. Since martensite, which has higher tensile strength than bainitic ferrite, a low yield ratio can be achieved. When the martensite is massive martensite having an aspect ratio of less than 5.0, the martensite can introduce more mobile dislocations into adjacent bainitic ferrite and effectively improve ductility. Martensite having an aspect ratio of 5.0 or more becomes rod-like martensite (non-massive martensite) and cannot achieve the desired low yield ratio. Nevertheless, rod-like martensite having an area fraction of less than 30% of the total amount of martensite is allowable. The massive martensite preferably has an area fraction of 70% or more of the total amount of martensite. The aspect ratio can be measured using the method described below in the examples.

[0048] Such effects require dispersion of massive martensite having an area fraction of 1.4% or more. It is difficult to achieve the desired low yield ratio with massive martensite having an area fraction of less than 1.4%. When the massive martensite has an area fraction of more than 15%, the low-temperature toughness is significantly decreased. Thus, the area fraction of massive martensite is limited to the range of 1.4% to 15%, preferably 10% or less. In addition to massive martensite, the second phase may contain bainite having an area fraction of approximately 7.0% or less.

[0049] The microstructure can be formed under certain manufacturing conditions, in particular, at a cumulative rolling reduction of 50% or more at a temperature of 930°C or less in finish rolling, and by sequentially performing a first cooling, second cooling, third cooling, and fourth cooling in a cooling step after the completion of the finish rolling. The first cooling includes cooling the hot-rolled steel sheet to a martensitic transformation start temperature (Ms point) or less at an average cooling rate of 100°C/s or more with respect to surface temperature. The second cooling includes, after the completion of the first cooling, holding the hot-rolled steel sheet for 1 s or more at a surface temperature of 600°C or more. The third cooling includes, after the completion of the second cooling, cooling the hot-rolled steel sheet to a cooling stop temperature in the range of 600°C to 450°C at an average cooling rate in the range of 5°C to 30°C/s with respect to the temperature at half the thickness of the hot-rolled steel sheet. The fourth cooling includes cooling the hot-rolled steel sheet from the cooling stop temperature of the third cooling to a coiling temperature at an average cooling rate of 2°C/s or less with respect to the temperature at half the thickness of the hot-rolled steel sheet or alternatively holding the hot-rolled steel sheet at a temperature in the range of the cooling stop temperature of the third cooling to the coiling temperature for 20 s or more.

[0050] The massive martensite preferably has a maximum size of 5.0 μm or less and an average size in the range of 0.5 to 3.0 μm. Coarse massive martensite having an average size of more than 3.0 μm tends to act as a starting point of brittle fracture or promote crack propagation and lowers the low-temperature toughness. Excessively fine massive martensite grains having an average size of less than 0.5 μm result in a decreased number of mobile dislocations introduced into adjacent bainitic ferrite. Massive martensite having a maximum size of more than 5.0 μm results in low toughness. Thus, the massive martensite preferably has a maximum size of 5.0 μm or less and an average size in the range of 0.5 to 3.0 μm. The term "diameter", as used herein in the context of the dimensions of massive martensite, refers to half the sum of the length along the major axis and the length along the minor axis. The maximum diameter is the "maximum" size of the massive martensite. The arithmetic mean of the "diameters" of grains is the "average" size of the massive martensite. At least 100 martensite grains are subjected to the measurement.

[0051] The microstructure can be formed under certain manufacturing conditions, in particular, at a cumulative rolling reduction of 50% or more at a temperature of 930°C or less in finish rolling, and by sequentially performing a first cooling, second cooling, third cooling, and fourth cooling in a cooling step after the completion of the finish rolling. The first cooling includes cooling the hot-rolled steel sheet to a martensitic transformation start temperature (Ms point) or less at an average cooling rate of 100°C/s or more with respect to surface temperature. The second cooling includes, after the completion of the first cooling, holding the hot-rolled steel sheet for 1 s or more at a surface temperature of 600°C or more. The third cooling includes, after the completion of the second cooling, cooling the hot-rolled steel sheet to a cooling stop temperature in the range of 600°C to 450°C at an average cooling rate in the range of 5°C to 30°C/s with respect to the temperature at half the thickness of the hot-rolled steel sheet. The fourth cooling includes cooling the hot-rolled steel sheet from the cooling stop temperature of the third cooling to a coiling temperature at an average cooling rate of 2°C/s or less with respect to the temperature at half the thickness of the hot-rolled steel sheet or alternatively holding the hot-rolled steel sheet at a temperature in the range of the cooling stop temperature of the third cooling to the coiling temperature for 20 s or more.

[0052] The microstructure, area fraction, and average grain size can be identified and calculated by observing and measuring using the methods described below in the examples.

[0053] A preferred method for manufacturing a high-strength hot-rolled steel sheet with a low yield ratio according to the present invention will be described below.

[0054] In the present invention, steel having a composition as described above is subjected to a hot-rolling step, a cooling step, and a coiling step to form a hot-rolled steel sheet.

[0055] The steel may be manufactured by any method. Preferably, molten steel having a composition as described above is smelted using a known melting method, such as using a converter or an electric furnace, and the molten steel is formed into steel, such as a slab, using a known casting method, such as a continuous casting process.

[0056] The steel is subjected to the hot-rolling step.

[0057] The hot-rolling step includes heating steel having a composition as described above to a heating temperature in the range of 1050°C to 1300°C, rough-rolling the heated steel to form a sheet bar, and finish-rolling the sheet bar such that the cumulative rolling reduction at a temperature of 930°C or less is 50% or more, thereby forming a hot-rolled steel sheet.

