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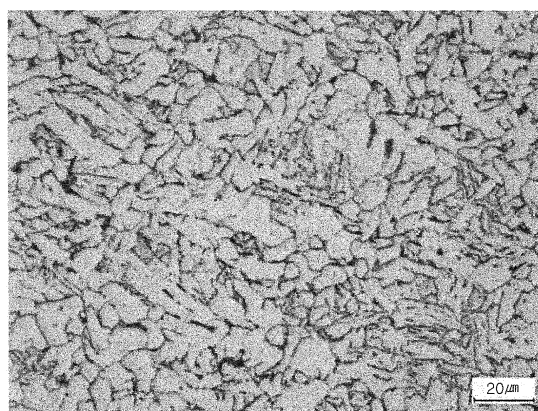
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(54) **LOW-YIELD RATIO AND HIGH-STRENGTH STEEL HAVING EXCELLENT STRESS CORROSION CRACKING RESISTANCE AND LOW TEMPERATURE TOUGHNESS**

(57) An aspect of the present invention relates to a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness, the steel comprising, by weight, 0.02-0.10% of carbon (C), 0.5-2.0% of manganese (Mn), 0.05-0.5% of silicon (Si), 0.05-1.0% of nickel (Ni), 0.005-0.1% of titanium (Ti), 0.005-0.5% of aluminum (Al), 0.005% or less of niobium (Nb), 0.015% or less of phosphorus (P), 0.015% or less of sulfur (S), and the balanced amount of Fe and inevitable impurities, the microstructure of which comprises: by area, 60% or more of acicular ferrite and a balanced amount of one or more phases of bainite, polygonal ferrite and martensite-austenite constituent (MA).

[FIGURE 3]



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Description

[Technical Field]

5 **[0001]** The present disclosure relates to a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness.

[Background Art]

10 **[0002]** Although varied according to types of a liquefied gas, a temperature for liquefying a gas is generally low (-52°C in the case of LPG) at normal pressure, and thus, steel used in a liquefied gas storage tank has been required to have excellent low temperature toughness in a welded part, as well as in a base material.

15 **[0003]** It is known that liquid ammonia (LAG) causes stress corrosion cracking (SCC) of steel, and thus, IGC CODE (International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk) regulates operating conditions at the time of manufacturing, such as oxygen partial pressure, temperature, and the like, limits the Ni content of steel to 5% or less, and defines actual yield strength to 440 MPa or less.

20 **[0004]** In addition, when a gas tank is manufactured by welding steel for a gas tank, removal of stress from a welded part is an important consideration. Therefore, methods for removing stress from a welded part include a post welding heat treatment (PWHT) based on a heat treatment and a mechanical stress relief (MSR) method of removing stress by adding hydrostatic pressure, or the like, to the welded part, or the like. In the case of removing stress from the welded part using the mechanical stress relieving (MSR) method, deformation is applied to a base material part due to water pressure, and thus, a yield ratio of the base material is limited to 0.8 or less. Here, in removing stress using MSR, if deformation equal to or greater than yield strength is applied to the base material part due to high pressure water injection, if a ratio of the yield strength and tensile strength is high, yield occurs, that is, tensile strength may be reached to cause damage, and thus, yield strength and tensile stress are limited, to be significantly different.

25 **[0005]** In particular, since gas tanks are basically required to be enlarged in size, it may be difficult to remove stress by the PWHT method and most shipbuilders prefer the MSR method, and thus, steel for manufacturing gas tanks is required to have low yield ratio characteristics.

30 **[0006]** In this manner, in the tanks in which the LPG and the LAG coexist, it is a significant issue to achieve both low temperature toughness and a low yield ratio accompanying the regulation of an upper limit of yield strength from liquid ammonia.

35 **[0007]** Meanwhile, Patent document 1 proposes a technique of adding 6.5 to 12.0% of Ni to achieve excellent low temperature toughness. Also, Patent document 2 proposes a technique of mixedly using tempered martensite and bainite by performing quench tempering on steel having a specific composition.

40 **[0008]** However, in general, if a large amount of Ni is added, a large amount of austenite phases having an FCC lattice structure, which is easily deformed due to a narrow interatomic gap, may be formed, and if repeated stress and a corrosive environment are applied to the easily deformed FCC lattice structure, corrosion may easily occur to cause cracking. Therefore, Patent document 1 has a problem of low economical efficiency due to high-priced Ni content and has a problem of degrading stress corrosion cracking (SCC) resistance.

45 **[0009]** Further, Patent document 3 proposes a technique of only softening a surface layer of a steel sheet to realize a low-yield ratio. This technique, however, may achieve low temperature toughness and low yield ratio separately but cannot obtain both low temperature toughness and low yield ratio together.

50 **[0010]** Meanwhile, in order to enhance strength of steel as another characteristic required for the steel, precipitation strengthening, solid solution strengthening, and martensite strengthening may be used but these methods degrade toughness and elongation, while enhancing strength.

55 **[0011]** In addition, in the case of increasing strength by refining crystal grains by applying various manufacturing conditions, high strength may be obtained and a degradation of toughness may be prevented due to a reduction in an impact toughness transition temperature. However, yield strength based on grain refinement may be increased to exceed 440 MPa, a yield strength upper limit, at which ammonia stress corrosion (SCC) occurs, and it is difficult to obtain low-yield ratio.

[0012] Therefore, there is a need to develop a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness and a manufacturing method thereof

<Related art document>

[0013]

(Patent document 1) Patent document 1: Japanese Patent Laid-Open Publication No. S63-290246

(Patent document 2) Patent document 2: Japanese Patent Laid-Open Publication No. S58-153730

(Patent document 3) Patent document 3: Japanese Patent Laid-Open Publication No. H4-17613

[Disclosure]

[Technical Problem]

[0014] An aspect of the present disclosure is to provide a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness, and a manufacturing method thereof.

[0015] Meanwhile, the aspect of the present disclosure is not limited to the above description. It will be understood by those of ordinary skill in the art that there is no difficulty in understanding the additional problems of the present disclosure.

[Technical Solution]

[0016] According to an aspect of the present disclosure, a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness includes: by weight percent (or percent by weight) (wt%), 0.02 to 0.10% of carbon (C), 0.5 to 2.0% of manganese (Mn), 0.05 to 0.5% of silicon (Si), 0.05 to 1.0% of nickel (Ni), 0.005 to 0.1% of titanium (Ti), 0.005 to 0.5% of aluminum (Al), 0.005% or less of niobium (Nb), 0.015% or less of phosphorus (P), 0.015% or less of sulfur (S), a balance of Fe and other inevitable impurities, and a microstructure includes, in area percent (%), 60% or more of acicular ferrite and the balance including at least one phase of bainite, polygonal ferrite and martensite-austenite constituent (MA).

