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(54) STEEL MATERIAL, HEAT-AFFECTED ZONE OF WELD, AND MANUFACTURING METHOD THEREFOR

(57) The present invention relates to a steel material applicable to liquefied gas storage tanks and the like, a heat-affected zone of a weld, and a method for manufacturing same.

EP 4 826 093 A1

Description

Technical Field

[0001] The present disclosure relates to a steel material applicable to a liquefied gas storage tank and a weld heat-affected zone and a manufacturing method thereof.

Background Art

[0002] Recently, as environmental regulations have been strengthened, demand for liquefied gas, an eco-friendly fuel, has increased, and accordingly, the construction of liquefied gas carriers that transport liquefied gas or gas propulsion ships that use liquefied gas as fuel has increased. Among the liquefied gases, liquefied natural gas and liquefied ethylene/ethane gas have very low liquefaction temperatures, and thus, high-Ni steel is generally used for storage thereof. However, LPG, ammonia, CO_2, and the like, are gases having liquefaction temperatures of -60°C, and carbon steel having improved strength and low-temperature toughness has been used to reduce the costs of building tanks or ships that accommodate these gases.

[0003] Since existing liquefied gas transport tanks mainly use large Type A tank designs that do not require high pressure, there was no demand for high strength or thick materials. However, recently, CO_2 tanks or ammonia fuel tanks that require high pressure during liquefaction are designed as Type C, and there is a trend to require high strength and thick materials for steel. In addition, since a post-weld heat treatment (PWHT) required by the IGC code is essential for the construction of Type C tanks, a steel material is additionally required to have properties guaranteed after PWHT.

[0004] The PWHT is a process of maintaining a material at a high temperature for a certain period of time to release the residual stress of the material after welding. During the PWHT process, a grain size and a precipitate size of a low-temperature structure increase, which deteriorates the material properties such as strength and toughness, making quality assurance difficult. Specifically, in the case of a steel material for CO_2 tanks, the classification society has recently required the quality of Crack Tip Opening Displacement (CTOD) in the weld heat-affected zone (HAZ) after PWHT as a structural compatibility evaluation item to improve the stability of tank design.

[0005] Meanwhile, in the case of liquefied CO_2, the liquefaction temperature varies depending on the pressure, and accordingly, a tank may be largely divided into low-pressure tanks and medium-pressure tanks.

[0006] In the case of low-pressure tanks with a typical operating pressure of 5 to 10 bars, since a temperature should be lowered to -60°C for CO_2 liquefaction, a steel material for storage tanks is also a steel material with a tensile strength (TS) of 600 to 650 MPa that may guarantee low-temperature impact toughness below -60°C. In order to maintain a low temperature after liquefaction, a separate cooling facility is required, which increases initial installation costs and maintenance costs.

[0007] In the case of medium-pressure tanks with a typical operating pressure of 18 to 20 bars, since the liquefaction temperature increases to -35°C, there is an advantage in that the storage and transport of liquefied CO_2 may be facilitated. However, because the operating pressure is high, a steel material for medium-pressure tanks uses also ultra-high strength steel with a strength of 780 MPa or higher, not the existing TS 600 to 650 MPa steel. Because steel including high alloy components is manufactured through a Quenching-Tempering (QT) heat treatment to secure high strength, it is not easy to secure weld quality.

[0008] Patent Document 1 discloses that a steel material capable of guaranteeing a low-temperature impact toughness guarantee of -40°C may be manufactured by heating a slab including alloy components including, by wt%, C: 0.06 to 0.12%, Si: 0.02 to 0.06%, Mn: 0.7 to 1.2%, Ti: 0.006 to 0.012%, Al: 0.002 to 0.01%, Cr: 0.3 to 0.5%, Mo: 0.3 to 0.4%, V: 0.03 to 0.04%, N: 0.002 to 0.003%, S: 0.002 to 0.01%, P: 0.007% or less and a balance of Fe and impurities to 1100 to 1200°C, and then rolling the slab at 800 to 900°C with a cumulative reduction ratio of 30% or more, air-cooling the slab, and quenching the slab again at 910 to 930°C, and then, performing a tempering heat treatment on the slab at 650 to 680°C.

[0009] The steel material provides a method to improve toughness by distributing uniform Al-Ti-MnS composite oxidizing inclusions in the weld heat-affected zone and refining HAZ grains, but steel material does not guarantee the quality of material after PWHT, and the tensile strength of the base material is low at 550 to 650 MPa, which makes it unsuitable as a steel material for medium-pressure liquefied CO_2 (LCO_2).

[0010] Meanwhile, Patent Document 2 discloses a method for manufacturing a P690QL2 steel material for LCO_2 storage tanks, which include, by wt%, C: 0.09 to 0.12%, Mn: 0.9 to 1.3%, Ti: 0.015% or less, S: 0.002% or less, Nb: 0.06 or less, V: 0.08 or less, Ni: 1.5 to 2.5%, Cr: 0.2 to 0.4%, Mo: 0.3 to 0.4%, Cu: 0.3% or less, Al: 0.03 to 0.05%, Ca: 0.0005 to 0.005%, N: 0.005% or less, H: 0.0003% or less, and a balance of Fe and impurities, and has a thickness of 50mm. The patent document 2 discloses that when the material is heated to a temperature of 1160 to 1210°C, rolled at 780 to 880°C, quenched at 890 to 920°C, and subject to a tempering heat treatment at a temperature of 630 to 680°C,

a tensile strength of 780MPa or more and an impact toughness of 47J or more at -60°C may be secured after PWHT.

[0011] However, since the CTOD guarantee temperature and standard of the HAZ do not meet a level required by the present disclosure, a practical method in which the material may be used as a steel material for medium-pressure LCO_2 storage tanks is not presented.