Heating temperature: 1050°C to 1300°C

[0058] Steel used in the present invention essentially contains Nb and Ti, as described above. In order to achieve the desired high strength by precipitation hardening, coarse carbide and nitride must be once dissolved in steel and then finely precipitated. Thus, the steel is heated to a heating temperature of 1050°C or more. At a heating temperature of less than 1050°C, the elements remain undissolved, and the resulting steel sheet cannot have the desired strength. A high heating temperature of more than 1300°C results in coarsening of crystal grains and steel sheets having low toughness. Thus, the heating temperature for the steel is limited to the range of 1050°C to 1300°C.

[0059] The steel heated to the heating temperature is subjected to rough rolling to form a sheet bar. The steel may be subjected to rough rolling under any conditions, provided that the sheet bar has the desired size and shape.

[0060] The sheet bar is then subjected to finish rolling to form a hot-rolled steel sheet having the desired size and shape. In the finish rolling, the cumulative rolling reduction at a temperature of 930°C or less is 50% or more.

Cumulative rolling reduction at a temperature of 930°C or less: 50% or more

[0061] The cumulative rolling reduction at a temperature of 930°C or less is 50% or more in order to decrease the size of bainitic ferrite and finely disperse massive martensite in the inner layer microstructure. A cumulative rolling reduction of less than 50% at a temperature of 930°C or less results in an insufficient rolling reduction and a lack of a fine bainitic ferrite main phase in the inner layer microstructure. This also results in insufficient dislocations that act as precipitation sites for NbC and the like, which promotes nucleation in $\gamma \rightarrow \alpha$ transformation, and insufficient formation of bainitic ferrite in grains. It is therefore impossible to keep a large number of finely dispersed massive untransformed γ grains for forming massive martensite. Thus, in the finish rolling, the cumulative rolling reduction at a temperature of 930°C or less is limited to 50% or more. The cumulative rolling reduction is preferably 80% or less. Such effects level off at a rolling reduction of more than 80%. Furthermore, a rolling reduction of more than 80% may result in a frequent occurrence of separation and low absorbed energy in a Charpy impact test.

[0062] The finishing temperature of the finish rolling preferably ranges from 850°C to 760°C in terms of steel sheet toughness, steel sheet strength, and rolling load. When the finishing temperature of the finish rolling is as high as more than 850°C, the rolling reduction per pass must be increased to achieve the cumulative rolling reduction of 50% or more at a temperature of 930°C or less, which sometimes results in increased rolling load. When the finishing temperature of the finish rolling is as low as less than 760°C, this sometimes results in the formation of ferrite during rolling, coarsening of the microstructure and precipitates, and decreases in low-temperature toughness and strength.

[0063] The hot-rolled steel sheet is then subjected to the cooling step.

[0064] The cooling step includes first cooling, second cooling, third cooling, and fourth cooling in this order. The first cooling is started immediately after the completion of the finish rolling and including cooling the hot-rolled steel sheet to a martensitic transformation start temperature (Ms point) or less at an average cooling rate of 100°C/s or more with respect to surface temperature. The second cooling includes, after the completion of the first cooling, holding the hot-rolled steel sheet for 1 s or more at a surface temperature of 600°C or more. The third cooling includes, after the completion of the second cooling, cooling the hot-rolled steel sheet to a cooling stop temperature in the range of 600°C to 450°C at an average cooling rate in the range of 5°C to 30°C/s with respect to the temperature at half the thickness of the hot-rolled steel sheet. The fourth cooling includes cooling the hot-rolled steel sheet from the cooling stop temperature of the third cooling to a coiling temperature at an average cooling rate of 2°C/s or less with respect to the temperature at half the thickness of the hot-rolled steel sheet or alternatively holding the hot-rolled steel sheet at a temperature in the range of the cooling stop temperature of the third cooling to the coiling temperature for 20 s or more. The coiling step includes coiling the hot-rolled steel sheet at a surface temperature of 450°C or more.

[0065] Cooling is started immediately, preferably within 15 s, after the completion of the finish rolling.

[0066] In the first cooling, the hot-rolled steel sheet is cooled to a martensitic transformation start temperature (Ms point) or less at an average cooling rate of 100°C/s or more with respect to surface temperature. The cooling rate in the first cooling is the average cooling rate in the temperature range of 600°C to 450°C with respect to surface temperature. In the first cooling, a single-phase microstructure composed of a martensite phase or a mixed microstructure composed of a martensite phase and a bainite phase is formed on the steel sheet outer layer. The average cooling rate in the first cooling has no particular upper limit. Depending on the capacity of a cooling apparatus, the hot-rolled steel sheet can be cooled at a higher cooling rate. The holding time at the martensitic transformation start temperature (Ms point) or less with respect to surface temperature depends on the desired surface microstructure and is 10 s or less, preferably 7 s or less. Holding the hot-rolled steel sheet at a temperature of the Ms point or less for a long time results in an excessively high occupied area of a single phase formed of a martensite phase or a mixed microstructure composed of a martensite phase and a bainite phase, which results in a lower thickness percentage of the desired microstructure.

[0067] In the second cooling after the first cooling, the hot-rolled steel sheet is held for 1 s or more at a surface temperature of 600°C or more utilizing internal recalescence without cooling or heating. In the second cooling, the martensite phase and the bainite phase are tempered, and the outer layer microstructure becomes a single-phase microstructure composed of the tempered martensite phase or a mixed microstructure composed of the tempered martensite phase and the tempered bainite phase. A steel sheet surface temperature of less than 600°C and a holding time of less than 1 s result in insufficient tempering of the outer layer microstructure. Thus, in the second cooling, the hot-rolled steel sheet is held at a surface temperature of 600°C or more for 1 s or more, preferably 600°C or more for 2 s or more. The holding time at a temperature of 600°C or more has no particular upper limit. However, in order to satisfy the third cooling conditions at half the thickness of the hot-rolled steel sheet and suppress the formation of polygonal ferrite, the holding time is preferably 6 s or less. The steel sheet surface temperature may be increased to 600°C or more using any method, for example, utilizing internal heat in the thickness direction or using an external heater. After the outer layer microstructure of the steel sheet is formed by the first cooling and the second cooling, the third cooling is performed to form an inner layer microstructure of the steel sheet, which includes a bainitic ferrite main phase and a massive martensite second phase.