[0017] According to another aspect of the present disclosure, a method of manufacturing a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness includes: heating a slab including, by weight percent (or percent by weight) (wt%), 0.02 to 0.10% of carbon (C), 0.5 to 2.0% of manganese (Mn), 0.05 to 0.5% of silicon (Si), 0.05 to 1.0% of nickel (Ni), 0.005 to 0.1% of titanium (Ti), 0.005 to 0.5% of aluminum (Al), 0.005% or less of niobium (Nb), 0.015% or less of phosphorus (P), 0.015% or less of sulfur (S), a balance of Fe and other inevitable impurities, to 1000 to 1200°C; rough-rolling the heated slab at a temperature of 1100 to 900°C; finishing-rolling at a temperature between $Ar_3 + 100^\circ\text{C}$ and $Ar_3 + 30^\circ\text{C}$ on the basis of a center temperature after the rough rolling; and cooling to a temperature of 300°C or lower after the finishing-rolling.

[0018] The foregoing technical solutions do not fully enumerate all of the features of the present invention. The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

[Advantageous Effects]

[0019] As set forth above, according to an exemplary embodiment in the present disclosure, by controlling an alloy composition and microstructure, the low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness and the manufacturing method thereof may be provided.

[Description of Drawings]

[0020]

FIG. 1 is a view illustrating phase transformation of inventive steel A according to a cooling rate.

FIG. 2 is a photograph (1-(1) in FIG. 1) obtained by observing a microstructure of the 1/4t portion of a steel sheet of A-5 as comparative example with an optical microscope.

FIG. 3 is a photograph (1-(2) in FIG. 1) obtained by observing a microstructure of the 1/4t portion of a steel sheet of A-1 as inventive example with an optical microscope.

FIG. 4 is a photograph (1-(3) in FIG. 1) obtained by observing a microstructure of the 1/4t portion of a steel sheet of A-6 as comparative example with an optical microscope.

[Best Mode for invention]

[0021] Hereinafter, preferred embodiments of the present disclosure will be described. However, the embodiments of the present disclosure may be modified into various other forms, and the scope of the present disclosure is not limited to the embodiments described below. Embodiments of the present invention are provided so that those skilled in the art may more completely understand the present invention.

[0022] The inventors of the present application recognized that it is difficult to make both ammonia stress corrosion

cracking resistance and low temperature toughness excellent and have studied to solve the problem.

[0023] As a result, the inventors confirmed that it is possible to provide a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness by controlling an alloy composition and a microstructure and a manufacturing method thereof, thereby completing the present disclosure.

[0024] Hereinafter, a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness according to an aspect of the present disclosure will be described in detail.

[0025] The low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness according to an aspect of the present disclosure includes, by weight percent (or percent by weight) (wt%), 0.02 to 0.10% of carbon (C), 0.5 to 2.0% of manganese (Mn), 0.05 to 0.5% of silicon (Si), 0.05 to 1.0% of nickel (Ni), 0.005 to 0.1% of titanium (Ti), 0.005 to 0.5% of aluminum (Al), 0.005% or less of niobium (Nb), 0.015% or less of phosphorus (P), 0.015% or less of sulfur (S), a balance of Fe and other inevitable impurities.

[0026] A microstructure includes, in area percent (%), 60% or more of acicular ferrite and the balance including at least one phase of bainite, polygonal ferrite and martensite-austenite constituent (MA).

[0027] First, an alloy composition of the low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness according to an aspect of the present disclosure will be described in detail. Hereinafter, the content of each component refers to weight percent (wt%).

C (carbon): 0.02 to 0.10%

[0028] Since C is the most important element for securing basic strength, it is necessary to be contained within an appropriate range in the steel, and in order to obtain an additive effect, preferably, C is added in an amount of 0.02% or more.

[0029] If the C content is less than 0.02%, strength may be reduced and the yield ratio may be lowered, which is not preferable. If the C content exceeds 0.10%, a large amount of low temperature transformation phases such as bainite, or the like, is generated to exceed an upper limit of yield strength that may cause ammonia stress corrosion cracking (SCC).

[0030] Therefore, the content of C is preferably limited to 0.02 to 0.10%. More preferably, it is 0.05 to 0.08%.

Si (silicon): 0.05 to 0.5%

[0031] Si has an effect of increasing strength due to the effect of solid solution strengthening and is advantageously used as a deoxidizing agent in steel making process.

[0032] If the Si content is less than 0.05%, the deoxidation effect and the strength improving effect may be insufficient. If the Si content exceeds 0.5%, the low-temperature toughness is lowered and weldability is deteriorated.

[0033] Therefore, the silicon content is preferably limited to 0.05 to 0.5%. More preferably, it is 0.05 to 0.3%.

Mn (manganese): 0.5 to 2.0%

[0034] Manganese contributes to ferrite grain refinement and is an element useful for improving strength by solid solution strengthening.

[0035] In order to obtain the effect of manganese, manganese is required to be added in an amount of 0.5% or more. If, however, the content exceeds 2.0%, hardenability may be excessively increased, which promotes formation of upper bainite and martensite to significantly reduce impact toughness and ammonia stress corrosion cracking (SCC) resistance and to reduce toughness of weld heat-affected zone as well.

[0036] Therefore, the Mn content is preferably limited to 0.5 to 2.0%. More preferably, it is 1.0 to 1.5%.

Ni (nickel): 0.05 to 1.0%

[0037] Ni is an important element for facilitating cross slip of dislocations at low temperatures to improve impact toughness and hardenability and to improve strength. In order to obtain such an effect, Ni is preferably added in an amount of 0.05% or more. If the Ni content exceeds 1.0%, ammonia stress corrosion cracking (SCC) may occur and manufacturing costs may be increased due to the high cost of Ni relative to other hardenable elements.

[0038] Therefore, the Ni content is preferably limited to 0.05 to 1.0%, and more preferably, 0.2 to 0.5%.

Nb (niobium): 0.005% or less

[0039] It is known that Nb dissolved in reheating at high temperatures is precipitated very finely in the form of NbC to inhibit the recrystallization of austenite, thereby making the structure finer.

