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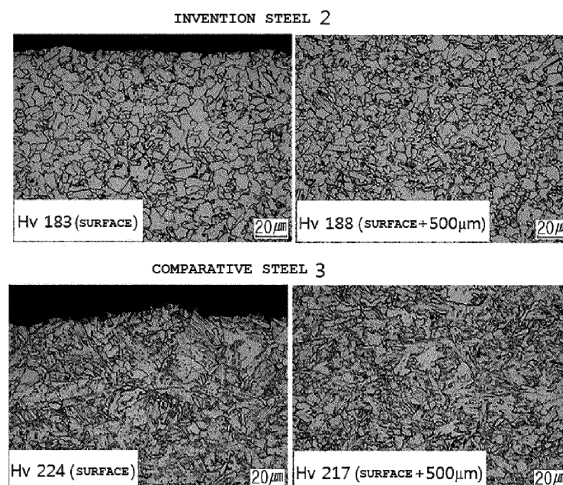
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(54) **STEEL MATERIAL HAVING EXCELLENT RESISTANCE TO SULFIDE STRESS CRACKING AND METHOD FOR MANUFACTURING SAME**

(57) The present invention relates to a thick steel material suitable for use as a line pipe, a sour-resistant material, or the like, and more specifically, to a high-strength steel material having excellent resistance to sulfide stress cracking while at the same time having excellent resistance to propagation of sulfide stress cracking, and a method for manufacturing the same.

[FIG. 1]



Description

[Technical Field]

[0001] The present disclosure relates to a thick steel material that is suitable for a line pipe, a sour-resistant material and, more particularly, to a high-strength steel material having excellent sulfide stress corrosion cracking resistance, and a method of manufacturing the steel material.

[Background Art]

[0002] Recently, the demand for an upper limit of surface hardness of line pipe steel materials is increasing. When the surface hardness of a line pipe is high, nonuniformity of roundness is caused when a pipe is machined, and cracks are formed due to high-hardness structures of the pipe surface when the pipe is machined and a deficit of toughness is caused in a use environment. Further, there is a high possibility that the high-hardness structures of the surface may cause brittle cracking due to hydrogen when the material is used in a sour environment with a lot of sulfides, so there is a high possibility of a significant accident.

[0003] There is an instance in which, in 2013, sulfide stress cracking (SSC) occurred in the high-hardness portions of a pipe surface within 2 weeks of a large-scale petroleum/natural gas exploitation project being started at the Caspian Sea, so pipelines at 200km below the sea were replaced with clad pipes. In this case, as the result of analysis, formation of hard spots that are high-hardness structures of the pipe surface is inferred as the reason of SSC.

[0004] The length is regulated at 2 inches or more and hardness is regulated at Hv 345 or more for hard spots under API standards, and DNV standards regulate the same sizes as API standards, but regulate the upper limit of hardness at Hv 250.

[0005] Meanwhile, steel materials for line pipe are manufactured generally by reheating, hot-rolling, and then accelerated-cooling a steel slab, and it is determined that hard spots (portions at which high-hardness structures are formed) are generated due to non-uniform rapid cooling of a surface portion in the accelerated cooling.

[0006] In a steel plate manufactured by common water cooling, the cooling rate is higher at the surface portion than the center portion because water is sprayed to the surface of the steel plate and hardness in the surface portion is higher than the center portion due to the cooling rate difference.

[0007] A method of attenuating a water-cooling process may be considered as a method for suppressing formation of high-hardness structures at the surface portion of a steel material. However, reducing surface hardness by attenuating water cooling is accompanied by strength reduction, which causes a problem that more alloy elements should be added, etc. Further, such an increase of alloy elements is also a factor that increases surface hardness.

[Related Art Document]

[Patent Document]

[0008] (Patent Document 1) Korean Patent Application Publication No. 1998-028324

[Disclosure]

[Technical Problem]

[0009] An aspect of the present disclosure is to provide a high-strength steel material having excellent sulfide stress corrosion cracking resistance by effectively reducing hardness at a surface portion in comparison to a thick-plate water-cooled material (TMCP) by optimizing alloy composition and manufacturing conditions, and a method of manufacturing the high-strength steel material.

[0010] In more detail, an aspect of the present disclosure is to provide a high-strength steel material having yield strength of 450MPa or more and having excellent sulfide stress corrosion cracking resistance in a high-pressure H₂S environment exceeding partial pressure of 1bar, and a method of manufacturing the high-strength steel material.

[0011] Further, an aspect of the present disclosure is to secure also a propagation resistance against sulfide stress corrosion cracking by increasing sulfide stress corrosion cracking resistance by effectively controlling hardness of a surface portion at a low level through optimization of alloy composition and manufacturing conditions, and by minimizing the content of chrome (Cr) that accelerates propagation of sulfide stress corrosion cracking in a high-pressure H₂S environment.

[0012] The objectives of the present disclosure are not limited to that described above. Those skilled in the art may understand additional objectives of the present disclosure without difficulty from the general contents in the specification.

[Technical Solution]

[0013] An aspect of the present disclosure provides a steel material that includes, by weight%, carbon (C): 0.02~0.06%, silicon (Si): 0.1~0.5%, manganese (Mn): 0.8~1.8%, chrome (Cr): less than 0.05%, phosphorous (P): 0.03% or less, sulfur (S): 0.003% or less, aluminum (Al): 0.06% or less, nitrogen (N): 0.01% or less, niobium (Nb): 0.005~0.08%, titanium (Ti): 0.005~0.05%, calcium (Ca): 0.0005~0.005%; one or more of nickel (Ni): 0.05~0.3%, molybdenum (Mo): 0.02~0.2%, and vanadium (V): 0.005~0.1%, and a balance of Fe and unavoidable impurities, in which the Ca and the S satisfy the following Equation 1, and the steel material has a microstructure of a surface portion composed of ferrite or a complex structure of ferrite and pearlite, and a microstructure of the center portion is composed of acicular ferrite,

[Equation 1]

$$0.5 \leq \text{Ca}/\text{S} \leq 5.0$$

where each element represents the content of each element by weight%.

[0014] Another aspect of the present disclosure provides a method of manufacturing a steel plate that includes: heating a steel slab satisfying the alloy composition described and Equation 1 at a temperature range of 1100~1300°C for 2 hours or more; manufacturing a hot-rolled plate by hot-rolling the heated steel slab; and cooling the hot-rolled plate after hot rolling, in which the cooling includes primary cooling, air cooling, and secondary cooling, and the primary cooling is performed at a cooling rate of 5~40°C/s such that a temperature of a surface portion of the hot-rolled plate becomes Ar1-50°C~Ar3-50°C and the secondary cooling is performed at a cooling rate of 50~500°C/s such that the temperature of the surface portion of the hot-rolled plate becomes 300~600°C.

[Advantageous Effects]

[0015] According to the present disclosure, when a thick steel material having a predetermined thickness, hardness at a surface portion is effectively reduced, so it is possible to provide a high-strength steel material having excellent resistance against sulfide stress corrosion cracking.