[0068] The average cooling rate of the third cooling at half the thickness of the hot-rolled steel sheet ranges from 5°C to 30°C/s in the polygonal ferrite formation temperature range, which ranges from 750°C to 600°C. An average cooling rate of less than 5°C/s results in an inner layer microstructure composed mainly of polygonal ferrite rather than the desired microstructure composed of a bainitic ferrite main phase. Rapid cooling at an average cooling rate of more than 30°C/s results in insufficient concentration of an alloying element in untransformed austenite, which makes it difficult to finely disperse a desired amount of massive martensite by the subsequent cooling and to provide a hot-rolled steel sheet having the desired low yield ratio and desired high low-temperature toughness. Thus, the cooling rate at half the thickness of the hot-rolled steel sheet is limited to the range of 5°C to 30°C/s, preferably 5°C to 25°C/s. The temperature at half the thickness of the hot-rolled steel sheet can be calculated by heat-transfer calculation based on the steel sheet surface temperature and the temperature and amount of cooling water.

[0069] The cooling stop temperature in the third cooling ranges from 600°C to 450°C. A cooling stop temperature above this temperature range makes it difficult to form the desired inner layer microstructure composed of a bainitic ferrite main phase. A cooling stop temperature below this temperature range results in substantial completion of transformation of untransformed γ and an insufficient amount of massive martensite.

[0070] In the present invention, the first to third cooling is followed by the fourth cooling. Fig. 1 schematically illustrates the temperature at half the thickness of the hot-rolled steel sheet in the fourth cooling in the temperature range from the cooling stop temperature of the third cooling to the coiling temperature. As illustrated in Fig. 1, the fourth cooling is slow cooling. Slow cooling in this temperature range allows alloying elements, such as C, to be further diffused into untransformed y, thereby stabilizing untransformed γ and facilitating the formation of massive martensite in the subsequent cooling. Such slow cooling is performed by cooling the hot-rolled steel sheet from the cooling stop temperature of the third cooling to the coiling temperature at an average cooling rate of 2°C/s or less, preferably 1.5°C/s or less, with respect to the temperature at half the thickness of the hot-rolled steel sheet or by holding the hot-rolled steel sheet at a temperature in the range of the cooling stop temperature of the third cooling to the coiling temperature for 20 s or more. Cooling from the cooling stop temperature of the second cooling to the coiling temperature at an average cooling rate of more than 2°C/s results in insufficient diffusion of alloying elements, such as C, into untransformed y, insufficient stabilization of the untransformed y, and formation of rod-like untransformed γ remaining between bainitic ferrite grains, as in cooling indicated by a dotted line in Fig. 1, thus making it difficult to form the desired massive martensite.

[0071] The fourth cooling is preferably performed by stopping water injection at the latter part of runout table. For a steel sheet having a small thickness, the desired cooling conditions are preferably ensured by completely removing cooling water remaining on the steel sheet or installing a heat-insulating cover. Furthermore, the transport speed is preferably adjusted in order to ensure a holding time of 20 s or more in the temperature range described above.

[0072] After the fourth cooling, the hot-rolled steel sheet is subjected to the coiling step.

[0073] The coiling step includes coiling the hot-rolled steel sheet at a surface temperature of 450°C or more. The desired low yield ratio cannot be achieved at a coiling temperature of less than 450°C. Thus, the coiling temperature is limited to 450°C or more. Through this step, the steel sheet can be held for at least a predetermined time in a temperature range where ferrite and austenite coexist.

[0074] A hot-rolled steel sheet manufactured by using the method described above is used as a material for pipe manufacturing to form spiral steel pipes and electric-resistance-welded (ERW) pipes through common pipe manufacturing steps. The pipe manufacturing steps are not particularly limited and may be common steps.

[0075] The present invention will be further described below with examples.

EXAMPLES

[0076] Molten steel having a composition listed in Table 1 was formed into a slab (thickness: 220 mm) using a continuous casting process. The slab was used as steel. The steel was subjected to a hot-rolling step, in which the steel was heated to a heating temperature listed in Table 2, rough-rolling the steel to form a sheet bar, and finish-rolling the sheet bar under the conditions listed in Table 2 to form a hot-rolled steel sheet (thickness: 8 to 25 mm). The hot-rolled steel sheet was subjected to a cooling step immediately after the completion of the finish rolling. The cooling step included first to fourth cooling listed in Table 2. After the cooling step, the hot-rolled steel sheet was subjected to a coiling step, which included coiling the hot-rolled steel sheet at a coiling temperature listed in Table 2 and allowing the coil to cool.

[0077] Test pieces were taken from the hot-rolled steel sheet and were subjected to microstructure observation, a tensile test, an impact test, and a hardness test.

[0078] The test methods are as follows:

(1) Microstructure Observation

[0079] A test piece for microstructure observation was taken from the hot-rolled steel sheet such that a cross section thereof in the rolling direction (L cross section) served as an observation surface. After the test piece was polished and was etched with nital, the microstructure of the test piece was observed and photographed with an optical microscope (magnification ratio: 500) or an electron microscope (magnification ratio: 2000). The type of microstructure, the fraction (area fraction) of the microstructure of each phase, and the average grain size were determined from the photograph of the inner layer microstructure with an image analyzing apparatus. For the outer layer, only the type of microstructure was identified from the microstructure photograph.