[0040] Since yield strength may be excessively increased due to microstructure refining, which may exceed the upper

limit of yield strength that may cause ammonia stress corrosion cracking (SCC), Nb is preferably controlled to 0.005% or less. More preferably, it is 0.003% or less.

Ti (titanium): 0.005 to 0.1%

[0041] Titanium forms oxides and nitrides in the steel to inhibit growth of crystal grains during reheating, thereby significantly improving low temperature toughness, and is also effective in refining the microstructure of a welded portion.

[0042] In order to obtain such an effect, titanium needs to be added in an amount of 0.005 wt% or more. If the content exceeds 0.1 wt%, low temperature toughness may be reduced due to clogging of a nozzle or crystallization of a central portion.

[0043] Therefore, the titanium content is preferably 0.005 to 0.1%. More preferably, it is 0.01 to 0.03%.

Al (aluminum): 0.005-0.5%

[0044] Aluminum is an element useful for deoxidizing molten steel, and to this end, aluminum needs to be added in an amount of 0.005 wt% or more. If the content exceeds 0.5 wt%, nozzle clogging may occur during continuous casting. Therefore, the aluminum content is preferably 0.005 to 0.5%. More preferably, it is 0.005 to 0.05%.

P (phosphorus): 0.015% or less

[0045] Phosphorus is an element that causes grain boundary segregation in a base material and a welded portion. Since phosphorus causes a problem of embrittling steel, an amount of phosphorus needs to be actively reduced. However, reducing phosphorus to an extreme limit may deepen a load of a steel making process and since the aforementioned problem does not significantly arise as long as the content of phosphorus is 0.015% or less, an upper limit thereof is limited to 0.015%, more preferably, to 0.010%.

S (sulfur): 0.015% or less

[0046] Sulfur (S), an element which causes red shortness, forms MnS, or the like, to significantly inhibit impact toughness. Therefore, sulfur is preferably controlled to as low as possible and the content is limited to 0.015 wt% or less, more preferably, to 0.005 wt%.

[0047] The balance of the present disclosure is iron (Fe). However, in the ordinary manufacturing process, impurities may be inevitably incorporated from a raw material or a surrounding environment, which may not be excluded. These impurities are known to any one skilled in the art in the ordinary manufacturing process and thus not specifically mentioned in this disclosure.

[0048] Next, a microstructure of the low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness according to one aspect of the present disclosure will be described in detail.

[0049] The microstructure of the steel of the present disclosure includes, in area %, 60% or more of acicular ferrite and a balance of at least one phase of bainite, polygonal ferrite and martensite-austenite constituent (MA).

[0050] If a fraction of the bainite is increased so the acicular ferrite is less than 60%, impact toughness may deteriorate due to an increase in a hard phase, and if a fraction of the polygonal ferrite is increased so the acicular ferrite is less than 60%, strength may deteriorate. Therefore, the area fraction of the acicular ferrite is preferably 60% or more.

[0051] In addition, the inclusion of pearlite may lower tensile strength and low-temperature impact toughness, and thus, the microstructure of the steel of the present disclosure may not contain pearlite.

[0052] Here, the acicular ferrite measured in terms of the equivalent of a circle diameter may be 30 μ m or less. If the size exceeds 30 μ m, impact toughness may be lowered.

[0053] Further, the bainite is preferably granular bainite and upper bainite.

[0054] Meanwhile, an area fraction of the bainite is preferably 30% or less. If the area fraction of the bainite exceeds 30%, an upper limit (440 MPa) of yield strength (440 MPa) which may cause ammonia stress corrosion cracking (SCC) may be exceeded, and thus, it is necessary to limit the fraction of the bainite.

[0055] The MA phase is preferably 10% by area or less and the size measured by the equivalent of a circle diameter is preferably 5 μ m or less. MA (Martensite-Austenite constituent) is also referred to as a martensitic island.

[0056] If the fraction of the MA phase exceeds 10% or if the equivalent of a circle diameter exceeds 5 μ m, toughness of the base material and the welded portion tends to be significantly lowered. Therefore, it is necessary to limit the fraction and size of the MA phase.

[0057] Meanwhile, the steel of the present disclosure satisfying the above conditions may have a yield ratio (YS/TS) of 0.85 or less, preferably, 0.8 or less. The steel may have tensile strength of 490 MPa or greater, for example, about 510 to 610 MPa, having excellent tensile strength.

[0058] In addition, an upper limit of yield strength of the steel is 440 MPa or less and does not exceed the upper limit of yield strength which causes ammonia stress corrosion cracking (SCC), and thus, ammonia stress corrosion cracking (SCC) resistance may be excellent.

[0059] In addition, since an impact transition temperature of the 1/4t portion in a thickness direction of the steel is -60°C or lower, low temperature toughness may be excellent. Here t represents a thickness of the steel.

[0060] Here, the steel has a thickness of 6 mm or greater, and preferably, 6 to 50 mm.

[0061] As described above, the steel of the present disclosure may secure all of high strength, low yield ratio, excellent low temperature toughness, and ammonia stress corrosion cracking (SCC) resistance.

[0062] Hereinafter, a method for manufacturing a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness according to another aspect of the present disclosure will be described in detail.

[0063] The method of manufacturing a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness according to another aspect of the present disclosure includes : heating a slab having the above-described alloy composition to 1000 to 1200°C;

rough-rolling the heated slab at a temperature of 1100 to 900°C;

finishing-rolling at a temperature between Ar3 + 100°C and Ar3 + 30°C on the basis of a center temperature after the rough rolling; and

cooling to a temperature of 300°C or lower after the finishing-rolling.

Heating

[0064] The slab having the above-described alloy composition is heated to 1000 to 1200°C.

[0065] The heating temperature of the slab is preferably 1000°C or higher, and this is to dissolve a Ti carbonitride formed during casting. If the heating temperature of the slab is too low, deformation resistance during rolling is too high, so that a reduction ratio per rolling pass may not be increased in a follow-up rolling process, and thus, a lower limit thereof is preferably limited to 1000°C. However, if heating is carried out at an excessively high temperature, austenite may be coarsened to lower toughness, and thus, an upper limit of the heating temperature is preferably 1200°C.

Rough rolling

[0066] The heated slab is subjected to rough rolling at a temperature of 1100 to 900°C.