[0012] Patent Document 3 discloses manufacturing a steel sheet including, by wt%, C: 0.03 to 0.18%, Si: 0.30% or less, Mn: 0.3 to 1.6%, P: 0.015% or less, S: 0.005% or less, Cu: 2.0% or less, Ni: 1.0 to 7.0%, Al: 0.01 to 0.20%, Ca: 0.005% or less, N: 0.0100% or less, O: 0.0060% or less, and a balance of Fe and impurities, wherein a content ratio of Mn and Ni, Mn/Ni, is 0.80 or less, a carbon equivalent Ceq based on WES is 0.430 to 0.900%, a tensile strength is 780 MPa or more and 930 MPa or less, a yield strength is 630 MPa or more and 750 MPa or less, and a yield ratio is 85% or less, an HAZ impact toughness evaluated at 0°C is 100J or more, a plate thickness is 40mm or more and 120mm or less, and a Vickers hardness of 225 points or more is measured at a location 1/4 of the plate thickness from ae surface, and when an average value of the Vickers hardness from a smaller side to 20% is defined as Hvmin and an average value of a larger side to 20% is defined as Hvmax, Hvmin/Hvmax is 0.85 or less. The strength satisfies the range required for the medium-pressure LCO_2 steel material, but the steel sheet may not be suitable because the impact toughness is not guaranteed at around -40°C, the temperature at which CO_2 liquefies. In addition, when Ceq and hardness are excessively high, a martensite fraction may become excessively high during quenching, which may make it difficult to secure impact toughness and HAZ CTOD characteristics.

[0013] Accordingly, in order to secure an appropriate low-temperature phase fraction, the range of Ceq and the corresponding surface hardness values is required, but since the technology does not describe this matter, this is not appropriate as a technology for manufacturing ultra-high strength steel for medium-pressure LCO_2.

[0014] Accordingly, the above-described conventional technology does not present a practical method for manufacturing ultra-high strength steel for medium-pressure LCO_2 that has a yield strength of 690 MPa or more and a tensile strength of 770 to 940 MPa after Post Weld Heat Treatment (PWHT), and that has a low-temperature impact toughness at -40°C or lower and a CTOD quality of 0.1 mm or more.

(Patent Document 1) Korean Patent Publication No. 10-2022-7030534 (Published on October 5, 2022)
(Patent Document 2) Chinese Patent Publication No. CN2022-11506158 (Published on November 29, 2022)
(Patent Document 3) PCT Patent Publication No. WO2021-255858-023761 (Published on December 23, 2021)

Summary of Invention

Technical Problem

[0015] An aspect of the present disclosure relates to a weld heat-affected zone having excellent strength and low-temperature impact toughness as well as excellent low-temperature CTODD quality after a post-weld heat treatment (PWHT) and a method of manufacturing the same.

[0016] In addition, another aspect of the present disclosure relates to a steel material having excellent strength and low-temperature impact toughness after the post-weld heat treatment (PWHT) and a method of manufacturing the same.

[0017] The aspect of the present disclosure is not limited to the matters described above. Additional aspects of the present disclosure are described in an overall content of the specification, and those skilled in the art to which the present disclosure pertains will have no difficulty in understanding the additional aspects of the present disclosure from the content described in the specification of the present disclosure.

Solution to Problem

[0018] An embodiment of the present disclosure relates to a steel material comprising: by wt%, C: 0.05 to 0.20%, Si: 0.05 to 0.50%, Mn: 0.5 to 2.0%, Al: 0.005 to 0.10%, P: 0.010% or less, S: 0.015% or less, Nb: 0.001 to 0.070%, V: 0.001 to 0.30%, Ti: 0.001 to 0.030%, Cr: 0.01 to 1.0%, Mo: 0.01 to 1.0%, Cu: 0.01 to 0.60%, Ni: 1.0 to 4.0%, B: 0.001 to 0.005%, Ca: 0.0005 to 0.0040%, O: 0.001%, and a balance of Fe and other inevitable impurities,

wherein Ceq defined in the following relational expression 1 satisfies a range of 0.50 to 0.70,
a microstructure comprises tempered martensite having an area fraction of 50% or more,
a packet size of the microstructure comprises 17μm or less, and
a maximum size of a $CaO-Al_2O_3$-X (where X is at least one of Ti, Mg or S) composite oxidation inclusion observed in an upper layer, which is a region of a surface layer to t/4 (where t is a thickness, unit: mm) in a thickness direction from a surface of the steel material, is 50μm or less, and the number of the inclusions per unit area of $1\mu m^2$ is 50 or less,

$$Ceq = [C] + [Mn]/6 + ([Cr] + [Mo] + [V])/5 + ([Ni] + [Cu])/15 \quad \text{[Relational Expression 1]}$$

in Relational Expression 1, [C], [Mn], [Cr], [Mo], [V], [Ni] and [Cu] represent the contents (wt%) of C, Mn, Cr, Mo, V, Ni and Cu included in the steel material, respectively, and when these components are not intentionally added, 0 is substituted.

[0019] The microstructure may comprise bainite and other inevitable structures.

[0020] When the tempered martensite exceeds 80%, a cross-sectional Brinell hardness of the steel material may be 220 to 290 HB.

[0021] In the steel material, the number of VC or VCN precipitates having a diameter of 5 to 15 nm, among precipitates observed in a cross-section of the steel material, may be at least 5 per 1 μm^2.

[0022] The microstructure may be observed within a prior austenite grain size having an average grain size of 30 μm or less.

[0023] The steel material may have a yield strength of 690 MPa or more, a tensile strength of 770 to 940 MPa, and a Charpy impact absorption energy of 50J or more at -40°C.