[0080] The average grain size of the bainitic ferrite main phase in the inner layer microstructure was determined using an intercept method in accordance with JIS G 0552. The aspect ratio of martensite grains was calculated as the ratio (the length along the major axis)/(the length along the minor axis) of the length of a grain in the longitudinal direction or in a direction of the maximum grain size (the length along the major axis) to the length of the grain in a direction perpendicular to the longitudinal direction (the length along the minor axis). Martensite grains having an aspect ratio of less than 5.0 were defined as massive martensite. Martensite grains having an aspect ratio of 5.0 or more were referred to as "rod-like" martensite. The average size of massive martensite in the steel sheet was calculated by determining half the sum of the length along the major axis and the length along the minor axis of each massive martensite grain as the diameter thereof and calculating the arithmetic mean of the diameters. The maximum diameter of each massive martensite grain was the maximum size of the massive martensite. At least 100 martensite grains were subjected to the measurement.

(2) Tensile Test

[0081] Test pieces for tensile test (full-thickness test pieces specified in API-5L, (width: 38.1 mm, GL: 50 mm)) were taken from the hot-rolled steel sheet such that the tensile direction was perpendicular to the rolling direction (sheet width direction) or at an angle of 30 degrees with the rolling direction. A tensile test was performed in accordance with the ASTM A 370 specification to determine tensile properties (yield strength YS and tensile strength TS) .

(3) Impact Test

[0082] V-notched test pieces were taken from the hot-rolled steel sheet such that the longitudinal direction of the test pieces was perpendicular to the rolling direction, and were subjected to a Charpy impact test in accordance with the ASTM A 370 specification to determine the fracture transition temperature vTrs (°C).

(4) Hardness Test

[0083] Test pieces for hardness measurement were taken from the hot-rolled steel sheet. The cross section hardness of the test pieces was measured with a Vickers hardness tester (test force: 4.9 N) (load: 500 g). The cross section hardness of each of the test pieces was continuously measured at intervals of 0.5 mm from a surface of the steel sheet in the thickness direction. The hardness at a depth of 0.5 mm from the surface of the steel sheet in the thickness direction (depth direction) and the maximum hardness in the thickness direction were determined. The hardness distribution was judged to be good when the maximum hardness in the thickness direction was 300 points or less, and the hardness at a depth of 0.5 mm from the surface was 95% or less of the maximum hardness in the thickness direction.

[0084] A spiral steel pipe (outer diameter: 1067 mmϕ) was then manufactured by using a spiral pipe manufacturing process using the hot-rolled steel sheet as a material for pipes. Test pieces for tensile test (test pieces specified in API) were taken from the steel pipe such that the tensile direction was the circumferential direction of the pipe, and were subjected to a tensile test in accordance with the ASTM A 370 specification to measure tensile properties (yield strength YS and tensile strength TS). ΔYS (= YS of steel pipe - 30-degree YS of steel sheet) was calculated from the results to determine the strength reduction due to pipe manufacturing. Table 3 shows the results.

[Table 1]

Steel No.	Chemical components (% by mass)														Note
	C	Si	Mn	P	S	Al	N	Nb	Ti	Mo	Cr	Ni	Cu,V,B	Ca	Moeq*	
A	0.064	0.22	1.64	0.008	0.0011	0.036	0.0039	0.065	0.014	0.29	0.08	0.02	-	-	1.58	Example
B	0.052	0.29	1.74	0.009	0.0006	0.035	0.0034	0.052	0.013	0.38	0.11	0.12	V:0.022	-	1.77	Example
C	0.070	0.46	1.88	0.007	0.0012	0.033	0.0032	0.071	0.017	0.24	0.23	0.21	V:0.039,B:0.0001	0.0021	1.79	Example
D	0.041	0.42	1.46	0.009	0.0014	0.039	0.0032	0.033	0.021	0.29	0.48	0.06	V:0.090	0.0023	1.59	Example
E	0.083	0.38	1.91	0.010	0.0023	0.042	0.0042	0.097	0.009	0.26	0.41	0.20	B:0.0004	-	1.89	Example
F	0.035	0.02	2.16	0.010	0.0015	0.035	0.0029	0.042	0.041	0.29	0.37	0.40	Cu:0.25	0.0024	2.11	Example
<u>G</u>	<u>0.162</u>	0.22	1.42	0.014	0.0019	0.035	0.0027	0.060	0.013	0.01	0.38	0.28	Cu:0.29	0.0022	1.26	Comparative Example
<u>H</u>	0.046	0.36	<u>1.15</u>	0.008	0.0025	0.051	0.0035	0.046	0.009	0.32	0.26	0.42	V:0.022,B:0.0002	0.0024	1.33	Comparative Example
<u>I</u>	0.051	0.17	1.57	0.007	0.0032	0.036	0.0038	0.051	0.012	0.09	<u>-</u>	<u>-</u>	V:0.055,B:0.0001	-	1.30	Comparative Example
<u>J</u>	0.040	0.17	1.65	0.009	0.0029	0.040	0.0046	0.042	0.015	<u>-</u>	<u>-</u>	0.18	V:0.025,Cu:0.15	-	1.27	Comparative Example
<u>K</u>	0.079	0.42	1.60	0.011	0.0012	0.046	0.0033	<u>0.129</u>	0.021	0.31	0.19	0.11	B:0.0003	0.0026	1.62	Comparative Example
<u>L</u>	0.063	0.22	1.64	0.009	0.0009	0.035	0.0028	0.054	<u>0.069</u>	0.18	0.28	0.10	-	-	1.55	Comparative Example
M	0.091	0.14	1.62	0.012	0.0007	0.037	0.0034	0.056	0.017	0.11	0.05	0.01	V:0.055	0.0019	1.38	Example