[0067] The rough rolling temperature is preferably set to be not lower than a temperature (T_{nr}) at which recrystallization of the austenite is stopped. An effect of breaking a cast structure such as dendrites formed during casting and reducing the size of austenite may be obtained through rolling. In order to obtain such an effect, the rough rolling temperature is preferably limited to 1100 to 900°C.

[0068] Here, the rough rolling may be performed so that the last three rolling passes have a reduction ratio of 10% or greater per pass.

[0069] In order to provide sufficient deformation to the center during rough rolling, it is preferred that the reduction ratio per pass is at least 10% and a total cumulative reduction ratio is at least 30% for the last three rolling passes during rough rolling.

[0070] During rough rolling, grain growth is made in a recrystallized structure due to a high temperature in initial rolling, but when the last three rolling passes are performed, a grain growth rate is slowed as a bar is air-cooled in a rolling atmosphere, and due thereto, a reduction ratio of the last three passes during rough rolling most significantly affects a grain size of a final microstructure.

[0071] Also, if the reduction ratio per pass in rough rolling is lowered, sufficient deformation is not transferred to the central portion, which may cause toughness degradation due to center coarsening. Therefore, the reduction ratio per pass of the last three passes is preferably limited to 10% or greater.

[0072] Meanwhile, in order to miniaturize the structure at the central portion, it is preferable to set a cumulative rolling reduction ratio at the time of rough rolling to 30% or greater.

Finishing rolling

[0073] After the rough rolling, finishing rolling is performed at a temperature between Ar3 + 100°C and Ar3 + 30°C on the basis of a temperature of the central portion.

[0074] This is to obtain a finer microstructure, and when finishing rolling is performed at Ar3 (ferrite transformation start temperature) + 100°C to Ar3 + 30°C, a large amount of deformation bands is generated in the austenite to secure a large amount of ferrite nucleation sites, obtaining an effect of securing a fine structure up to the central portion of the steel.

[0075] If the temperature for finishing rolling is lowered to below Ar3 + 30°C, the ferrite grain size becomes too fine to

exceed the yield strength upper limit (440 MPa) causing ammonia stress corrosion cracking (SCC). Also, finishing rolling performed at a temperature exceeding $Ar_3 + 100^\circ\text{C}$ is not effective in miniaturizing the grain size. Thus, it is preferable to carry out the finishing rolling at a temperature between $Ar_3 + 100^\circ\text{C}$ and $Ar_3 + 30^\circ\text{C}$ and a microstructure of the steel sheet to be subjected to finishing rolling under such conditions may be a composite structure having the features mentioned above.

[0076] Here, the Ar_3 may be calculated as $Ar_3 = 910 - (310 \cdot C) - (80 \cdot Mn) - (55 \cdot Ni)$, each element symbol represents the content of each element measured in wt%, and the unit of Ar_3 is $^\circ\text{C}$.

[0077] Further, in order to effectively generate a large amount of deformation bands in the austenite, it is more preferable to maintain the cumulative reduction ratio at 60% or greater during finishing rolling and to maintain the reduction ratio per pass, excluding the final shape sizing phase, at 10% or more.

Cooling

[0078] After the finishing rolling, the steel sheet is cooled to a temperature of 300°C or lower.

[0079] After the finishing rolling, the cooling is preferably started at a temperature of $Ar_3 + 30^\circ\text{C}$ to Ar_3 and cooled to a finish cooling temperature (FCT) of 300°C or lower, for example, about 100 to 300°C .

[0080] If the finish cooling temperature (FCT) is higher than 300°C , the fine MA phase may be decomposed due to a tempering effect to make it difficult to realize a low yield ratio. Thus, the finish cooling temperature is preferably 300°C or lower.

[0081] Here, in performing cooling, first cooling may be performed such that a cooling rate at the central portion is 15°C/s or greater up to $B_s - 10^\circ\text{C}$ to $B_s + 10^\circ\text{C}$, and second cooling may be performed up to 300°C or lower such that a cooling rate at the central portion is 10 to 50°C/s .

[0082] The cooling start temperature may be $Ar_3 + 30^\circ\text{C}$ to Ar_3 .

[0083] The above-mentioned first cooling preferably starts, after finishing rolling, to perform cooling at a temperature of $Ar_3 + 30^\circ\text{C}$ to Ar_3 up to $B_s - 10^\circ\text{C}$ at a cooling rate of 15°C/s or higher, for example, 30°C/s or higher, in the central portion of the steel sheet.

[0084] If the cooling rate of the central portion of the steel sheet is lower than 15°C/s up to $B_s - 10^\circ\text{C}$ to $B_s + 10^\circ\text{C}$ in the first cooling, it is possible to form a coarse polygonal ferrite to lower tensile strength and impact toughness.

[0085] Here, B_s may be calculated as $B_s = 830 - (270 \cdot C) - (90 \cdot Mn) - (37 \cdot Ni)$, each element symbol represents the content of each element measured in wt%, and the unit of B_s is $^\circ\text{C}$.

[0086] The second cooling is preferably performed after the first cooling up to the finish cooling temperature of 300°C or lower, for example, 100 to 300°C , at a cooling rate of 10°C/s to 50°C/s in the central portion of the steel sheet.

[0087] If the cooling rate of the steel sheet exceeds 50°C/s in the second cooling, the bainite fraction is formed to be 30% or greater by area as in the microstructure of 1- (1) of FIG. 1 to exceed the yield strength upper limit (440 MPa) causing ammonia stress corrosion cracking (SCC), and the excessive increase in strength may lower elongation and impact toughness.

[0088] Meanwhile, if the cooling rate of the steel sheet is lower than 10°C/s in the second cooling, a coarse polygonal ferrite and pearlite, rather than the fine acicular ferrite like the microstructure of 1-(3) of FIG. 1, may be formed, leading to a possibility that tensile strength is 490 MPa or less and Charpy transition temperature is -60°C or higher.

[0089] According to the above-described manufacturing method, it is possible to manufacture a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness.

[Mode for invention]

[0090] Hereinafter, the present disclosure will be described in detail by way of examples. It should be noted, however, that the following examples are intended to illustrate the present disclosure in more detail and not to limit the scope of the present disclosure and the scope of the present disclosure is determined by the matters described in the claims and the matters reasonably inferred therefrom.

[0091] A 300 mm-thick steel slab having the composition shown in Table 1 below was reheated to a temperature of 1100°C and then subjected to rough rolling at a temperature of 1050°C to prepare a bar. A cumulative reduction ratio during rough rolling was applied equally as 30%. Also, Ar_3 and B_s temperatures according to compositions of each steel were calculated and are shown in Table 1 below.