[0016] Further, according to the present disclosure, it is possible to provide a high-strength steel material having excellent resistance against sulfide stress corrosion cracking and excellent resistance against propagation of sulfide stress corrosion cracking too. This steel material of the present disclosure can be advantageously applied as not only the material of pipes such as a line pipe, but a sour-resistant material, and particularly, it is possible to provide a high-strength steel material having an excellent sulfide stress corrosion cracking characteristic even in a high-pressure H₂S environment over partial pressure of 1bar.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0017] FIG. 1 shows microstructures and hardness of surface portions of invention steel and comparative steel in an experimental example of the present disclosure

[Best Mode]

[0018] At present, Thermo-Mechanical Control Process (TMCP) materials that are supplied to the market of thick plate materials and hot rolling has a characteristic that hardness is higher at the surface portion than the center portion due to an avoidable phenomenon that is generated in cooling after hot rolling (a phenomenon that the cooling rate becomes higher at the surface portion than the center portion).

[0019] Accordingly, as the strength of a material is increased, hardness is considerably increased at the surface portion than the center portion, and such an increase in hardness at a surface portion is a factor that causes cracking or deteriorates low-temperature toughness in machining. Further, there is a problem that the increase is the onset point of hydrogen embrittlement when a steel material is applied to a sour environment. In spite of such problem of the related art, at present, a steel material having excellent sulfide stress corrosion cracking resistance under a high-pressure H₂S environment is not provided.

[0020] Accordingly, the inventors, as the result of recognizing and minutely examining the problem of the related art, have found out and achieved a steel material that can effectively suppress sulfide stress corrosion cracking resistance due to hard spots and does not easily propagate cracks even if cracks are generated at a surface portion due to hard spots.

[0021] In detail, the inventors, as an aspect of the present disclosure, have intended to provide a steel material securing resistance against cracking and propagation resistance against cracking and having high strength by effectively de-

creasing hardness of a surface portion in a thick steel plate having a predetermined thickness or more.

[0022] The inventors has conceived a new cooling control technique rather than the common cooling method of the related art, whereby the inventors have conceived a technique that can attenuate hardness of a surface portion separating phase transformation at a surface portion and a center portion.

[0023] That is, the inventors have develop a technique that can reduce hardenability of a surface portion by promoting decarburization of the surface portion in the process of heating and rolling, and can form ferrite at the surface portion. Further, the inventors of the present disclosure intend to provide a technique of manufacturing a steel plate having excellent sulfide stress corrosion cracking resistance even under a high-pressure H₂S environment by optimizing the components of steel and conditions such as manufacturing process (heating, hot rolling, cooling, etc.) because they have found out that when Cr is added as an alloy elements in a steel material propagation resistance against sulfide stress corrosion cracking resistance is deteriorated.

[0024] Hereafter, the component system of a steel material according to the present disclosure is described first.

[0025] A steel material according to an embodiment of the present disclosure may include, in percent by weight, carbon (C): 0.02~0.06%, silicon (Si): 0.1~0.5%, manganese (Mn): 0.8~1.8%, chrome (Cr): less than 0.05%, phosphorous (P): 0.03% or less, sulfur (S): 0.003% or less, aluminum (Al): 0.06% or less, nitrogen (N): 0.01% or less, niobium (Nb): 0.005~0.08%, titanium (Ti): 0.005~0.05%, calcium (Ca): 0.0005~0.005%; one or more of nickel (Ni): 0.05~0.3%, molybdenum (Mo): 0.02~0.2%, and vanadium (V): 0.005~0.1%, and a balance of Fe and unavoidable impurities.

[0026] Hereafter, the reason of limiting the alloy composition of the steel material provided in the present disclosure, as described above, is described in detail.

[0027] Meanwhile, unless specifically stated in the present disclosure, the content of each element is based on weight and the ratio of structures is based on an area.

Carbon (C): 0.02~0.06%

[0028] Carbon is an element having the largest influence on the properties of steel. When the content of C is less than 0.02%, there is a problem that an excessive component control cost is generated in the steel manufacturing process and welding heat-influenced portions are excessively softened. However, when the content exceeds 0.06%, hydrogen induced cracking resistance of a steel plate is decreased and weldability may be deteriorated. Accordingly, in the present disclosure, C may be included at 0.02~0.06%, and more preferably, 0.03~0.05%.

Silicon (Si): 0.1~0.5%

[0029] Silicon (Si) is an element that not only is used as a deoxidizer in a steel manufacturing process, but serves to increase strength of steel. When the content of Si exceeds 0.5%, low-temperature toughness of a material, weldability, and scale separability in rolling are deteriorated. Meanwhile, the manufacturing cost is increased to reduce the content of Si less than 0.1%, so the content of Si may be limited at 0.1~0.5%, and more preferably, 0.2~0.4%.

Manganese (Mn): 0.8.0~1.8%

[0030] Manganese (Mn), which is an element that improves hardenability of steel without deteriorating low-temperature toughness, may be included at 0.8% or more. However, when the content exceeds 1.8%, centerline segregation occurs, so there is a problem that low-temperature toughness is deteriorated, hardenability of steel is increased, and weldability is deteriorated. Further, centerline segregation of Mn is a factor that causes hydrogen induced cracking. Accordingly, Mn may be included at 0.8~1.8% in the present disclosure. Alternatively, in terms of centerline segregation, Mn may be included preferably at 0.8~1.6%, and more preferably, 1~1.4%.

Chrome (Cr): less than 0.05%

[0031] Chrome (Cr) is solidified in austenite when a slab is reheated, thereby contributing to increasing hardenability of a steel material and securing strength of a steel plate. However, the inventors have found out that when Cr is added at 0.05% or more, propagation of sulfide stress corrosion cracking may be promoted. That is, the content of Cr is limited less than 0.05% in a steel material, thereby achieving an effect that resistance against propagation of sulfide stress corrosion cracking. Meanwhile, the steel material according to an aspect of the present disclosure may include Cr more than 0% and less than 0.05%, more preferably, 0.04% of less, and the most preferably, 0.02% or less. However, since Cr may not be added when strength can be secured, the lower limit of the content of Cr may be 0%, and preferably, 0.0005%.

Phosphorous: 0.03% or less

[0032] Phosphorous (P) is an element that is unavoidably added in steel, and when the content exceeds 0.03%, there is a problem that not only weldability is remarkably decreased, but low-temperature toughness is reduced. Accordingly, it is required to limit the content of P at 0.03% or less, and, in terms of securing low-temperature toughness, more preferably, P may be included at 0.01% or less. However, 0% may be excluded as the lower limit of the content of Cr in consideration of load in the steel manufacturing process, and more preferably, the lower limit of the content of Cr may be 0.0001%.