*) Moeq(%)=Mo+0.36Cr+0.77Mn+0.07Ni

[Table 2]

Steel sheet No.	Steel No.	Hot-rolling step					Cooling step										Coiling step	Note
		Heating	Rough rolling	Finish rolling			Cooling start time (s)	First cooling*2			Second cooling*2		Third cooling*3		Fourth cooling*3		Coiling temperature *11 (°C)	
		Heating temperature (°C)	Thickness of sheet bar (mm)	Finish rolling temperature (°C)	Rolling reduction *1 (%)	Thickness (mm)		Average cooling rate *4 (°C/s)	Cooling stop temperature *5 (°C)	Ms (°C)	Final surface temperature *6 (°C)	Holding time *7 (s)	Average cooling rate *8 (°C/s)	Cooling stop temperature (°C)	Average cooling rate *9 (°C/s)	Holding time *10 (s)		
1	A	1059	51	768	74	8	2.4	111	373	406	608	1.4	18	551	1.5	-	538	Example
2	A	1091	55	759	55	25	7.6	145	372	406	613	2.7	28	558	0.5	-	536	Example
3	A	1099	51	777	61	16	4.8	122	372	406	603	2.0	22	555	-	28	522	Example
4	A	1261	58	762	70	14	4.2	123	371	406	605	1.8	25	556	4.5	-	468	Comparative Example
5	A	1158	59	761	61	23	7.0	124	366	406	601	2.4	29	551	-	12	522	Comparative Example
6	A	1247	58	772	69	16	4.8	117	361	406	617	1.9	22	454	2.0	-	323	Comparative Example
7	A	1388	53	758	70	16	4.8	125	366	406	617	1.8	19	550	1.0	-	536	Comparative Example
8	A	1281	57	759	19	14	4.2	124	362	406	604	2.0	15	557	2.0	-	537	Comparative Example
9	A	1232	60	762	67	16	4.8	68	367	406	418	2.3	19	437	-	28	424	Comparative Example
10	A	1252	59	768	70	14	4.2	119	674	406	684	2.0	27	551	1.0	-	531	Comparative Example
11	A	1264	57	769	69	16	4.8	128	375	406	460	2.1	17	552	1.0	-	529	Comparative Example
12	A	1155	59	773	64	21	6.4	131	377	406	613	1.0	20	445	0.5	-	460	Comparative Example
13	A	1164	56	765	55	25	7.6	140	361	406	603	2.6	55	553	1.0	-	540	Comparative Example
14	A	1270	57	766	67	19	5.8	135	368	406	607	2.4	30	405	0.5	-	521	Comparative Example
15	B	1195	58	776	81	11	3.3	114	374	404	621	2.0	21	533	1.0	-	514	Example
16	C	1185	51	782	78	10	3.0	117	347	390	603	1.8	21	527	1.0	-	508	Example
17	D	1182	52	801	62	18	5.5	125	375	415	628	2.1	27	550	1.0	-	526	Example
18	E	1168	55	763	64	16	4.8	127	341	380	632	2.0	30	501	1.0	-	471	Example
19	F	1300	51	772	50	21	6.4	137	354	391	618	2.4	28	486	0.5	-	451	Example
20	G	1206	52	734	66	16	4.8	125	329	363	632	1.8	22	543	1.0	-	521	Comparative Example
21	H	1291	58	814	79	11	3.3	119	376	420	645	1.6	23	561	0.5	-	541	Comparative Example
22	I	1241	59	780	58	25	7.6	147	385	420	693	2.3	20	604	0.5	-	576	Comparative Example
23	J	1193	54	772	55	22	6.7	125	376	422	697	2.6	18	607	0.5	-	580	Comparative Example
24	K	1199	56	785	76	11	3.3	115	360	396	628	1.7	15	535	0.5	-	513	Comparative Example
25	L	1156	52	785	66	14	4.2	123	359	404	634	1.8	15	561	1.0	-	538	Comparative Example
26	M	1176	55	773	68	14	4.2	123	361	398	660	2.1	21	584	0.5	-	566	Example

*1) Cumulative rolling reduction (%) at a temperature of 930°C or less
*2) Surface temperature control of the steel sheet
*3) Temperature control at half the thickness of the steel sheet by heat-transfer calculation
*4) Average cooling rate in the range of 600°C to 450°C (For steel sheet No. 10, average cooling rate in the range of cooling start temperature to first cooling stop temperature)
*5) By heat-transfer calculation
*6) By measurement with surface thermometer
*7) Holding time at a surface temperature of 600°C or more
*8) Average cooling rate in the range of 750°C to 600°C
*9) Average cooling rate in the range of third cooling stop temperature to fourth coiling temperature
*10) Holding time from third cooling stop temperature to fourth coiling temperature
*11) Surface temperature

[Table 3]