[0092] After the rough rolling, finishing rolling was performed to satisfy the difference between the finishing rolling temperature and the Ar_3 temperature shown in Table 2 below to obtain a steel sheet having the thickness shown in Table 2, and thereafter, cooling performed at various cooling rates through multistage cooling. Here, a finish cooling temperature of first cooling was equal to the B_s temperature of each steel.

[0093] The microstructure, yield strength, tensile strength, yield ratio, Charpy impact transition temperature, and ammonia stress corrosion cracking (SCC) test were performed on the steel sheet prepared as described above, and the

results are shown in Table 3.

[0094] A sample of the microstructure was taken from the 1/4t portion of the steel sheet, mirror-polished, corroded using a Nital corrosion solution, and observed using an optical microscopy, and thereafter, a phase ratio was obtained through an image analysis.

[0095] A sample was taken from a 1/4t portion of the steel sheet, mirror-polished, corroded using a LePera corrosion solution, and observed using an optical microscope, and thereafter, a phase ratio of the MA phase was obtained through an image analysis.

[0096] A sample of No. JIS4 was taken from a 1/4t portion of the steel sheet in a direction perpendicular to a rolling direction and subjected to a tensile test at room temperature to measure yield strength, tensile strength and A yield ratio.

[0097] As for the low-temperature impact toughness, a sample was taken from a 1/4t portion of the steel sheet in a direction perpendicular to the rolling direction to manufacture a V-notch test sample and Charpy impact test was performed three times at each temperature at temperatures from -20 to -100°C at an interval of 20°C to derive a regression equation of each temperature average value, and low-temperature impact toughness was obtained at a temperature of 100J as a transition temperature.

[0098] In addition, the ammonia stress corrosion cracking (SCC) test was carried out using the test solution under the test conditions described in Table 4 by making proof ring test samples. 80% of actual yield stress was applied, and samples which were not broken for 720 hours were evaluated as pass and samples which were broken before 720 hours were evaluated as fail.

[Table 1]

Steel type	Steel composition (wt%)									Ar ₃ (°C)	Bs (°C)
	c	Si	Mn	Ni	Ti	Al	Nb	P (ppm)	S (ppm)		
Inventive steel A	0.08	0.3	1.5	0.2	0.01	0.03	0.003	59	25	754	666
Inventive steel B	0.072	0.27	1.32	0.34	0.012	0.024	0.001	46	31	763	679
Comparative Steel C	0.12	0.16	1.25	0.63	0.018	0.013	0.001	49	9	738	662
Comparative Steel D	0.062	0.32	2.11	0.65	0.011	0.026	0.002	55	17	686	599
Comparative Steel E	0.07	0.21	1.32	1.62	0.013	0.032	0.001	79	24	694	632
Comparative Steel F	0.069	0.23	1.41	0.52	0.021	0.033	0.035	81	33	747	665

[Table 2]

Steel type	Classification		Finishing rolling temperature -Ar ₃ temperature (°C)	Product thickness (mm)	First cooling rate (°C/s)	Second cooling rate (°C/s)	Finish cooling temperature (°C)
Inventive steel A	A-1	Inventive example	45	20	40	45	250
	A-2	Comparative example	150	20	38	25	280
	A-3	Comparative example	-30	20	35	30	150
	A-4	Comparative example	30	30	8	15	240
	A-5	Comparative example	18	15	50	75	150
	A-6	Comparative example	50	35	15	7	300
	A-7	Comparative example	50	35	15	25	450

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(continued)

Steel type	Classification		Finishing rolling temperature -Ar ₃ temperature (°C)	Product thickness (mm)	First cooling rate (°C/s)	Second cooling rate (°C/s)	Finish cooling temperature (°C)
Inventive steel B	B-1	Inventive example	50	9	52	30	210
	B-2	Comparative example	200	50	15	10	150
	B-3	Comparative example	-55	9	50	45	150
	B-4	Comparative example	30	50	5	15	140
	B-5	Comparative example	18	10	55	80	210
	B-6	Comparative example	90	50	16	5	230
	B-7	Comparative example	45	12	54	44	420
Comparative Steel C	C-1	Comparative example	10	9	55	41	200
Comparative Steel D	D-1	Comparative example	15	12	52	35	150
Comparative Steel E	E-1	Comparative example	18	9	60	45	150
Comparative Steel F	F-1	Comparative example	10	8	65	48	150

[Table 3]

Steel type	Classification	Microstructure phase fraction (area%)				Yield strength (MPa)	Tensile strength (MPa)	Yield ratio	Impact transition temperature (°C)	Evaluation of Ammonia stress corrosion cracking (SCC)
		AF	B	PF	MA					
Inventive steel A	A-1	75	20	0	5	412	556	0.74	-78	Pass
	A-2	32	5	55	8	355	446	0.80	-54	Pass
	A-3	51	0	45	4	468	542	0.86	-72	Fail
	A-4	30	3	62	5	367	471	0.78	-48	Pass
	A-5	36	60	0	4	510	632	0.81	-31	Fail
	A-6	23	0	75	2	322	451	0.71	-46	Pass
	A-7	55	15	30	0	465	518	0.90	-51	Pass
Inventive steel B	B-1	80	12	0	8	424	563	0.75	-90	Pass
	B-2	34	12	50	4	326	451	0.72	-44	Pass
	B-3	50	0	48	2	459	512	0.90	-95	Fail
	B-4	35	5	58	2	325	425	0.76	-32	Pass
	B-5	20	77	0	3	583	642	0.91	-65	Fail
	B-6	25	0	70	5	333	423	0.79	-62	Pass
	B-7	32	36	32	0	486	521	0.93	-65	fail

(continued)

Steel type	Classification		Microstructure phase fraction (area%)					Yield strength (MPa)	Tensile strength (MPa)	Yield ratio	Impact transition temperature (°C)	Evaluation of Ammonia stress corrosion cracking (SCC)
			AF	B	PF	MA						
Comparative Steel C	C-1	Comparative example	42	56	0	2	512	680	0.75	-23	fail	
Comparative Steel D	D-1	Comparative example	30	68	0	2	543	625	0.87	-36	fail	
Comparative Steel E	E-1	Comparative example	70	15	0	15	435	552	0.79	-80	fail	
Comparative Steel F	F-1	Comparative example	78	2	15	5	556	612	0.91	-90	fail	

[0099] In Table 3, AF: Acicular Ferrite, B: Bainite, PF: Polygonal ferrite and MA: Martensite/Austenite.