Sulfur (S): 0.003% or less

[0033] Sulfur (S) is an element that is unavoidably added in steel, when the content exceeds 0.003%, there is a problem that ductility, low-toughness, and weldability of steel are reduced. Accordingly, the content of S needs to be limited at 0.003% or less. Meanwhile, S produces a MnS inclusion by bonding with Mn in steel, and in this case, the hydrogen induced cracking resistance of steel is deteriorated, so, more preferably, S may be included in 0.002% or less. However, 0% may be excluded as the lower limit of the content of S in consideration of load in the steel manufacturing process, and more preferably, the lower limit of the content of S may be 0.0001%.

Aluminum (Al): 0.06% or less (excluding 0%)

[0034] Aluminum (Al) usually functions as a deoxidizer that removes oxygen by reacting with oxygen (O) existing in molten steel. Accordingly, Al may be added such that it has a sufficient decarburization ability in steel. However, when the content exceeds 0.06%, a large amount of oxide-based inclusion is produced and deteriorates low-temperature toughness, hydrogen induced cracking resistance, and sulfide stress corrosion cracking resistance, which is not preferable. Accordingly, Al may be included at 0.06% or less, and more preferably, 0.04% or less. However, 0% may be excluded as the lower limit of the content of S in consideration of that Al is necessarily included as a deoxidizer, and more preferably, the lower limit of the content of Al may be 0.005%.

Nitrogen (N); 0.01% or less (excluding 0%)

[0035] Nitrogen (N) is difficult to be industrially completely removed from steel, so the upper limit thereof is 0.01% that is an allowable range in a manufacturing process. Meanwhile, since N produces nitrides by reacting with Al, Ti, Nb, V, etc. in steel, N suppresses growth of austenite grains, which has a good influence on improvement of toughness and strength of a material. However, when N is excessively added over 0.01%, N exists in a solidified state, which has a bad influence on low-temperature toughness. Accordingly, N may be included at 0.01% or less, and more preferably, 0.009% or less. However, 0% may be excluded as the lower limit of the content of N in consideration of load in the steel manufacturing process, and more preferably, the lower limit of the content of N may be 0.0005%.

Niobium (Nb): 0.005~0.08%

[0036] Niobium (Nb) is an element that solidifies when a slab is heated, thereby suppressing growth of austenite grains and effectively improving strength of steel through precipitation. Further, Nb is precipitated as a carbide by bonding with C in steel, thereby serving to minimize an increase of a yield ratio and improving strength of steel. When the content of Nb is less than 0.005%, the above effect cannot be sufficiently obtained, but when the content exceeds 0.08%, there is a problem that not only austenite grains are unnecessarily excessively micronized, but low-temperature toughness and hydrogen induced cracking resistance are deteriorated due to production of coarse precipitates. Accordingly, Nb may be included within 0.005~0.08% in the present disclosure. Meanwhile, the lower limit of the content of Nb may be more preferably 0.02% and the upper limit of the content of Nb may be 0.05%.

Titanium (Ti): 0.005~0.05%

[0037] Titanium (Ti) is precipitated as TiN by bonding with N when a slab is heated, which is effective in suppression of growth of austenite grains. When Ti is added less than 0.005%, austenite grains are coarsened, so low-temperature toughness is reduced. However, when the content exceeds 0.05%, coarse Ti-based precipitates are produced, so low-temperature toughness and hydrogen induced cracking resistance are reduced. Accordingly, Ti may be included within 0.005~0.05% in the present disclosure. Meanwhile, the lower limit of the content of Ti may be more preferably 0.006% and the upper limit of the content of Ti may be preferably 0.03% in terms of securing low-temperature toughness.

Calcium (Ca): 0.0005~0.005%

[0038] Calcium (Ca) produces CaS by bonding with S in a steel manufacturing process, thereby suppressing segregation of MnS that causes hydrogen induced cracking. It is required to add Ca at 0.005% or more in order to sufficiently achieve the effect of suppressing segregation of MnS, but when the content exceeds 0.005%, not only CaS, but CaO inclusions are produced, so hydrogen induced cracking is caused by the inclusions. Accordingly, in the present disclosure, Ca may be included at 0.0005~0.005%, and more preferably, 0.001~0.003% in terms of securing hydrogen induced cracking resistance.

[0039] The steel material according to the present disclosure contains Ca and S, as described above, in which it is preferable that the composition ratio of Ca and S ($[Ca]/[S]$) satisfies the following Equation 1.

[Equation 1]

$$0.5 \leq [Ca]/[S] \leq 5.0$$

where $[Ca]$ is the average content of Ca in a steel material by weight% and $[S]$ is the average content of S in a steel material by weight%. That is, the composition ratio of Ca and S is a representative index for core segregation of MnS and production of coarse inclusions, and when the $[Ca]/[S]$ value is less than 0.5, MnS is produced at the center portion in the thickness direction of a steel material, which may cause a problem of reduction of hydrogen induced cracking resistance. On the contrary, when the $[Ca]/[S]$ value exceeds 5.0, Ca-based coarse inclusions are produced, which deteriorates hydrogen induced cracking resistance. Accordingly, it is preferable that the composition ratio of Ca and S ($[Ca]/[S]$) satisfies Equation 1, and in order to further improve the above effect, more preferably, the $[Ca]/[S]$ value may be within the range of 1.4~3.2.

[0040] Meanwhile, the steel material of the present disclosure may further include elements that can further improve properties other than the alloy composition described above, and in detail, may further include one or more of Nickel (Ni): 0.05~0.3%, Molybdenum (Mo): 0.02~0.2%, and Vanadium (V): 0.005~0.1%. In this case, the steel material has only to include one or more of Ni, Mo, and V within the range of being able to achieve the objectives of the present disclosure, and all of Ni, Mo, and V are not necessarily included in the present disclosure.

Nickel (Ni): 0.05~0.3%

[0041] Nickel (Ni) is an element that has an effect in improvement of strength of steel without deterioration of low-temperature toughness. Ni may be added at 0.05% or more to achieve the effect of increasing strength without deteriorating low-temperature toughness, but Ni is an expensive element and the manufacturing process is considerably increased when the content of Ni exceeds 0.3%. Accordingly, Ni may be included at 0.05~0.3% when Ni is added in the present disclosure. Meanwhile, the lower limit of the content of Ni may be preferably 0.08%, and more preferably, 0.1%. Alternatively, the upper limit of the content of Ni may be preferably 0.28%, and more preferably, 0.21%.

Molybdenum (Mo): 0.02~0.2%

[0042] Molybdenum (Mo), similar to Cr, improves hardenability of a steel material and increases strength. Mo may be added at 0.02% or more to achieve the effect of improving hardenability described above, but when the content exceeds 0.2%, there is a problem that a structure that is vulnerable to low-temperature toughness such as upper bainite is produced, and hydrogen induced cracking resistance and sulfide stress corrosion cracking resistance are deteriorated. Accordingly, Mo may be included at 0.02~0.2% when Mo is added in the present disclosure. Meanwhile, the lower limit of the content of Mo may be more preferably 0.05% and the upper limit of the content of Mo may be 0.15%.