[0024] Another embodiment of the present disclosure relates to a manufacturing method of a steel material comprising: manufacturing a steel slab satisfying the above-described composition and Ceq, wherein a maximum size of a $CaO-Al_2O_3$-X (where X is at least one of Ti, Mg or S) composite oxidation inclusion observed in an upper layer, which is a region of a surface layer to t/4 (where t is a thickness, unit: mm) in a thickness direction from a surface of the steel slab, is 50μm or less, and the number of the inclusions per unit area of 1μm^2 is 50 or less;

reheating the steel slab to a temperature range of 1050 to 1300°C;
manufacturing a steel material by hot-rolling the steel slab at a finishing hot-rolling temperature of 830 to 1050°C;
heating the steel material to a temperature range of 820 to 950°C and holding the heated steel material for 10 to 40 minutes, and then cooling the steel material to a temperature of 300°C or less at a cooling rate of 3°C/s to 80°C/s based on a steel thickness t/4 temperature; and
a tempering heat treatment operation of heating the steel material to 550 to 700°C and maintaining the steel material for 5 to 60 minutes after the cooling.

[0025] The manufacturing a steel slab may comprise:

inputting a metal Ca wire into molten steel after secondary refining so that an amount of Ca input is 0.015 to 0.15 kg/ton; and
performing clean bubbling for 5 to 40 minutes so that an inert gas blowing amount in a ladle is 10 to 50 liter/min after the Ca input,
wherein an input velocity of the Ca wire is 100 to 300 meters/min, and the number of inert gas blowing points in the ladle is 2.

[0026] The manufacturing method of a steel material further may comprise performing multistage stacking cooling in a temperature range from 200°C to room temperature after the hot rolling.

[0027] The manufacturing method of a steel material of may further comprise performing a post-weld heat treatment on the steel material.

[0028] The post-weld heat treatment may be performed at 595°C to 625°C for 180 to 540 minutes (min).

[0029] When temperatures of the tempering heat treatment and the post-weld heat treatment are identical to each other, LMP according to the following relational expression 2 may be 17.0 to 19.5.

[Relational Expression 2]

$$LMP = T_k\ (\text{Log}\ t + 20)$$

where T_k = Kelvin temperature of tempering and PWHT, and t = tempering and PWHT time (hour)

[0030] When temperatures of the tempering heat treatment and the post-weld heat treatment are different from each other, the LMP according to the following relationship 3 may be 17.0 to 19.5.

[Relational Expression 3]

$$T(\log t_{eq}+20) = T_i(\log t_i+20)$$

$$\text{Total LMP} = T_i[\log(t_i+t_{eq})+20]$$

where T_i: Kelvin temperature of PWHT, t_i: PWHT time (hour), T: tempering Kelvin temperature, and t_{eq}: Equivalent tempering time (hour) when converted to a PWHT temperature.

[0031] Another embodiment of the present disclosure relates to a weld heat affect zone satisfying the above-described composition and Ceq,

wherein a maximum size of a $CaO\text{-}Al_2O_3$-X (where X is at least one of Ti, Mg or S) composite oxidation inclusion observed in an upper layer, which is a region of a surface layer to t/4 (where t is a thickness, unit: mm) in a thickness direction from a surface of the steel slab, is 50μm or less, and the number of the inclusions per unit area of $1\mu m^2$ is 50 or less,
a grain boundary occupancy ratio of cementite existing in a grain boundary is 10% or less, and an average size of cementite is 1μm or less, and
a cross-sectional hardness is 200 to 300 HB.

$$Ceq = [C] + [Mn]/6 + ([Cr] + [Mo] + [V])/5 + ([Ni] + [Cu])/15 \quad \text{[Relational Expression 1]}$$

[0032] In Relational Expression 1, [C], [Mn], [Cr], [Mo], [V], [Ni] and [Cu] represent the contents (wt%) of C, Mn, Cr, Mo, V, Ni and Cu included in a steel material, respectively, and when these components are not added intentionally, 0 is substituted.

[0033] Another embodiment of the present disclosure relates to a manufacturing method of a weld heat-affected zone including:

manufacturing a steel material satisfying the above-described composition and Ceq,
wherein a maximum size of a $CaO\text{-}Al_2O_3$-X (where X is at least one of Ti, Mg or S) composite oxidation inclusion observed in an upper layer, which is a region of a surface layer to t/4 (where t is a thickness, unit: mm) in a thickness direction from a surface of the steel slab, is 50μm or less, and the number of the inclusions per unit area of $1\mu m^2$ is 50 or less;
welding the steel material; and
performing a post-weld heat treatment on the welded steel material.

Advantageous Effects of Invention

[0034] According to an aspect of the present disclosure, even after a post-weld heat treatment (PWHT), the deterioration of physical properties may be minimized, and thus, a steel material having excellent strength and low-temperature impact toughness and a method of manufacturing the same may be provided.

[0035] According to another aspect of the present disclosure, a weld heat-affected zone having excellent low-temperature impact toughness and low-temperature CTOD characteristics after post-weld heat treatment (PWHT) and a method for manufacturing the same may be provided.

[0036] Advantages and effects of the present application are not limited to the foregoing content and may be more easily understood in the process of describing a specific embodiment of the present disclosure.

Best Mode for Invention

[0037] The terms used in the present specification are intended to describe specific embodiments and are not intended to limit the present disclosure. In addition, singular forms used in the present specification include plural forms unless the relevant definition indicates the opposite meaning.

[0038] The meaning of "include" and "comprise" used in the specification specifies the configuration and does not exclude the existence or addition of other configurations.

[0039] Unless otherwise defined, all terms including technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which example embodiments of the present disclosure belong. It will be further understood that the terms, such as those defined in commonly used dictionaries, should be interpreted as having meanings consistent with the relevant technical literature and the currently disclosed

content.

[0040] Hereinafter, preferred embodiments of the present disclosure will be described. These embodiments of the present disclosure may be modified in various forms, and the scope of the present disclosure should not be construed as being limited to the embodiments described below. These embodiments are provided to further detail the present invention to those skilled in the art.

[0041] First, the composition of a steel material, which is an example of the present disclosure, will be described in detail.