[Table 4]

Sample	Proof ring sample
Test solution	Liquefied ammonia 5 wt% of ammonium carbamate 0.1% of O ₂ is contained
Test temperature	25°C
Test time	720 hours

[0100] As shown in Tables 1 to 3, it can be seen that the inventive examples satisfying the compositions and manufacturing conditions proposed in the present disclosure are steel having excellent ammonia stress corrosion cracking (SCC) resistance, as well as having high strength and high toughness, and having a yield ratio of 0.8 or less, low yield ratio characteristics. Also, the microstructure of the inventive example A-1 was observed with a microscope and the results showed that the microstructure was a mixed structure including, in area %, 60% of more of acicular ferrite and the balance including at least one phase of bainite, polygonal ferrite and martensite-austenite constituent (MA) as illustrated in 1-(2) of FIG. 1.

[0101] Meanwhile, in the case of Comparative Examples A-2, A-4, A-6, B-2, B-4 and B-6 in which the compositions satisfied the present disclosure but manufacturing conditions did not satisfy the present disclosure, the polygonal ferrite fraction was too high or the ferrite grain size was too coarse to secure tensile strength and low temperature toughness.

[0102] Meanwhile, in the case of Comparative Examples A-3, A-5, A-7 to B-3, B-5 and B-7, the acicular ferrite grain size was too small or the bainite fraction was too high, or the MA phase was not produced, and thus, the yield strength upper limit (440 MPa) at which the ammonia stress corrosion cracking (SCC) may occur was exceeded to cause the ammonia stress corrosion cracking (SCC) and it was impossible to secure a low yield ratio and low temperature toughness.

[0103] Also, in the case of Comparative Examples C-1 to F-4 in which the manufacturing conditions satisfied the present disclosure but the compositions did not satisfy the present disclosure, the bainite fraction was too high, the acicular ferrite grain size was too small, or the fraction of MA phase was too high, and thus, the yield strength upper limit (440 MPa) at which the ammonia stress corrosion cracking (SCC) may occur was exceeded to cause the ammonia stress corrosion cracking (SCC) and it was impossible to secure a low yield ratio and low temperature toughness.

[0104] While example embodiments have been shown and described above, it will be apparent to those skilled in the art that modifications and variations could be made without departing from the scope of the present invention as defined by the appended claims.

Claims

1. A low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness, comprising:

by weight percent, 0.02 to 0.10% of carbon (C), 0.5 to 2.0% of manganese (Mn), 0.05 to 0.5% of silicon (Si), 0.05 to 1.0% of nickel (Ni), 0.005 to 0.1% of titanium (Ti), 0.005 to 0.5% of aluminum (Al), 0.005% or less of niobium (Nb), 0.015% or less of phosphorus (P), 0.015% or less of sulfur (S), a balance of Fe and other inevitable impurities,

wherein a microstructure includes, in area percent (%), 60% or more of acicular ferrite and the balance including at least one phase of bainite, polygonal ferrite and martensite-austenite constituent (MA).

2. The steel of claim 1, wherein a size of the acicular ferrite measured in terms of the equivalent of a circle diameter is 30 μ m or less.

3. The steel of claim 1, wherein the bainite has a 30 area% or less.

4. The steel of claim 1, wherein the MA phase is 10 area% or less, and a size of the MA phase measured in terms of the equivalent of a circle diameter is 5 μ m or less.

5. The steel of claim 1, wherein
a yield ratio of the steel is 0.85 or less and tensile strength of the steel is 490 MPa or greater.

6. The steel of claim 1, wherein
yield strength of the steel is 440 MPa or less.

7. The steel of claim 1, wherein
an impact transition temperature of the steel is -60°C or lower.

8. A method of manufacturing a low yield ratio and high-strength steel having excellent stress corrosion cracking resistance and low temperature toughness, the method comprising:

heating a slab including, by weight percent, 0.02 to 0.10% of carbon (C), 0.5 to 2.0% of manganese (Mn), 0.05 to 0.5% of silicon (Si), 0.05 to 1.0% of nickel (Ni), 0.005 to 0.1% of titanium (Ti), 0.005 to 0.5% of aluminum (Al), 0.005% or less of niobium (Nb), 0.015% or less of phosphorus (P), 0.015% or less of sulfur (S), a balance of Fe and other inevitable impurities, to 1000 to 1200°C;

rough-rolling the heated slab at a temperature of 1100 to 900°C;

finishing-rolling at a temperature between $Ar_3 + 100^\circ\text{C}$ and $Ar_3 + 30^\circ\text{C}$ on the basis of a center temperature after the rough rolling; and

cooling to a temperature of 300°C or lower after the finishing-rolling.