Vanadium (V): 0.005~0.1%

[0043] Vanadium (V) is an element that improves strength by increasing hardenability of a steel material and may be added at 0.005% or more to achieve this effect. However, when the content exceeds 0.1%, hardenability of steel excessively increases, so structures that are vulnerable to low-temperature toughness are formed and hydrogen induced cracking resistance is reduced. Accordingly, V may be included at 0.005~0.1% when V is added in the present disclosure. Meanwhile, the lower limit of the content of V may be more preferably 0.005% and the upper limit of the content of V may be more preferably 0.05%.

[0044] The balance is F in the present disclosure. However, since unintended impurities may be unavoidably mixed

from a raw material or a surrounding environment in a common manufacturing process, it cannot be excluded. Since anyone of those skilled in a common manufacturing process can know such impurities, they are not all specifically stated therein.

[0045] The steel material having the above alloy composition according to an aspect of the present disclosure is characterized in that the microstructure of the surface portion is composed of ferrite or a complex structure of ferrite and pearlite, whereby Vickers hardness of the surface portion may be controlled at 200Hv or less.

[0046] Meanwhile, the surface portion is the portion from the surface to a point at 1000 μ m in the thickness direction, which may be applied to both sides of a steel material. Further, the center portion is the other region except for the surface portion.

[0047] Further, in the present disclosure, the hardness of the surface portion is a maximum hardness value measured under 1kgf load using Vickers hardness from the surface to a point at 1000 μ m in the thickness direction. In general, hardness may be measured around 5 times at each position.

[0048] That is, in the steel material according to the present disclosure, the microstructure is composed of ferrite or a complex structure of ferrite and pearlite and the microstructure of the center portion is composed of acicular ferrite, so it is possible to form a soft microstructure at the surface portion in comparison to the center portion, whereby it is possible to provide a steel material of which the hardness in the surface portion is lower than those of existing TMCP steel materials.

[0049] In detail, the same or high strength is secured in the steel material according to an aspect of the present disclosure in comparison to existing TMCP steel materials, so the steel material has yield strength of 450MPa or more, the hardness of the surface portion is remarkably reduced, and the content of Cr is minimized, whereby it is possible to effectively suppress formation and propagation of sulfide stress corrosion cracks.

[0050] Meanwhile, a method of manufacturing the steel material according to the present disclosure described above is described in detail hereafter.

[0051] The steel material of the present disclosure may be manufactured through a process of [slab heating - hot rolling - cooling] and each of the process conditions are described in detail hereafter.

[Slab heating]

[0052] A steel slab that satisfies the alloy composition and component relationship proposed in the present disclosure may be prepared and then heated, which may be performed at 1100~1300°C for 2 hours.

[0053] When the heating temperature exceeds 1300°C, not only a scale defect increases, but austenite grains are coarsened, so hardness of the steel may be increased. Further, the fracture of structures that are vulnerable to low-temperature toughness such as upper bainite is increased at the center portion, so there is a problem that hydrogen induced cracking resistance and low-temperature toughness resistance are deteriorated.

[0054] However, when the temperature is less than 1100°C or the heating time is less than 2 hours, decarburization at the surface portion is insufficient, which not only adversely influences formation of ferrite at the surface portion, but decrease the re-solidification ratio of alloy elements. Accordingly, in the present disclosure, the steel slab described above may also be heated for 2 hours or more in the temperature range of 1100~1300°C, and more preferably, for 3.0 hours or more in the temperature range of 1145~1250°C. Meanwhile, the upper limit of the slab heating time is not specifically fixed, and generally, since the more the heating time, the higher the component uniformity, the heating time may be 50 hours or less, 20 hours or less, or 6 hours or less.

Hot rolling

[0055] A hot-rolled plate may be manufactured by hot-rolling the heated steel slab. In this case, hot rolling may be performed at an accumulated reduction ratio of 50% or more within the temperature range of Ar3+80°C~Ar3+200°C, and resting may be maintained for 30 seconds or more (air cooling) after hot rolling.

[0056] When the temperature is higher than Ar3+200°C in hot rolling, structures that are vulnerable to low-temperature toughness such as upper bainite are formed due to an increase of hardenability by growth of grains, so that hydrogen induced cracking characteristics and low-temperature toughness may be deteriorated.

[0057] However, when the temperature is lower than Ar3+80°C, the temperature at which following cooling is started is excessively low, so the fracture of air-cooled ferrite excessively increases and strength may be decreased. Further, decarburization at the surface portion is suppressed, so it is difficult to contribute to form ferrite at the center portion in the following process. Accordingly, it is preferable in the present disclosure that the finishing rolling temperature of hot rolling is Ar3+80°C~Ar3+200°C.

[0058] When the accumulated reduction ratio is less than 50% in hot rolling in the temperature range described above, recrystallization by rolling even to the center portion of the steel material does not occur, so there is a problem that grains are coarsened in the center portion and low-temperature toughness is deteriorated. Accordingly, it is preferable in the present disclosure that the accumulated reduction ratio is 50% or more in hot rolling.

[0059] Meanwhile, the maintaining time is less than 30 seconds after hot rolling, the time for decarburization at the surface portion is insufficiency, so it is difficult to contribute to forming ferrite at the surface portion in the following process. Accordingly, it is preferable in the present disclosure that the maintaining time after finishing hot rolling is 30 seconds or more. The upper limit of the maintaining time after finishing hot rolling is not specifically fixed, but may be preferably 30 minutes or less, 10 minutes or less, or 5 minutes or less. Further, since such maintaining time is provided, cooling start temperature to be described below can be secured from air cooling.

[Cooling]

[0060] The hot-rolled plate manufactured through such hot rolling can be cooled, and particularly, it would be technically meaningful to provide an optimal cooling process that can obtain a steel material of which hardness in the surface portion is effectively reduced in the present disclosure.

[0061] In detail, the cooling includes primary cooling; air cooling, and secondary cooling, and each of the process conditions are described in more detail hereafter.

[0062] In this case, the primary cooling and the secondary cooling may be performed by applying a specific cooling means, and for example, water cooling may be performed.

Primary cooling

[0063] In the present disclosure, primary cooling may be performed after hot rolling- maintaining time over 30 seconds described above is maintained. In detail, it is preferable to start primary cooling when the surface temperature of the hot-rolled plate obtained through the process described above is $Ar3-20^{\circ}C \sim Ar3+50^{\circ}C$.

[0064] When the start temperature of primary cooling exceeds $Ar3+50^{\circ}C$, phase transformation into ferrite is not sufficiently made at the surface portion during primary cooling, so a hardness reduction effect at the surface portion cannot be achieved. However, when the start temperature of primary cooling is less than $Ar3-20^{\circ}C$, ferrite transformation is excessive generated even to the center portion, which is a factor that reduces strength of steel.