Steel sheet No.	Steel No.	Outer layer: Type *1	Outer layer: Hardness of outer layer/maximum hardness *2	Outer layer: Maximum hardness *3 HV0.5	Inner layer: Type*1	Inner layer: BF Fraction (% by area)	Inner layer: BF Average grain size (μm)	Inner layer: Second phase, Massive martensite Fraction (% by area)	Inner layer: Second phase, Massive martensite Average size (μm)	Inner layer: Second phase, Massive martensite Maximum size (μm)	Inner layer: Second phase, Massive martensite Aspect ratio	Inner layer: Second phase, Rod-like M Fraction *4 (% by area)	Inner layer: Second phase, Others Type *1:% by area	Tensile properties: YS (MPa)	Tensile properties: TS (MPa)	Tensile properties: YR (%)	Tensile properties: 30-degreeYS *5 (MPa)	Toughness: vTrs (°C)	Tensile properties of steel pipe: YS (MPa)	Tensile properties of steel pipe: TS (MPa)	Tensile properties of steel pipe: YR (%)	Variation in strength: ΔYS*6	Note
1	A	TM	91	261	BF+M	95.2	3.9	4.3	1.5	4.4	4.0	0.5	-	580	699	83	558	-115	571	671	85	13	Example
2	A	TM	92	268	BF+M+B	95.6	4.9	3.4	1.2	4.2	3.5	0.5	B:0.5	586	697	84	563	-85	583	671	87	20	Example
3	A	TM+TB	93	264	BF+M	95.3	5.0	4.2	1.4	4.2	3.5	0.5	-	585	697	84	568	-110	576	669	86	7	Example
4	A	TM	94	269	BF+M	95.6	4.7	0.9	0.3	2.9	2.5	3.5	-	621	714	87	606	-120	588	692	85	-18	Comparative Example
5	A	TM	94	267	BF+M	98.3	4.8	1.2	0.5	2.9	3.0	0.5	-	595	684	87	585	-110	538	656	82	-47	Comparative Example
6	A	TM	91	264	BF+M	95.2	4.7	1.3	0.8	3.4	3.0	2.5	-	595	709	86	578	-75	585	688	85	7	Comparative Example
7	A	TM	92	268	BF+M	94.6	11.9	4.9	1.7	6.2	3.0	0.5	-	581	717	81	564	-65	585	696	84	21	Comparative Example
8	A	TM	95	263	BF+M	94.9	10.5	0.6	0.3	7.5	3.0	4.5	-	678	770	88	639	-20	619	746	83	-20	Comparative Example
9	A	TM	91	263	BF+M	95.8	10.8	3.2	1.2	5.5	3.0	1.0	-	586	715	82	571	-65	583	694	84	12	Comparative Example
10	A	M+B	99	306	BF+M	95.9	4.5	1.6	0.6	2.9	2.5	2.5	-	613	704	87	591	-120	579	681	85	-12	Comparative Example
11	A	TM	96	294	BF+B	95.0	4.5	0.0	-	-	-	-	B:5.0	590	671	88	575	-60	537	647	83	-38	Comparative Example
12	A	TM	98	304	BF	100.0	4.6	0.0	-	-	-	-	-	622	699	89	595	-110	544	672	81	-51	Comparative Example
13	A	TM	94	262	BF+M	95.0	5.0	0.5	0.2	2.7	3.5	4.5	-	606	722	84	590	-70	580	698	83	-11	Comparative Example
14	A	TM	93	269	BF	98.9	5.1	0.2	0.2	2.4	3.0	0.9	-	581	683	86	566	-80	539	657	82	-28	Comparative Example
15	B	TM	93	264	BF+M	95.5	4.0	3.4	1.2	3.9	3.5	1.1	-	551	735	75	530	-105	568	710	80	38	Example
16	C	TM	91	264	BF+M	94.6	4.4	4.9	1.7	4.8	4.5	0.5	-	547	739	74	537	-100	603	718	84	66	Example
17	D	TM	93	262	BF+M+B	91.5	4.9	3.9	1.4	4.4	2.5	1.6	B:3.0	623	742	84	605	-95	614	714	86	9	Example
18	E	TM+TB	93	269	BF+M+B	88.3	4.4	4.2	1.4	4.2	2.0	0.5	B:7.0	610	735	83	592	-90	598	712	84	6	Example
19	F	TM+TB	92	262	BF+M	94.4	4.8	4.0	1.4	4.6	3.0	1.6	-	521	754	69	516	-110	584	730	80	68	Example
20	G	TM+TB	91	262	BF+B	80.0	5.0	0.0	-	-	-	-	B:20	548	615	89	529	-40	464	595	78	-65	Comparative Example
21	H	TM	95	263	BF+P	90.0	13.2	0.0	-	-	-	-	P:10	534	607	88	509	-50	462	585	79	-47	Comparative Example
22	I	TM	93	263	BF	100.0	5.3	0.0	-	-	-	-	-	566	636	89	565	-100	491	613	80	-75	Comparative Example
23	J	TM	92	264	BF	100.0	5.3	0.0	-	-	-	-	-	606	666	91	600	-120	532	641	83	-67	Comparative Example
24	K	TM	93	262	BF+M	94.8	4.5	4.1	1.4	4.5	4.0	1.1	-	643	739	87	628	-80	571	714	80	-57	Comparative Example
25	L	TM	95	268	BF+M+F	94.6	11.1	3.9	1.4	5.3	3.5	0.5	F:1.0	621	739	84	609	-50	594	715	83	-16	Comparative Example
26	M	TM	94	263	BF+M+B	95.5	4.8	2.9	1.0	3.8	3.0	0.6	B:1.0	606	721	84	579	-95	593	698	85	14	Example

*1) F: Ferrite, P: Pearlite, B: Bainite, BF: Bainitic ferrite, M: Martensite, TM: Tempered martensite, TB: Tempered bainite
*2) (Hardness at a depth of 0.5 mm from a surface)/(Maximum hardness in the thickness direction)
*3) Maximum hardness in the thickness direction
*4) (Amount of martensite having an aspect ratio of 5.0 or more)/(Total amount of martensite)
*5) Yield strength at 30 degrees with respect to rolling direction
*6) ΔYS = YS of steel pipe - 30-degree YS of steel sheet

[0085] All the examples provided high-strength high-toughness hot-rolled steel sheets having a low yield ratio without particular heat treatment. These hot-rolled steel sheets had a yield strength of 480 MPa or more at an angle of 30 degrees with the rolling direction, a tensile strength of 600 MPa or more in the sheet width direction, high toughness represented by a fracture transition temperature vTrs of - 80°C or less, and a yield ratio of 85% or less. The comparative examples outside the scope of the present invention could not provide hot-rolled steel sheets having the desired characteristics because of low toughness or a high yield ratio.