[0042] The steel material comprises, C: 0.05 to 0.20%, Si: 0.05 to 0.50%, Mn: 0.5 to 2.0%, Al: 0.005 to 0.10%, P: 0.010% or less, S: 0.0050% or less, Nb: 0.001 to 0.070%, V: 0.001 to 0.30%, Ti: 0.001 to 0.030%, Cr: 0.01 to 1.0%, Mo: 0.01 to 1.0%, Cu: 0.01 to 0.60%, Ni: 1.0 to 4.0%, B: 0.001 to 0.005%, Ca: 0.0005 to 0.0040%, O: 0.002% or less, and a balance of Fe and other inevitable impurities.

[0043] Ceq defined by the following relational expression 1, may be 0.50 to 0.70.

$$Ceq = [C] + [Mn]/6 + ([Cr] + [Mo] + [V])/5 + ([Ni] + [Cu])/15 \quad \text{[Relational Expression 1]}$$

[0044] In Relational Expression 1, [C], [Mn], [Cr], [Mo], [V], [Ni], and [Cu] represent the contents (wt%) of C, Mn, Cr, Mo, V, Ni, and Cu included in the steel material, respectively, and when these components are not intentionally added, 0 is substituted.

[0045] The composition of the steel material may be the same as a composition of not only a steel slab, but also a composition of a parent material of a steel material before welding, a steel material after welding, and a steel material after a welding heat treatment, as well as a composition of the weld heat-affected zone (HAZ).

[0046] Hereinafter, the composition will be described in detail. Hereinafter, unless otherwise specified, % and ppm described in relation to the alloy composition are based on weight.

Carbon (C): 0.05 to 0.20%

[0047] Carbon (C) is the most important element for securing basic strength, and thus, carbon (C) needs to be included in steel within an appropriate range, and in order to obtain this addition effect, 0.05% or more carbon (C) may be added. Preferably, 0.10% or more carbon (C) may be included. On the other hand, when the content of the carbon (C) exceeds a certain level, the fraction of martensite becomes excessively high, the hardness of the weld heat-affected zone (HAZ) increases, and the fraction of grain boundary cementite increases, so that the impact propagation resistance decreases during an impact test or CTOD test, and thus the toughness value required in the present disclosure may not be secured. Accordingly, the present disclosure may be performed with a carbon (C) content of 0.20%. An upper limit of a more preferable carbon (C) content may be 0.18%.

Silicon (Si): 0.05~0.50%

[0048] Silicon (Si) is a substitutional element that improves the strength of the steel material through solid solution strengthening and has a strong deoxidation effect, and thus, silicon (Si) is an essential element for manufacturing clean steel. Therefore, silicon (Si) may be included in an amount of 0.05% or more, and preferably in an amount of 0.20% or more. On the other hand, when silicon (Si) is included in a large amount, silicon (Si) may generate a Martensite-Austenite (MA) phase and excessively increase the matrix strength of the martensite phase, thereby deteriorating the low-temperature impact toughness, and thus, an upper limit of a content thereof may be included as being 0.50%. A more preferable upper limit of the silicon (Si) content may be 0.40%.

Manganese (Mn): 0.5 to 2.0%

[0049] Manganese (Mn) is a useful element improving strength through solid solution strengthening and enhancing hardenability so that a low-temperature transformation phase is generated. Accordingly, in order to secure a yield strength of 690 MPa or more, 0.5% or more of manganese (Mn) may be preferably included. A more preferable manganese (Mn) content may be 0.7% or more. On the other hand, manganese (Mn) may form MnS, a non-metallic inclusion that is elongated with sulfur (S), thereby lowering toughness and acting as an impact initiation point, which may be a factor that rapidly lowers the low-temperature impact toughness of the steel material. Accordingly, the content of the manganese (Mn) may be preferably managed to being 2.0% or less, and a more preferable manganese (Mn) content may be 1.5% or less.

Aluminum (Al): 0.005 to 0.10%

[0050] Aluminum (Al) is one of the powerful deoxidizers in the steelmaking process along with silicon (Si), and 0.005% or more may be preferably included to obtain this effect. A more preferable lower limit of the aluminum (Al) content may be 0.01%. On the other hand, when the content of aluminum (Al) is excessive, a fraction of Al_2O_3, among the oxidizing inclusions generated as a result of deoxidation, increases excessively, and a size thereof becomes coarse, and it may be difficult to remove the inclusions during refining, which may be a factor that reduces the low-temperature impact toughness. Accordingly, the content of aluminum (Al) may be preferably managed to being 0.10% or less. A more preferable aluminum (Al) content may be 0.07% or less.

Phosphorus (P): 0.010% or less (including 0%) and sulfur (S): 0.0050% or less (including 0%)

[0051] Phosphorus (P) and sulfur (S) are elements causing embrittlement at grain boundaries or forming coarse inclusions, which may cause embrittlement. Accordingly, it is preferable not to include the phosphorus (P) and sulfur (S). In order to improve the brittle crack propagation resistance, phosphorus (P) may be preferably included in an amount of 0.010% or less, and sulfur (S) may be preferably included in an amount of 0.0050% or less.

Niobium (Nb): 0.001 to 0.070%

[0052] Niobium (Nb) is an element improving the strength of the base material by precipitating in the form of NbC or NbCN. In addition, niobium (Nb) subject to solid solution during high-temperature reheating is significantly finely precipitated in the form of NbC during rolling, which inhibits recrystallization of austenite, thus having the effect of refining the structure. Accordingly, niobium (Nb) may be preferably included in an amount of 0.001% or more, and a more preferable niobium (Nb) content may be 0.005% or more. On the other hand, when niobium (Nb) is included excessively, undissolved niobium (Nb) may be generated in the form of TiNb (C,N), which becomes a factor inhibiting low-temperature impact toughness, so that an upper limit of the niobium (Nb) content may preferably be 0.070%. An upper limit of the more preferable niobium (Nb) content may be 0.065% or less.