[0065] Further, it is preferable to perform the primary cooling at a cooling rate of $5 \sim 40^{\circ}C/s$ such that the surface temperature of the hot-rolled plate becomes $Ar1-50^{\circ}C \sim Ar3-50^{\circ}C$.

[0066] That is, when the end temperature of the primary cooling exceeds $Ar3-50^{\circ}C$, the fracture of phase transformation into ferrite at the surface portion of the primarily cooled hot-rolled plate is low, so the hardness reduction effect at the surface portion cannot be sufficiently achieved. However, when the temperature is less than $Ar1-50^{\circ}C$, ferrite phase transformation excessively occurs even to the center portion, so it is difficult to secure strength at a target level.

[0067] Further, when the cooling rate in the primary cooling is excessively low less than $5^{\circ}C/s$, it is difficult to primary cooling end temperature described above, but when the cooling rate exceeds $40^{\circ}C/s$, the fracture of phase transformation into acicular ferrite, so a soft structure cannot be formed at the surface portion. Accordingly, in the primary cooling, for the temperature at the surface portion, it is possible to control the average cooling rate at $5 \sim 40^{\circ}C/s$, and more preferably, $17 \sim 40^{\circ}C/s$.

[0068] When the primary cooling is ended, the temperature at the center portion of the hot-rolled plate may be controlled at $Ar3-30^{\circ}C \sim Ar3+30^{\circ}C$. That is, when the temperature at the center portion of the hot-rolled plate exceeds $Ar3+30^{\circ}C$ at the end of the primary cooling, the temperature of the surface portion cooled within a specific temperature range is increased, so the fracture of ferrite phase transformation of the surface portion is decreased. Accordingly, the temperature at the center portion of the hot-rolled plate may be controlled preferably at $730 \sim 810^{\circ}C$ at the end of the primary cooling.

[0069] However, when the temperature at the center portion of the hot-rolled plate is less than $Ar3-30^{\circ}C$, the temperature of the center portion of the hot-rolled plate is excessively decreases and the temperature at which the surface portion can be recuperated in the following cooling decreases, so a tempering effect cannot be achieved, which decreases the hardness reduction effect at the surface portion.

Air cooling

[0070] It is preferable to air-cool the hot-rolled plate that has undergone primary cooling under the conditions described above, and an effect of recuperation of the surface portion can be obtained by the center portion that is a relatively high temperature through the air-cooling process.

[0071] It is preferable to end the air cooling when the temperature of the surface portion of the hot-rolled plate becomes the rang $Ar3-50^{\circ}C \sim Ar3-10^{\circ}C$.

[0072] When the temperature of the surface portion of the hot-rolled plate is lower than $Ar3-50^{\circ}C$ after the air cooling is finished, not only the time for formation of air-cooled ferrite is insufficient, but the tempering effect by recuperation of the surface portion is insufficient, which is disadvantageous in hardness reduction of the surface portion. However, when the temperature of the surface portion of the hot-rolled plate exceeds than $Ar3-50^{\circ}C$ after the air cooling is finished,

cooling time excessively increases and ferrite phase transformation occurs at the center portion, so it is difficult to secure strength at a target level.

Secondary cooling

[0073] It is preferable to perform secondary cooling immediately after the air cooling is finished within the temperature range described above (based on the temperature of the surface portion), and the temperature of the surface portion at the end of air cooling is the same as the start point in secondary cooling.

[0074] Meanwhile, it is preferable that the secondary cooling is performed at a cooling rate of 50~500°C/s such that the temperature of the surface portion becomes 300~600°C.

[0075] That is, when the end temperature of the secondary cooling is less than 300°C, the fracture on MA increases, which has a bad influence on security of low-temperature toughness and suppression of hydrogen embrittlement. However, when the end temperature of the secondary cooling exceeds 600°C, phase transformation is not completed in the center portion, so it is difficult to secure strength.

[0076] Further, the cooling rate is less than 50°C/s in secondary cooling within the temperature range described above, the grains at the center portion are coarsened, so it is difficult to secure strength at a target level. However, when the cooling rate exceeds 500°C/s, the fracture of a phase vulnerable to low-temperature toughness such as upper bainite is increased due to a microstructure at the center portion, so hydrogen induced cracking resistance is deteriorated, which is disadvantageous. Accordingly, in the secondary cooling, for the temperature at the surface portion, it is possible to control the average cooling rate at 50~500°C/s, and more preferably, 245~500°C/s.

[0077] Meanwhile, according to an aspect of the present disclosure, a steel material manufactured through the sequence of processes may have thickness of 5~50mm.

[Mode for Invention]

[0078] Hereafter, the present disclosure is described in more detail through embodiments. However, it should be noted that the following embodiments are provided only to describe the present disclosure in more detail through exemplification rather than limiting the right range of the present disclosure. This is because the right range of the present disclosure is determined the matters described in claims and matters reasonably inferred from the matters.

(Embodiment)

[0079] Steel slabs having the alloy composition and properties shown in the following Tables 1 and 2 were prepared. In this case, the content of the following alloy composition is described in percent by weight and the balance includes Fe and other unavoidable impurities. Steel materials were manufactured by heating, hot-rolling, and cooling the prepared steel slabs, respectively, under the conditions shown in Tables 3 and 4.

[0080] The invention steel and comparative steel described in Tables 1 and 2 were manufactured through the same processes except for following the manufacturing conditions described in Tables 3 and 4.

[0081] In detail, the steel materials of the invention steel and comparative steel were obtained by heating slabs having the composition described in the following Table 1 under the conditions described in Table 3, performing rough rolling under common conditions, performing finishing hot-rolling under the conditions described in Table 3, and then performing water cooling after maintaining resting for a predetermined time. Cooling described Table 4 was controlled by performing intermediate air cooling and then secondary cooling after primary cooling.

[Table 1]

	C	Si	Mn	P	s	Al	N	Ni	Cr	Mo	Nb	Ti	V	Ca
IS* 1	0.043	0.25	1.32	0.006	0.007	0.024	0.003	0.21	0.002	0.12	0.043	0.012	0.02	0.0018
IS 2	0.044	0.24	1.31	0.008	0.0005	0.023	0.004	0.18	0.007	0.14	0.041	0.013	0	0.0016
IS 3	0.043	0.23	1.33	0.009	0.0008	0.025	0.004	0.15	0.02	0.12	0.046	0.011	0	0.0011

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(continued)