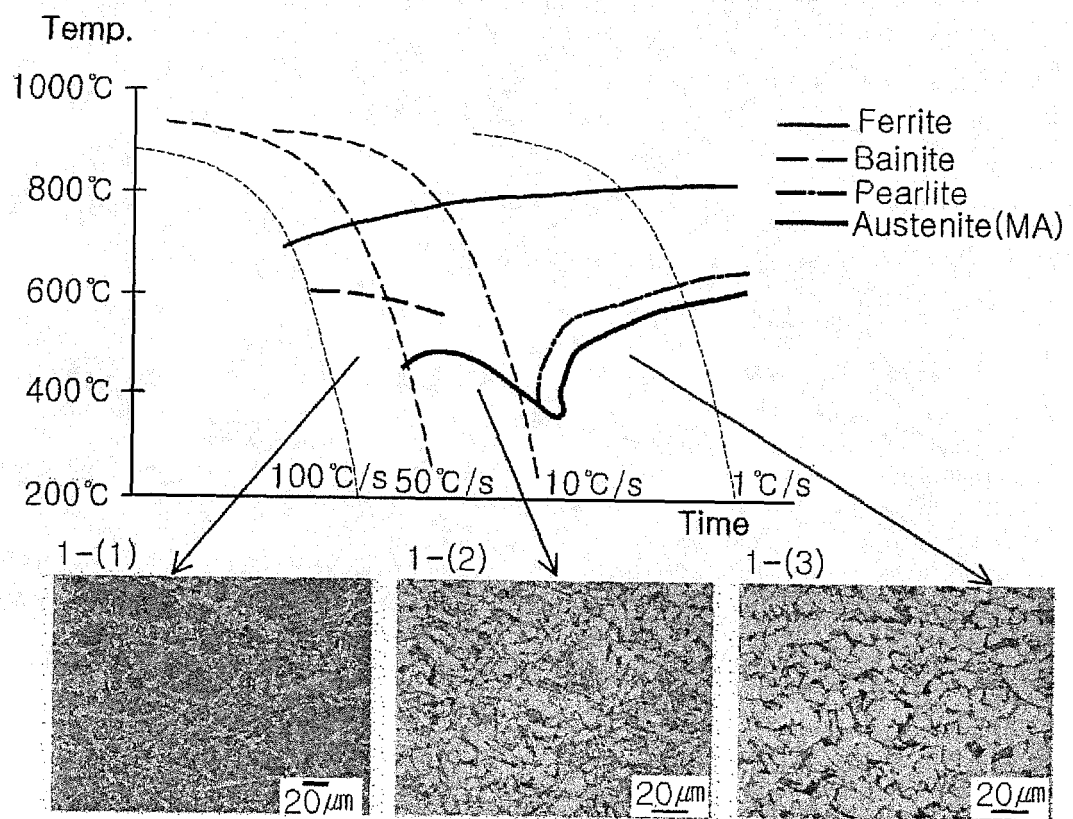
9. The method of claim 8, wherein
in performing cooling, first cooling is performed such that a cooling rate at the central portion is 15°C/s or greater up to $B_s - 10^\circ\text{C}$ to $B_s + 10^\circ\text{C}$, and
second cooling is performed up to 300°C or lower such that a cooling rate at the central portion is 10 to 50°C/s.

10. The method of claim 8, wherein
a cooling start temperature is $Ar_3 + 30^\circ\text{C}$ to Ar_3 .

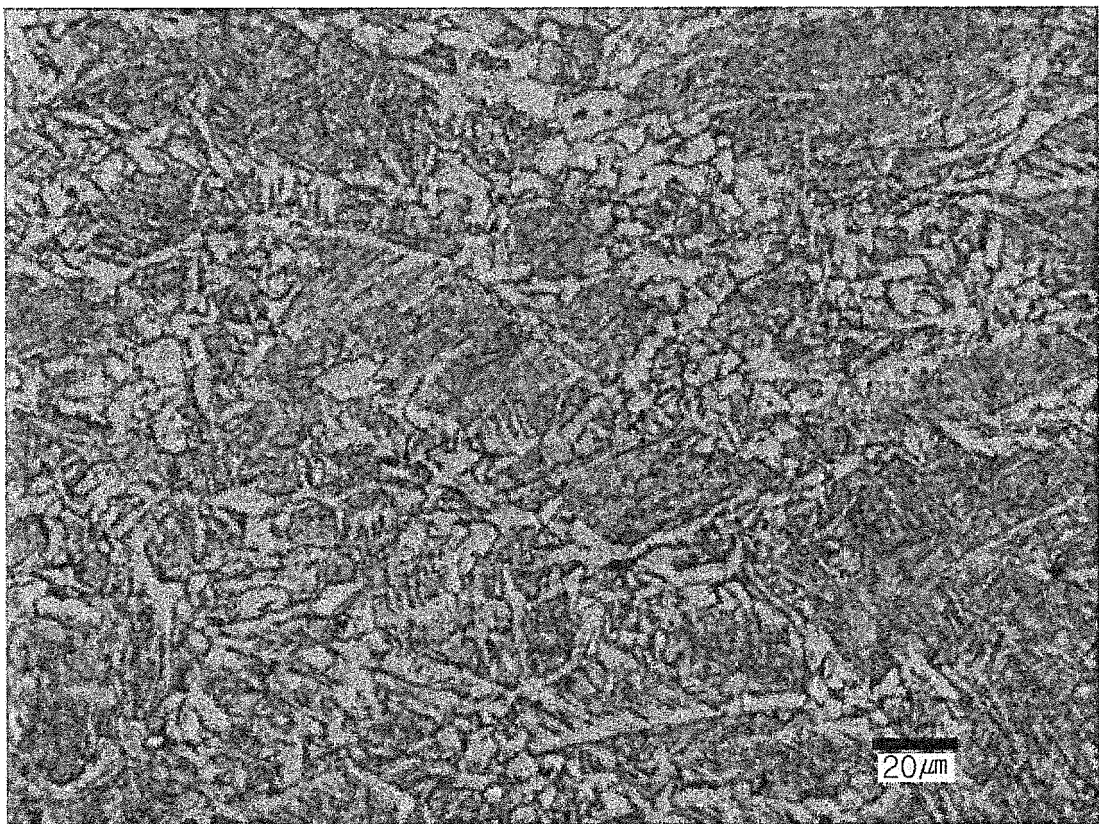
11. The method of claim 8, wherein
the rough rolling is performed so that the last three rolling passes have a reduction ratio of 10% or greater per pass .

12. The method of claim 8, wherein
the finishing rolling is performed such that a reduction ratio per pass is 10% or greater and a cumulative reduction ratio is 60% or greater.