Vanadium (V): 0.001 to 0.30%

[0053] Since vanadium (V) is almost completely subject to solid solution again during reheating, the strengthening effect by precipitation or solid solution during subsequent rolling is minimal, but vanadium (V) has the effect of improving strength by precipitating significantly fine carbonitrides during tempering heat treatment or PWHT. In order to sufficiently obtain this effect, it is necessary to add 0.001% or more vanadium (V). A lower limit of a more preferable vanadium (V) content may be 0.01%. On the other hand, when the content is excessive, a slab surface hardness may increase excessively due to high hardenability, which may act as a factor such as surface cracks during flange processing, and manufacturing costs may also increase rapidly, which is not commercially advantageous. Accordingly, the content of vanadium (V) may be limited to 0.3% or less. A more preferable vanadium (V) content may be 0.25% or less.

Titanium (Ti): 0.001 to 0.030%

[0054] Titanium (Ti) is a component significantly improving low-temperature toughness by precipitating as TiN during reheating and inhibiting the growth of prior austenite grains at high temperatures. To achieve this effect, it may be preferable to include 0.001% or more of titanium (Ti). On the other hand, when titanium (Ti) is included excessively, low-temperature toughness may be reduced due to clogging of a casting nozzle or centerline inclusions. In addition, since titanium (Ti) combines with nitrogen (N) to form coarse TiN precipitates in a center of a thickness, the elongation of a product is reduced, and thus, a uniform elongation is reduced during a forging process to cause surface cracks. Accordingly, the content of titanium (Ti) may be 0.030% or less. An upper limit of the preferable titanium (Ti) content may be 0.025% or less, and a more preferable titanium (Ti) content may be 0.018% or less.

Chromium (Cr): 0.01 to 1.0%

[0055] Chromium (Cr) is a component increasing the yield strength and tensile strength by increasing the quench-ability and forming a low-temperature transformation structure. Chromium (Cr) is also a component having an effect of preventing the decrease in strength by slowing down the spheroidization rate of cementite. For this effect, 0.01% or more of chromium (Cr) may be included. On the other hand, when the content of chromium (Cr) is excessive, the size and fraction of Cr-rich coarse carbides such as $M_{23}C_6$ increase, which reduces the impact toughness of the steel, and

the solubility of niobium (Nb) in the steel material and the fraction of fine precipitates such as NbC decrease, which may reduce the strength of the product. Accordingly, an upper limit of the chromium (Cr) content of the present disclosure may be 1.0%. An upper limit of the preferable chromium (Cr) content may be 0.8%.

Molybdenum (Mo): 0.01 to 1.0%

[0056] Molybdenum (Mo) is an element increasing grain boundary strength and having a large effect of solid solution strengthening in ferrite, and is an element effectively contributing to increasing the strength and ductility of the product. In addition, molybdenum (Mo) has an effect of preventing the deterioration of toughness due to grain boundary segregation of impurity elements such as phosphorus (P). For this effect, 0.01% or more of molybdenum (Mo) may be added. However, since molybdenum (Mo) is an expensive element, excessive addition may significantly increase the manufacturing costs, so that an upper limit of the molybdenum (Mo) content may preferably be 1.0%.

Copper (Cu): 0.01 to 0.60%

[0057] Copper (Cu) may significantly improve the strength of a matrix by solid solution strengthening in ferrite, and also has an effect of suppressing corrosion in a wet hydrogen sulfide atmosphere, and is an advantageous element in the present disclosure. For this effect, 0.01% or more of copper (Cu) may be included. A more preferable copper (Cu) content may be 0.03% or more. However, when the copper (Cu) content is excessive, the possibility of causing star cracks on a surface of a steel sheet increases, and since copper (Cu) is an expensive element, there may be a problem that the manufacturing costs increases significantly. Accordingly, an upper limit of the copper (Cu) content may preferably be 0.60%, and a more preferable upper limit of the copper (Cu) content may be 0.35%.

Nickel (Ni): 1.0 to 4.0%

[0058] Nickel (Ni) is an element enhancing stacking faults at low temperatures, making cross-slip of dislocations easier, thus improving impact toughness, and effectively contributing to improving strength by improving hardenability. For this effect, 1.0% or more of nickel (Ni) may be included. A preferable nickel (Ni) content may be 0.10% or more. On the other hand, when nickel (Ni) is excessively added, the manufacturing costs may also increase due to the high costs, and thus, an upper limit of the nickel (Ni) content may preferably be 4.0%, and a more preferable upper limit of the nickel (Ni) content may be 3.0%.

Calcium (Ca): 0.0005 to 0.0040%

[0059] When calcium (Ca) is added after deoxidation by aluminum (Al), calcium (Ca) suppresses the formation of MnS by combining with sulfur (S) forming MnS inclusions, and simultaneously forms spherical CaS to suppress the occurrence of cracks due to hydrogen-induced cracking. In order to sufficiently form sulfur (S) CaS included as impurities, calcium (Ca) of 0.0005% or more may be preferably included. However, when the amount added is excessive, CaS may be formed and the remaining calcium (Ca) may combine with oxygen (O) to create coarse oxidizing inclusions, which may be elongated and destroyed during rolling, which may lower the lamella tearing characteristics. Accordingly, an upper limit of the calcium (Ca) content may preferably be 0.0040%.

Boron (B): 0.001 to 0.005%

[0060] Boron (B) is an effective element for improving the hardenability of a hot-rolled steel sheet by delaying the transformation of austenite into ferrite during cooling transformation. In order to obtain this effect, boron (B) may be preferably added in an amount of 0.001% or more, but when the content exceeds 0.005%, the strength increases excessively, which causes a problem of lowering the impact toughness. In addition, boron oxide may be formed, which may lower the surface quality of a steel sheet.