	C	Si	Mn	P	s	A1	N	Ni	Cr	Mo	Nb	Ti	V	Ca
CS* 1	0.11	0.2 5	1.44	0.00 8	0. 00 08	0.03 1	0.00 5	0. 21	0.03	0. 06	0.05	0. 01 1	0. 02	0.00 15
CS 2	0.03 6	0.2 4	1.55	0.00 8	0. 00 08	0.02 9	0.00 6	0	0.21	0	0.03 5	0. 01 2	0. 02	0.00 11
CS 3	0.03 7	0.2 2	1.22	0.00 6	0. 00 1	0.03 8	0.00 4	0. 16	0.19	0	0.04 4	0. 01 3	0	0.00 04
CS 4	0.04 3	0.2 5	1.32	0.00 6	0. 00 07	0.02 4	0.00 3	0. 21	0.00 2	0. 12	0.04 3	0. 01 2	0. 02	0.00 18
CS 5	0.04 3	0.2 5	1.32	0.00 6	0. 00 07	0.02 4	0.00 3	0. 21	0.00 2	0. 12	0.04 3	0. 01 2	0. 02	0.00 18
CS 6	0.04 3	0.2 5	1.32	0.00 6	0. 00 07	0.02 4	0.00 3	0. 21	0.00 2	0. 12	0.04 3	0. 01 2	0. 02	0.00 18
CS 7	0.04 3	0.2 5	1.32	0.00 6	0. 00 07	0.02 4	0.00 3	0. 21	0.00 2	0. 12	0.04 3	0. 01 2	0. 02	0.00 18
CS 8	0.04 3	0.2 5	1.32	0.00 6	0. 00 07	0.02 4	0.00 3	0. 21	0.00 2	0. 12	0.04 3	0. 01 2	0. 02	0.00 18
CS 9	0.04 3	0.2 5	1.32	0.00 6	0. 00 07	0.02 4	0.00 3	0. 21	0.00 2	0. 12	0.04 3	0. 01 2	0. 02	0.00 18
IS*: Inventive steel CS*: Comparative steel														

[Table 2]

	Ca/S	Ar3 (°C)	Ar1 (°C)
IS 1	2.6	778	717
IS 2	3.2	775	718
IS 3	1.4	776	719
CS 1	1.9	752	715
CS 2	1.4	780	726
CS 3	0.4	797	722
CS 4	2.6	777	717
CS 5	2.6	777	717
CS 6	2.6	777	717
CS 7	2.6	777	717
CS 8	2.6	777	717
CS 9	2.6	777	717
Ar3 = 910 - 310×C - 80×Mn - 20×Cu - 15×Cr - 55×Ni - 80×Mo + 0.35×(thickness [mm] - 8) Ar1 = 742 - 7.1×C - 14.1×Mn + 16.3×Si + 11.5×Cr - 49.7×Ni			

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[Table 3]

	Thickn ess [mm]	Slab heating		Hot rolling		Maintain ing time after finishin g rolling [sec]
		Heating temperatur e [°C]	Heating time [hr]	Finishing temperature [°C]	Accumulate d reduction ratio [%]	
IS 1	30.5	1166	4.3	893	80	72
IS 2	21.5	1158	4	918	77	135
IS 3	19.5	1145	3.9	905	77	188
CS 1	30.5	1129	4.3	850	75	122
CS 2	30.5	1127	4.2	875	75	135
CS 3	30.5	1133	3.9	895	77	138
CS 4	30.5	1131	4.5	888	80	180
CS 5	30.5	1132	3.7	895	77	185
CS 6	30.5	1145	4.3	879	75	194
CS 7	30.5	1155	3.6	834	75	171
CS 8	30.5	1050	3.1	870	75	139
CS 9	30.5	1145	4.4	865	75	11

[Table 4]

	2- step cool ing or not	Primar y coolin g start temper ature [°C]	Primar y coolin g end temper ature of surfac e portio n [°C]	Primar y coolin g end temper ature of center portio n [°C]	Prima ry cooli ng rate of surfa ce porti on [°C/s]	Temper ature of surfac e portio n after interm ediate air coolin g [°C]	Second ary coolin g end temper ature of surfac e portio n [°C]	Secondary coolin g rate of surfa ce porti on [°C/s]
IS 1	0	825	710	802	22	750	466	345
IS 2	0	815	699	799	13	754	489	321
IS 3	0	822	703	799	17	748	443	245
CS 1	X	815	492	495	245	-	-	-
CS 2	X	780	488	494	255	-	-	-
CS 3	X	823	503	495	261	-	-	-

(continued)

	2- step cool ing or not	Primar y cool in g start temper ature [°C]	Primar y cool in g end temper ature of surfac e portio n [°C]	Primar y cool in g endtemper ature of center portio n [°C]	Prima ry cool in g rate of surfa ce portio n [°C/s]	Temper ature of surfac e portio n after interm ediate air cool in g [°C]	Second ary cool in g end temper ature of surfac e portio n [°C]	Secondary cool in g rate of surfa ce portio n [°C/s]
CS 4	X	823	465	483	359	-	-	-
CS 5	0	823	611	732	25	642	455	324
CS 6	0	820	718	789	123	760	444	359
CS 7	0	743	616	702	21	688	466	321
CS 8	0	818	698	794	16	754	455	324
CS 9	0	820	700	795	15	755	454	333

[0082] Yield strength, Vickers hardness in the surface portion, sulfide stress corrosion cracking resistance, a micro-structure of each of the steel materials manufactured through the manufacturing process described above were observed, and the result was shown in the following Table 5.

[0083] In this case, yield strength is 0.5% under-load yield strength, API-5L specimens were taken in a direction perpendicular to the rolling direction as the tension samples, and the tests were performed.

[0084] Hardness of the steel materials was measured on thickness cross-sections under 1kgf load using a Vickers hardness tester, and hardness of the surface portions were measured from the surface portion to positions at 100 μ m and were shown in the following Table 5.

[0085] Meanwhile, microstructures were measured using an optical microscope and the kinds of phases were observed using an image analyzer.

[0086] A 4 Point Bent Beam Test was performed for characteristic analysis of sulfide stress corrosion cracking (SSC) under NACE standard test method (TM-0177), and whether cracking occurred was estimated by adding 90% of yield strength of each steel plate to a strong acid Sol. A solution and then exposing the solution in an H₂S environment of 10bar for 720 hours.

[Table 5]

		Structure of surface portion	Structur e of center portion	Hardnes s of surface portion [Hv]	Yield strengt h [MPa]	Sulfide stress corrosion cracking [SSC]
Invention steel	IS 1	F+P	AF	172	478	Not generated
	IS 2	F+P	AF	183	489	Not generated
	IS 3	F+P	AF	178	490	Not generated

(continued)

		Structure of surface portion	Structure of center portion	Hardness of surface portion [Hv]	Yield strength [MPa]	Sulfide stress corrosion cracking [SSC]
Comparative steel	CS 1	UB	AF + IJB	284	534	Generated
	CS 2	UB	AF + UB	275	545	Generated
	CS 3	AF	AF	224	483	Generated
	CS 4	AF	AF	228	478	Generated
	CS 5	F+P	AF+F+P	175	421	Not generated
	CS 6	AF	AF	224	475	Generated
	CS 7	F+P	F+P	175	411	Generated
	CS 8	F+AF	AF+F	202	452	Generated
	CS 9	F+AF	AF+F	205	475	Generated
F: Ferrite, P: Pearlite, AF: Acicular Ferrite, UB: Upper Bainite						

[0087] In Tables 1 to 5, the invention steels satisfied both the composition and manufacturing conditions of the present disclosure and the comparative steels did not satisfy any one or more the composition and manufacturing conditions of the present disclosure.