[0086] The examples provided hot-rolled steel sheets that had little strength reduction due to pipe manufacturing even after formed into steel pipes by pipe manufacturing and are suitable as materials for spiral steel pipes and electric-resistance-welded (ERW) pipes.

Claims

1. A hot-rolled steel sheet having a composition, comprising, on a mass percent basis:

C: 0.03% to 0.10%, Si: 0.01% to 0.50%, Mn: 1.4% to 2.2%, P: 0.025% or less, S: 0.005% or less, Al: 0.005% to 0.10%, Nb: 0.02% to 0.10%, Ti: 0.001% to 0.030%, Mo: 0.01% to 0.50%, Cr: 0.01% to 0.50%, Ni: 0.01% to 0.50%, and a remainder of Fe and incidental impurities,
wherein the hot-rolled steel sheet includes an inner layer having a microstructure that contains a main phase and a second phase, the main phase being bainitic ferrite having an average grain size of 10 μm or less, the second phase having an area fraction in the range of 1.4% to 15% and containing massive martensite having an aspect ratio of less than 5.0, and
the hot-rolled steel sheet includes an outer layer having a microstructure that contains a tempered martensite phase or a tempered martensite phase and a tempered bainite phase.

2. The hot-rolled steel sheet according to Claim 1, wherein the composition has Moeq defined by the following formula (1) in the range of 1.4% to 2.2% by mass:

$$\mathrm{Moeq}\ (\%) = \mathrm{Mo} + 0.36\mathrm{Cr} + 0.77\mathrm{Mn} + 0.07\mathrm{Ni} \quad (1)$$

wherein Mn, Ni, Cr, and Mo denote the corresponding element contents (% by mass).

3. The hot-rolled steel sheet according to Claim 1 or 2, further comprising, on a mass percent basis, one or two or more selected from Cu: 0.50% or less, V: 0.10% or less, and B: 0.0005% or less.

4. The hot-rolled steel sheet according to any one of Claims 1 to 3, further comprising Ca: 0.0005% to 0.0050% by mass.

5. The hot-rolled steel sheet according to any one of Claims 1 to 4, wherein the massive martensite has a maximum size of 5.0 μm or less and an average size in the range of 0.5 to 3.0 μm.

6. The hot-rolled steel sheet according to any one of Claims 1 to 5, wherein the hardness of the hot-rolled steel sheet at a depth of 0.5 mm from a surface thereof in the thickness direction is 95% or less of the maximum hardness in the thickness direction.

7. A method for manufacturing a hot-rolled steel sheet, comprising:

subjecting steel to a hot-rolling step, a cooling step, and a coiling step to form the hot-rolled steel sheet,
wherein the steel contains, on a mass percent basis, C: 0.03% to 0.10%, Si: 0.01% to 0.50%, Mn: 1.4% to 2.2%, P: 0.025% or less, S: 0.005% or less, A1: 0.005% to 0.10%, Nb: 0.02% to 0.10%, Ti: 0.001% to 0.030%, Mo: 0.01% to 0.50%, Cr: 0.01% to 0.50%, Ni: 0.01% to 0.50%, and a remainder of Fe and incidental impurities,
the hot-rolling step includes heating the steel to a heating temperature in the range of 1050°C to 1300°C, rough-rolling the heated steel to form a sheet bar, and finish-rolling the sheet bar such that the cumulative rolling reduction at a temperature of 930°C or less is 50% or more, thereby forming a hot-rolled steel sheet,
the cooling step includes first cooling, second cooling, third cooling, and fourth cooling in this order, the first cooling being started immediately after completion of the finish rolling and including cooling the hot-rolled steel sheet to a martensitic transformation start temperature or less at an average cooling rate of 100°C/s or more

with respect to surface temperature, the second cooling including, after completion of the first cooling, holding the hot-rolled steel sheet for 1 s or more at a surface temperature of 600°C or more, the third cooling including, after completion of the second cooling, cooling the hot-rolled steel sheet to a cooling stop temperature in the range of 600°C to 450°C at an average cooling rate in the range of 5°C to 30°C/s with respect to the temperature at half the thickness of the hot-rolled steel sheet, the fourth cooling including cooling the hot-rolled steel sheet from the cooling stop temperature of the third cooling to a coiling temperature at an average cooling rate of 2°C/s or less with respect to the temperature at half the thickness of the hot-rolled steel sheet or alternatively holding the hot-rolled steel sheet at a temperature in the range of the cooling stop temperature of the third cooling to the coiling temperature for 20 s or more, and
the coiling step includes coiling the hot-rolled steel sheet at a surface temperature of 450°C or more.