Oxygen (O): 0.002% or less

[0061] Oxygen (O) is combined with Ca or Al in molten steel to exist in the form of CaO or Al_2O_3 or CaO-Al_2O_3 complex oxidizing inclusions. The oxidizing inclusions generated at high temperatures are crushed in a rough rolling operation of a slab and are elongated in a rolling direction, and remain without dissolution not only during a rolling/heat treatment process of a parent metal but also in the HAZ during welding. Since an end of the crushed oxidizing inclusions may act as a starting point of destruction when evaluating impacts and CTOD due to a notch effect, it is recommended to remove them through flotation separation in a secondary refining process as much as possible, so

that an oxygen concentration in the molten steel may preferably be 20 ppm or less. The present disclosure proposes a secondary refining method that may extremely control oxidizing inclusions, and after applying this process, a total oxygen content may be more preferably 15 ppm or less, and most preferably 10 ppm or less.

[0062] In addition to the aforementioned components, the balance of Fe and other unavoidable impurities may be included. However, since unintended impurities may inevitably be mixed in from raw materials or the surrounding environment during the normal manufacturing process, Fe and other unavoidable impurities may not be completely excluded. Since these impurities are known to anyone with ordinary knowledge in this technical field, all of their contents are not specifically mentioned in this specification.

[0063] In addition, the addition of additional effective components other than the aforementioned components is not completely excluded.

[0064] The composition may have a Ceq of 0.50 to 0.70, as defined by the following relational expression 1.

$$Ceq = [C] + [Mn]/6 + ([Cr] + [Mo] + [V])/5 + ([Ni] + [Cu])/15 \quad \text{[Relational Expression 1]}$$

[0065] In Relational Expression 1, [C], [Mn], [Cr], [Mo], [V], [Ni] and [Cu] represent the contents (wt%) of C, Mn, Cr, Mo, V, Ni and Cu included in the steel material, respectively, and when these components are not added intentionally, 0 is substituted.

[0066] When Ceq by the relational expression 1 is less than 0.50, the high yield strength value required in the present disclosure may not be secured because the martensite fraction decreases, and since the bainite fraction increases excessively, an occupancy ratio of grain boundary cementite in the weld heat-affected zone (HAZ), especially in the coarse grained heat-affected zone (CGHAZ), after the post-weld heat treatment (PWHT), increases, and thus, an appropriate impact toughness and a HAZ CTOD value required in the present disclosure may not be secured. In addition, when the Ceq value exceeds 0.70, the hardness may increase excessively and a cleavage fracture may be induced, and thus, the crack propagation resistance decreases, which may make it difficult to secure an appropriate impact toughness and CTOD characteristics in the weld heat-affected zone.

[0067] In the steel material of the present disclosure, a maximum size of $CaO\text{-}Al_2O_3\text{-}X$ (where X is at least one of Ti, Mg or S) composite oxidation inclusions observed in an upper layer, which is a region from a surface layer to t/4 (t: thickness) in a thickness direction from a surface of a surface of the steel material, based on a cross-section, may be 50μm or less, and the number of the inclusions per unit area of 1μm^2 is 50 or less.

[0068] The composite oxidation inclusions may be observed not only in the steel slab, but also in a parent material of a steel material before welding, a steel material after welding, and a steel material after a welding heat treatment and in the heat-affected zone (HAZ).

[0069] When the composite oxidation inclusions are formed in a steel slab manufacturing operation, ae shape and a fraction do not change in a subsequent product manufacturing operation, and during rough rolling, the composite oxidation inclusions may be crushed and elongated in a rolling direction. The crushed oxidized inclusions may act as a position in which stress is concentrated, and may act as a starting point when a fracture occurs. Thus, when an amount or size of the oxidized inclusions generated during the steel slab manufacturing process is large, the amount of the crushed oxidized inclusions after rough rolling increases, which becomes a major cause of the deterioration of the impact toughness and CTOD quality. Accordingly, when the size of the composite oxidized inclusions in an upper layer of a product, which is a region from a surface layer to t/4, exceeds 50μm, or the number per 1μm^2 exceeds 50, it may be difficult to secure the low-temperature impact toughness at -40°C based on the parent material and the HAZ CTOD quality at -35°C or lower.

[0070] The steel material of the present disclosure has tempered martensite or a tempered martensite-bainite mixed structure as a base structure. Specifically, the steel material may include 50% or more of tempered martensite in terms of area fraction, and may include a balance of bainite and inevitably occurring structures.

[0071] When the matrix structure is a tempered martensite-bainite mixed structure, an area fraction of tempered martensite may be 50 to 80%.

[0072] When the matrix structure is comprised of a single structure exceeding 80% of tempered martensite, a hardness of a cross-section of the parent material of the steel material after PWHT may be 220 to 290HB by Brinell.

[0073] The inevitably occurring structures may be Martensite-Austenite (MA) Constituent, and the like.

[0074] A packet size of the low-temperature structure of the tempered martensite or bainite may be 17μm or less.

[0075] An average grain size of the prior austenite of the steel may be 30μm or less.

[0076] A fine VC or VCN precipitate having a precipitate diameter of 5 to 15 nm observed on a cross-section of the steel material may include 5 or more precipitates per 1 μm^2.

[0077] The microstructural characteristics may be the same in the steel material before welding, the base material after the welding, and the base material of the steel material subjected a heat treatment after the welding.

[0078] An average grain size of a prior austenite of the steel material may be 30μm or less. A post-weld heat

treatment (PWHT) is generally performed at a high temperature of 595°C or higher to prevent cracks in a weld zone through stress relieving after welding. In this case, a dislocation density decreases, and a cross-sectional hardness may decrease, so that the soundness of the weld zone may increase. However, in a process of holding at a high temperature for a long time, the cementite generated at a bainite lath interface is decomposed, and long-range diffusion of carbon occurs into an austenite grain boundary. Accordingly, when a grain size increases, a grain boundary area that may be occupied by cementite decreases, so that the segregation increases, which may deteriorate the impact toughness. Accordingly, it is necessary to control a prior austenite grain size under appropriate low-temperature pressure. Accordingly, the prior austenite grain size is preferably 30μm or less, and more preferably 25μm or less.