[0088] In detail, the comparative steels 1 to 4 did not satisfy both the composition and manufacturing conditions of the present disclosure, and particularly, the 2-step cooling method proposed in the present disclosure was not applied in cooling.

[0089] Meanwhile, the comparative steels 4 to 9 used steel slabs having the same composition as the invention steel 1 of the present disclosure and did not satisfy the manufacturing conditions of the present disclosure. That is, the 2-step cooling method proposed in the present disclosure was not applied to the comparative steel 4, and, in the comparative steel 5, a primary cooling end temperature of the surface portion and the temperature of the surface portion after intermediate air cooling were out of the range proposed in the present disclosure.

[0090] Further, the primary cooling rate of the surface portion was out of the range proposed in the present disclosure in the comparative steel 6, the finishing temperature of hot rolling was out of the lower limit range proposed in the present disclosure in comparative steel 7, and the finishing temperature of hot rolling was decreased, so all of the primary cooling start temperature, the primary cooling end temperatures of the surface portion and the center portion, and the temperature of the surface portion after intermediate air cooling were all out of the ranges proposed in the present disclosure.

[0091] The heating temperature of the slab was out of the lower limit range proposed in the present disclosure in the comparative steel 8, and the maintaining time after finishing hot rolling was out of the lower limit range proposed in the present disclosure in the comparative steel 9.

[0092] The 2-step cooling proposed in the present disclosure was not applied to the comparative steels 1 to 4, so a ferrite structure of a complex structure of ferrite and pearlite proposed in the present disclosure was not formed in the microstructures of the surface portions. Accordingly, the hardness in the surface portions exceeded 200Hv in the comparative steels 1 to 4, so sulfide stress corrosion cracking was generated due to high hardness in the surface portions.

[0093] 2-step cooling proposed in the present disclosure was not applied to the comparative steel 1, but the primary cooling end temperature of the center portion and the temperature of the surface portion after intermediate air cooling were low, so ferrite transformation was generated before secondary cooling. In the comparative steel 5, sulfide stress corrosion cracking was the generated, but the yield strength did not satisfy 450MPa or more that is the range set in the present disclosure.

[0094] In the comparative steel 6, the primary cooling rate exceeded the upper limit proposed in the present disclosure and ferrite was not formed at the surface portion, so sulfide stress corrosion cracking was generated.

[0095] In the comparative steel 7, the finishing temperature of hot rolling did not satisfy the lower limit proposed in the present disclosure, in which the cooling temperature after hot rolling also did not satisfy the range proposed in the present disclosure, so ferrite transformation was generated even to the center portion, and accordingly, the yield strength was insufficient.

[0096] The heating temperature of the slab was out of the range proposed in the present disclosure in the comparative steel 8 and the maintaining time after hot rolling was out of the range proposed in the present disclosure in the comparative steel 9. In the comparative steels 8 and 9, since ferrite transformation was insufficient at the surface portions, so a complex structure of ferrite and acicular ferrite was formed, whereby the surface portion hardness reduction effect was not sufficiently achieved and sulfide stress corrosion cracking was generated.

[0097] As described above, in the invention steels 1 to 3 that satisfy both the alloy composition and the manufacturing conditions proposed in the present disclosure, the hardness in the surface portions is 200Hv or less, so the hardness in the surface portion is remarkably low and yield strength of 450MPa or more could be secured. Further, it could be seen that resistance against sulfide stress corrosion cracking was also excellent.

[0098] However, in the comparative steels 1~9 that did not satisfy the alloy composition of the present disclosure or did not satisfy the manufacturing conditions of the present disclosure, the hardness in the surface portions of the steel materials was not sufficiently low, so sulfide stress corrosion cracking was generated or yield strength of 450MPa or more could not be secured.

[0099] Meanwhile, microstructure pictures at the surface portions and the hardness values at the surface portions measured by an optical microscope for the invention steel 2 and the comparative steel 3 of the above test examples were shown in FIG. 1. In detail, in FIG. 2, the left pictures show hardness measured from a surface to a position at 100 μ m using a Vickers hardness tester, and the right pictures show hardness measured from a surface to a position at 500 μ m.

[0100] As can be seen from FIG. 1, it can be seen that the steel material of the present disclosure has hardness of 200Hv at the surface portion, but the hardness in the surface portion exceeds 200Hv in the comparative steel 3 to which 2-step cooling proposed in the present disclosure was not applied.

Claims

1. A steel material comprising, by weight%, carbon (C): 0.02~0.06%, silicon (Si): 0.1~0.5%, manganese (Mn): 0.8~1.8%, chrome (Cr): less than 0.05%, phosphorous (P): 0.03% or less, sulfur (S): 0.003% or less, aluminum (Al): 0.06% or less, nitrogen (N): 0.01% or less, niobium (Nb): 0.005~0.08%, titanium (Ti): 0.005~0.05%, calcium (Ca): 0.0005~0.005%; one or more of nickel (Ni): 0.05~0.3%, molybdenum (Mo): 0.02~0.2%, and vanadium (V): 0.005~0.1%, and a balance of Fe and unavoidable impurities,

wherein the Ca and the S satisfy the following Equation 1,
the steel material has a microstructure of a surface portion composed of ferrite or a complex structure of ferrite and pearlite, and
a microstructure of the center portion is composed of acicular ferrite,

[Equation 1]

$$0.5 \leq \text{Ca/S} \leq 5.0$$

where each element represents the content of each element by weight%.

2. The steel material of claim 1, wherein Vickers hardness in the surface portion is 200Hv or less.
3. The steel material of claim 1, wherein the steel material has yield strength of 450MPa or more.
4. A method of manufacturing a steel material, the method comprising: heating a steel slab, which includes, by weight%, carbon (C): 0.02~0.06%, silicon (Si): 0.1~0.5%, manganese (Mn): 0.8~1.8%, chrome (Cr): less than 0.05%, phosphorous (P): 0.03% or less, sulfur (S): 0.003% or less, aluminum (Al): 0.06% or less, nitrogen (N): 0.01% or less, niobium (Nb): 0.005~0.08%, titanium (Ti): 0.005~0.05%, calcium (Ca): 0.0005~0.005%; one or more of nickel (Ni): 0.05~0.3%, molybdenum (Mo): 0.02~0.2%, and vanadium (V): 0.005~0.1%, and a balance of Fe and unavoidable

impurities and in which the Ca and the S satisfy the following Equation 1, at a temperature range of 1100~1300°C for 2 hours or more;

obtaining a hot-rolled plate by hot-rolling the heated steel slab; and
cooling the hot-rolled plate after hot rolling,
wherein the cooling includes primary cooling, air cooling, and secondary cooling, and
the primary cooling is performed at a cooling rate of 5~40°C/s such that a temperature of a surface portion of
the hot-rolled plate becomes Ar1-50°C~Ar3-50°C and the secondary cooling is performed at a cooling rate of
50~500°C/s such that the temperature of the surface portion of the hot-rolled plate becomes 300~600°C.