8. The method for manufacturing a hot-rolled steel sheet according to Claim 7, wherein the composition has Moeq defined by the following formula (1) in the range of 1.4% to 2.2% by mass:

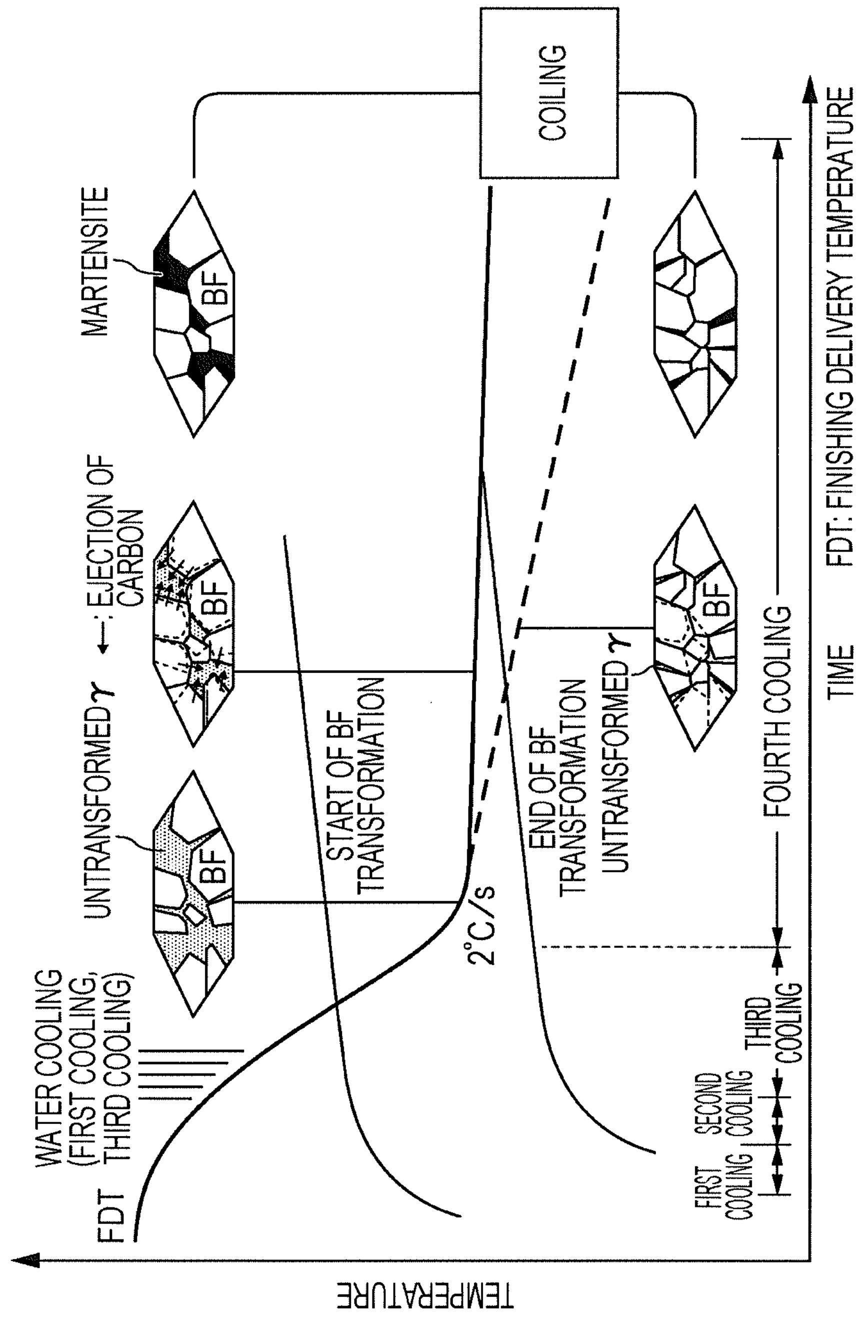
$$\mathrm{Moeq}\ (\%) = \mathrm{Mo} + 0.36\mathrm{Cr} + 0.77\mathrm{Mn} + 0.07\mathrm{Ni} \quad (1)$$

wherein Mn, Ni, Cr, and Mo denote the corresponding element contents (% by mass).

9. The method for manufacturing a hot-rolled steel sheet according to Claim 7 or 8, wherein the hot-rolled steel sheet further contains, on a mass percent basis, one or two or more selected from Cu: 0.50% or less, V: 0.10% or less, and B: 0.0005% or less.

10. The method for manufacturing a hot-rolled steel sheet according to any one of Claims 7 to 9, wherein the hot-rolled steel sheet further contains Ca: 0.0005% to 0.0050% by mass.

FIG. 1


TEMPERATURE
TIME
FDT
WATER COOLING (FIRST COOLING, THIRD COOLING)
UNTRANSFORMED γ
BF
←: EJECTION OF CARBON
MARTENSITE
COILING
START OF BF TRANSFORMATION
2°C/s
END OF BF TRANSFORMATION
UNTRANSFORMED γ
FIRST COOLING
SECOND COOLING
THIRD COOLING
FOURTH COOLING
FDT: FINISHING DELIVERY TEMPERATURE
BF: BAINITIC FERRITE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/005388

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *B21B3/02*(2006.01)i, *C21D8/02*(2006.01)i, *C22C38/58*(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)
C22C1/00-49/14, B21B3/02, C21D8/02

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2008-248384 A (Nippon Steel Corp.), 16 October 2008 (16.10.2008), & US 2010/0059149 A1 & EP 2133441 A1 & WO 2008/108487 A1 & CA 2680036 A & CN 101631887 A & TW 200904997 A & KR 10-2009-0109571 A	1-10
A	JP 2010-209471 A (Nippon Steel Corp.), 24 September 2010 (24.09.2010), & US 2010/0119860 A1 & EP 2192203 A1 & WO 2009/014238 A1 & KR 10-2010-0033413 A & CN 101755068 A	1-10
P,A	JP 2013-7101 A (Kobe Steel, Ltd.), 10 January 2013 (10.01.2013), (Family: none)	1-10

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 December, 2013 (04.12.13)	17 December, 2013 (17.12.13)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2006299413 A **[0007]**
- JP 2010059472 A **[0007]**