[0079] As the temperature and time of the PWHT increase, coarse cementite is spheroidized at an prior austenite grain boundary, and some thereof is formed as film-like cementite. When such cementite is formed at the grain boundary, a grain boundary strength becomes lower than a shear strength, which ultimately becomes a main cause of intergranular fracture. Accordingly, in order to prevent intergranular fracture after PWHT, martensite, which only causes short-range diffusion, should be included in an appropriate fraction or more. However, when a proportion of martensite is significantly high, the cross-sectional hardness becomes excessively high, and even if the intergranular fracture occurs, an impact absorption energy value decreases, which ultimately causes the toughness to deteriorate. Accordingly, the steel microstructure may be preferably formed of a mixed structure of tempered martensite and bainite, and in this case, a fraction of tempered martensite may preferably be 50 to 80% in area fraction.

[0080] However, when the base structure as the steel microstructure is tempered martensite, that is, when martensite exceeds 80% (including 100%), a tempering temperature should be further increased to maintain the cross-sectional hardness of the parent material at 200 to 290 HB, and when the temperature deviates from a range of the cross-sectional hardness, it is difficult to secure the low-temperature impact toughness and CTOD value required in the present disclosure.

[0081] A packet size of the low-temperature structure of the tempered martensite or bainite may be 17 μm or less. The packet size is a group unit of laths having the same orientation relationship in low-temperature transformation structures such as bainite or martensite, and may be understood as a domain boundary that may have resistance (characteristics that cracks are bent at the boundary when the crack propagates) when a physical crack propagates. As an example of the packet size measurement, a packet size may be measured as a grain boundary that may be confirmed when domains within 15 degrees of the orientation relationship are set to the same orientation using Electro-back-scattered diffraction (EBSD) equipment. Since the bainite or martensite grows only within the grains of the prior austenite crystals, this is smaller than the size of the prior austenite crystal grain. When the packet size exceeds 17μm, it is difficult to secure sufficient impact toughness because it is difficult to secure sufficient crack propagation resistance, and thus, the packet size may be preferably 17μm or less.

[0082] On the other hand, during tempering and PWHT, the strength is reduced because the dislocation density of the steel material decreases. When fine precipitates are used to appropriately compensate for such reduction, a strength deterioration phenomenon during the heat treatment process may be reduced. Normalizing materials or Thermo-Mechanical Control Process (TMCP) materials frequently utilize precipitates such as NbC and NbCN, but a temperature at which the precipitates are generated is 800 to 900°C, and are generated by deformation induction, and thus, the precipitates are not suitable for a Quenching-Tempering (QT) heat treatment steel material. Accordingly, it is easy to utilize vanadium carbides/carbonitrides such as VC and VCN generated in the temperature range of 550 to 700°C. When a diameter of the VC or VCN fine precipitates is less than 5 nm, a size thereof may be significantly minimal to have a minimal strength improvement effect, and when the size thereof exceeds 15 nm, the strength improvement effect is also reduced because the fine precipitates is significantly coarse. Therefore, it is appropriate that the size of the fine precipitate is 5 to 15 nm. On the other hand, when the density of VC and VCN is less than 5 per unit area of 1 μm^2, the above-described precipitation strengthening effect also decreases, so 5 or more per unit area of 1 μm^2 is preferable. The generation of the precipitates is determined by the chemical potential and temperature determined by the composition of the steel. The 5 to 15nm-sized precipitates may be generated in large quantities, but when the number increases, the precipitates aggregate with each other and become larger in size, and thus, the 5 to 15nm-sized precipitates are not formed indefinitely. Accordingly, even if an upper limit of the number of fine precipitates is not limited to those skilled in the art, it is not necessarily unclear.

[0083] In the meantime, the microstructure of the weld heat-affected zone (HAZ), which is an example of the present disclosure, will be described in detail. The HAZ may be a HAZ after post-weld heat treatment (PWHT), and specifically, may be a coarse grained heat-affected zone (CGHAZ).

[0084] The weld heat-affected zone (HAZ) may have a grain boundary occupation ratio of cementite existing at the grain boundary of 10% or less.

[0085] The grain boundary occupancy ratio may be understood as a length ratio of film-like cementite occupied at the grain boundary, and becomes an area ratio in three dimensions. As an example of measuring the occupancy ratio, a specimen is etched with nital and observed using SEM, and the like, and general grain boundaries and grain boundaries having the film-like cementite therein may be distinguished and measured.

[0086] Meanwhile, an average size of the cementite may be 1μm or less.

[0087] After the post-weld heat treatment (PWHT), in the HAZ, especially the CGHAZ microstructure, tempered martensite may preferably be 50% or more in area fraction. In addition to the tempered martensite, the balance may be bainite and other structures. When the tempered martensite area fraction is less than 50%, the film-like cementite occupancy ratio at the grain boundary increases after PWHT, and since the crystal grains become coarser, it is difficult to secure an appropriate CTOD value of 0.1 mm or more at - 35°C or lower. For the same reason, the grain boundary occupancy ratio of cementite existing at the grain boundary after PWHT may preferably be 10% or less, and an average size of cementite existing at the grain boundary may preferably be 1μm or less.