[Equation 1]

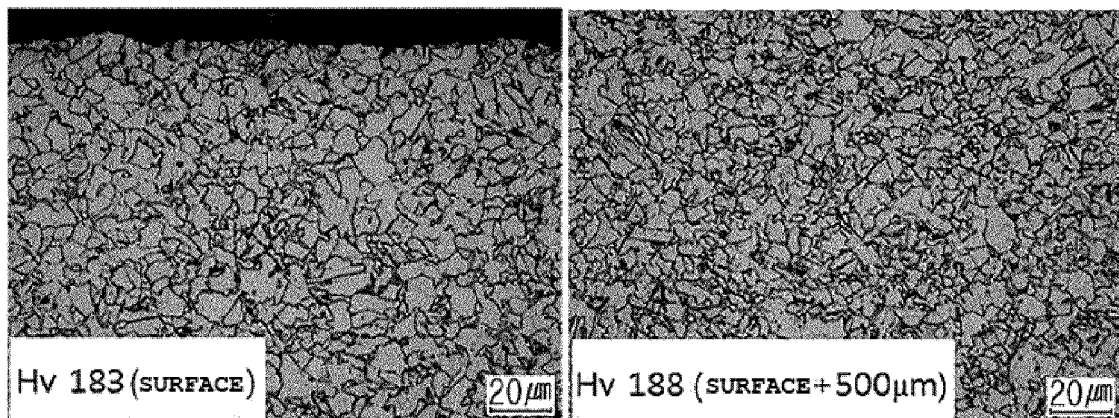
$$0.5 \leq \text{Ca/S} \leq 5.0$$

where each element represents the content of each element by weight%.

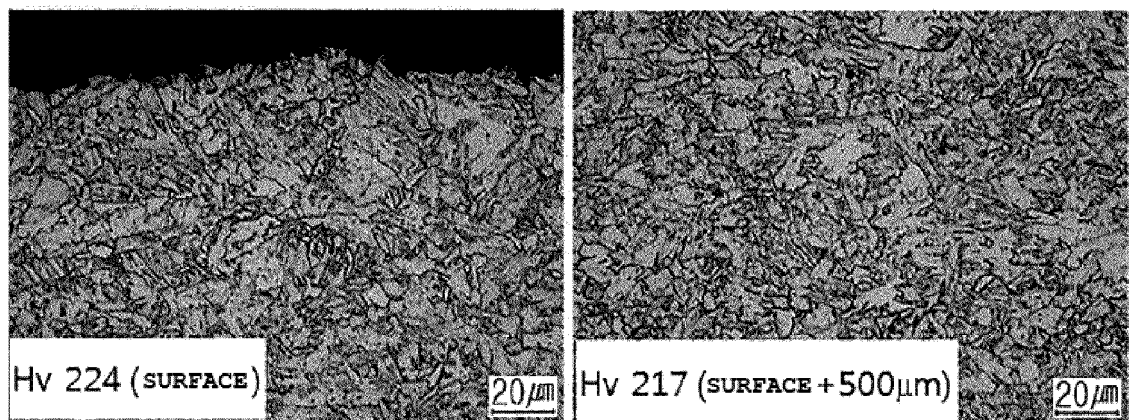
5. The method of claim 4, wherein the hot rolling is performed at an accumulated reduction ratio of 50% or more in a temperature range of Ar3+80°C~Ar3+200°C.
6. The method of claim 4, further comprising maintaining for 30 second or more before cooling after the hot rolling.
7. The method of claim 4, wherein the primary cooling is started when the temperature of the surface of the hot-rolled plate is Ar3-20°C~Ar3+50°C.
8. The method of claim 4, wherein a temperature of a center portion of the hot-rolled plate is Ar3-30°C~Ar3+30°C after the primary cooling is finished.
9. The method of claim 4, wherein the temperature of the surface portion of the hot-rolled plate is Ar3-10°C~Ar3-50°C after the air cooling is finished.

[FIG. 1]

INVENTION STEEL 2



COMPARATIVE STEEL 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2020/018309

A. CLASSIFICATION OF SUBJECT MATTER C22C 38/58(2006.01)i; C22C 38/48(2006.01)i; C22C 38/50(2006.01)i; C22C 38/44(2006.01)i; C22C 38/46(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 38/58(2006.01); C21D 8/02(2006.01); C22C 38/00(2006.01); C22C 38/04(2006.01); C22C 38/22(2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models: IPC as above Japanese utility models and applications for utility models: IPC as above Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal) & keywords: 페라이트(ferrite), 에시칼리(accicular), 황화물(sulfide), 균열(cracking), 크롬(chrome), 알루미늄(aluminum)																					
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>JP 10-298645 A (SUMITOMO METAL IND. LTD.) 10 November 1998 (1998-11-10) See paragraph [0020], claims 1-2 and table 5.</td> <td>1-4,7-9</td> </tr> <tr> <td>Y</td> <td></td> <td>5-6</td> </tr> <tr> <td>Y</td> <td>KR 10-2016-0078845 A (POSCO) 05 July 2016 (2016-07-05) See paragraphs [0069] and [0071].</td> <td>5-6</td> </tr> <tr> <td>A</td> <td>KR 10-2016-0077392 A (POSCO) 04 July 2016 (2016-07-04) See paragraph [0041] and claims 1 and 3-4.</td> <td>1-9</td> </tr> <tr> <td>A</td> <td>KR 10-2011-0110278 A (JFE STEEL CORPORATION) 06 October 2011 (2011-10-06) See paragraph [0109] and claims 1-3.</td> <td>1-9</td> </tr> <tr> <td>A</td> <td>KR 10-2016-0099113 A (JFE STEEL CORPORATION) 19 August 2016 (2016-08-19) See claims 1-4.</td> <td>1-9</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	JP 10-298645 A (SUMITOMO METAL IND. LTD.) 10 November 1998 (1998-11-10) See paragraph [0020], claims 1-2 and table 5.	1-4,7-9	Y		5-6	Y	KR 10-2016-0078845 A (POSCO) 05 July 2016 (2016-07-05) See paragraphs [0069] and [0071].	5-6	A	KR 10-2016-0077392 A (POSCO) 04 July 2016 (2016-07-04) See paragraph [0041] and claims 1 and 3-4.	1-9	A	KR 10-2011-0110278 A (JFE STEEL CORPORATION) 06 October 2011 (2011-10-06) See paragraph [0109] and claims 1-3.	1-9	A	KR 10-2016-0099113 A (JFE STEEL CORPORATION) 19 August 2016 (2016-08-19) See claims 1-4.	1-9
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A	KR 10-2016-0099113 A (JFE STEEL CORPORATION) 19 August 2016 (2016-08-19) See claims 1-4.	1-9																			
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International application No.

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