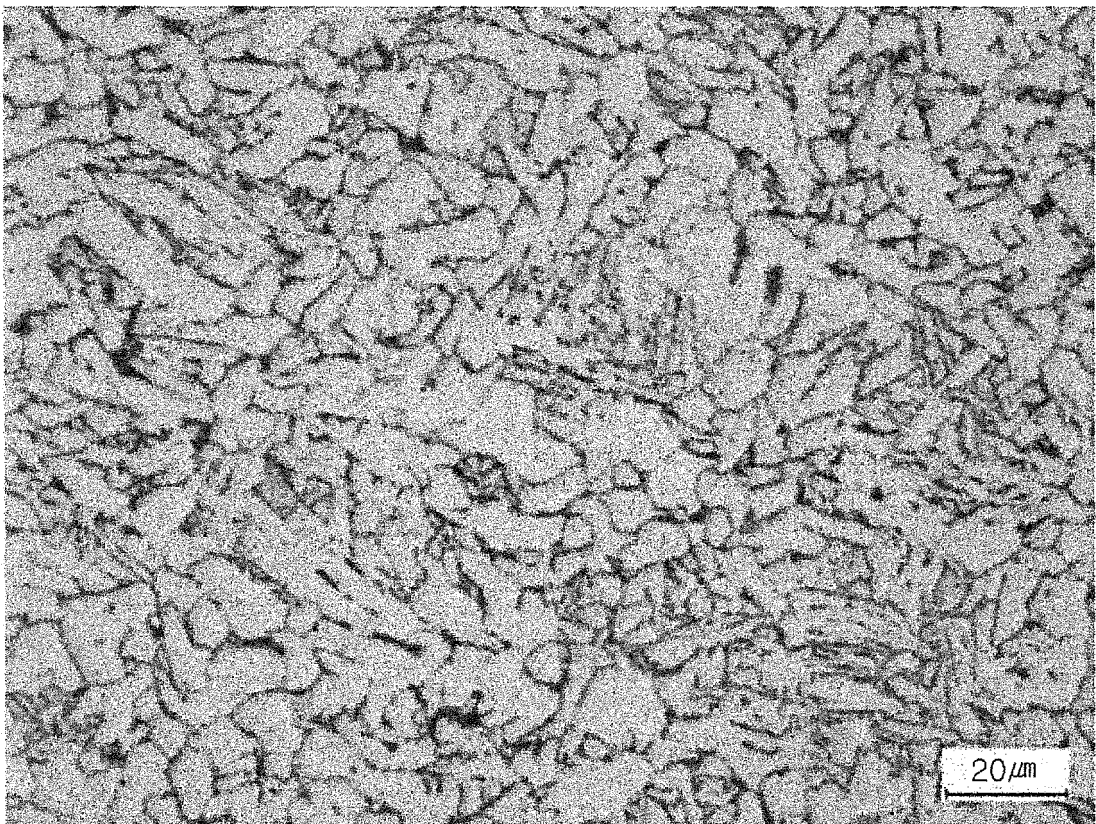
【FIGURE 1】



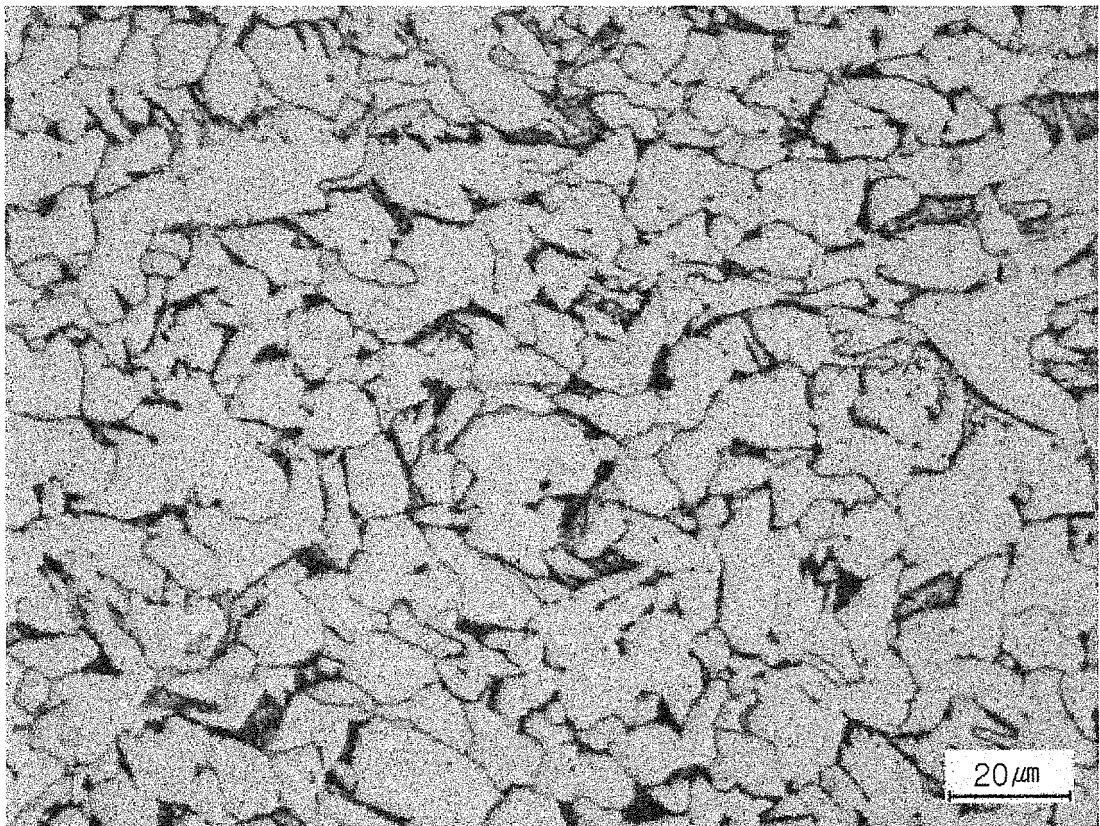
【FIGURE 2】



【FIGURE 3】



【FIGURE 4】



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2016/015156

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/14(2006.01)i, C22C 38/12(2006.01)i, C22C 38/08(2006.01)i, C22C 38/06(2006.01)i, C22C 38/04(2006.01)i, C22C 38/02(2006.01)i, C21D 8/02(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 38/14; C21D 8/02; C22C 38/00; C22C 38/58; C22C 38/12; C22C 38/08; C22C 38/06; C22C 38/04; C22C 38/02

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: manganese, nickel, titanium, niobium, acicular ferrite, bainite, polygonal ferrite, impact transition temperature, cooling

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2012-107310 A (JFE STEEL CORP.) 07 June 2012 See paragraphs [0051], [0052], [0058], [0093] and claims 1, 4.	1-12
A	KR 10-2011-0116760 A (KOREA INSTITUTE OF MACHINERY & MATERIALS) 26 October 2011 See paragraph [0079] and claims 1-4.	1-12
A	KR 10-2011-0075627 A (POSCO) 06 July 2011 See paragraphs [0064]-[0070] and claims 1-3.	1-12
A	KR 10-2014-0023787 A (POSTECH ACADEMY-INDUSTRY FOUNDATION) 27 February 2014 See paragraphs [0068]-[0072] and claim 1.	1-12
A	KR 10-2013-0110643 A (HYUNDAI STEEL COMPANY) 10 October 2013 See paragraph [0084] and claims 1, 4.	1-12

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

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Date of the actual completion of the international search

14 MARCH 2017 (14.03.2017)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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PCT/KR2016/015156

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REFERENCES CITED IN THE DESCRIPTION

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- JP S58153730 B [0013]
- JP H417613 B [0013]