[0088] The average grain size of the prior austenite in the heat-affected zone (HAZ) may be 200μm or less. The HAZ microstructure is determined by the microstructure of the parent material and the welding condition influences such as a welding heat input/a preheating temperature/a laminar temperature. Specifically, since the CGHAZ is a section in which the crystal grains become very coarser as compared to the parent material, the material may be inferior to the parent material. The average grain size of the prior austenite according to the CGHAZ may preferably be 200μm or less, and when the average grain size exceeds 200μm, the hardenability increases excessively and the cross-sectional hardness increases, so that the average grain size of the CGHAZ may preferably be 200μm or less. The average grain size of the prior austenite may not differ before and after PWHT. In order for the grain size to change, the prior austenite should be reversely transformed to an austenite single-phase region, and thus, a temperature should be heated to 800°C or higher, but since the PWHT temperature is around 500 to 600°C, there may be no change in the AGS itself.

[0089] The heat-affected zone (HAZ) may have a grain boundary occupancy ratio of cementite existing at the grain boundary of 10% or less.

[0090] The grain boundary occupancy ratio may be understood as a length ratio of film-like cementite occupied at the grain boundary, and becomes an area ratio in in three dimensions. As an example of the occupancy ratio measurement, after etching the specimen with nital, the specimen may be observed using SEM, or the like, and general grain boundaries and the grain boundaries having film-shaped cementite formed therein may be distinguished and measured.

[0091] The steel material of the present disclosure may secure the strength and low-temperature impact toughness of the parent material after PWHT. Specifically, the steel material may has a yield strength of 690 MPa or more, a tensile strength of 770 to 940 MPa, and the low-temperature impact toughness absorption energy of the parent material may be 50 J or more in a Charpy V-Notch Test performed at - 40°C or lower.

[0092] Meanwhile, the weld heat-affected zone, especially the CGHAZ, after the PWHT, may secure excellent low-temperature impact toughness and CTOD properties. Specifically, the low-temperature impact toughness absorption energy may be 40 J or more in a Charpy V-Notch Test performed at -40°C or lower, and the CTOD property at -35°C or lower may be 0.1 mm or more.

[0093] Hereinafter, an example of a method of manufacturing a steel material of the present disclosure will be described in detail.

[0094] The manufacturing method may manufacture a steel slab satisfying the alloy composition and Ceq range of the relational expression 1 described above, and may manufacture a steel material by performing heating, hot rolling, reheating, quenching, and tempering on the steel slab. This may be referred to as the so-called RQT method by performing the reheating-quenching-tempering process.

[0095] Welding and post-weld heat treatment (PWHT) may be performed on the steel material manufactured in this manner.

[0096] Each process may be described in detail below.

Manufacturing of Steel Slab

[0097] A steel slab is manufactured in which the Ceq defined in the alloy composition and the relational expression 1 described above satisfies the range of 0.50 to 0.70, a maximum size of the CaO-Al_2O_3-X (where X is at least one of Ti, Mg or S) composite oxidation inclusions observed in the upper layer, which is a region from a surface layer to t/4 (t: thickness, unit: mm) in a thickness direction from the steel slab surface, is 50μm or less, and the number of inclusions per unit area of $1\mu m^2$ is 50 or less.

[0098] As an example of a method of manufacturing the steel slab, a calcium (Ca) raw material may be added to the secondary refined molten steel and a clean bubbling process may be performed. As a specific example, a metal Ca wire may be added to the molten steel after the secondary refinement, and an amount of Ca may be input so that the input amount is 0.015 to 0.15 kg/ton. The metal Ca wire may be formed of a steel material wrapping Ca alloys, a thickness of the steel material may be 1.2 to 1.4 mm, and input velocity of the metal Ca wire may be 100 to 300 meters/min.

[0099] After inputting Ca, clean bubbling may be performed so that the amount of inert gas blew into the ladle is 10

to 50 liters/min. The number of inert gas blowing points in the ladle may be two, and the clean bubbling time may be 5 to 40 minutes.

[0100] The present disclosure does not specifically limit the process before the secondary refining, and any conventional method may be applied. The present disclosure does not specifically limit the process after the Ca input and clean bubbling processes, and the molten steel may be cooled under conventional conditions to manufacture a slab. In addition, as the amount of Al_2O_3 in the molten steel increases, the generation and coarsening of inclusions including both Ca and Al progress, which increases the crushing inclusions during rolling, and thus, the low-temperature impact toughness and CTOD quality of the HAZ may not be secured, so that the total amount of inclusions in the molten steel before inputting Ca may be limited to 2 to 5ppm.

[0101] Hereinafter, the Ca input process and the clean bubbling process will be described in detail.

(1) Inputting of Calcium (Ca)

[0102] When manufacturing a steel slab, a metal Ca wire may be input into the molten steel after secondary refining so that a Ca input amount is 0.015 to 0.15kg/ton. The metal Ca wire is formed of a steel material wrapping Ca alloys, a thickness of the steel material may be 1.2 to 1.4mm, and the input velocity of the metal Ca wire may be 100 to 300 meter/min.

[0103] When Ca is input, if the thickness of the steel covering the Ca alloy of the metal Ca wire is less than 1.2 mm, Ca melts in an upper portion of the ladle to reduce the effect of the static pressure, resulting in a poor Ca yield, which increases the input amount. On the other hand, if the thickness exceeds 1.4 mm, the metal Ca wire is in contact with a basal portion of the ladle to causes a problem in which the refractory of the ladle is melted, and thus, the stability of the operation may not be secured.

[0104] When Ca is input into the molten steel, in order to secure the Ca yield along with the thickness of the metal Ca wire, the input velocity of the wire into the molten steel must be controlled. when the input velocity of the wire is less than 100 meters/min, Ca melts in the upper portion of the ladle to reduce the effect of the static pressure, resulting in a poor Ca yield, which increases the input amount. On the other hand, if the input velocity of the wire exceeds 300 meters/min, the Ca wire is in contact with the basal portion of the ladle, which causes a problem in which the refractory of the ladle is melted, and thus, the stability of the operation may not be secured. In addition, preferable input velocity may be 120 to 300 meters/min, and more preferably 140 to 180 meters/min.

[0105] When the Ca input amount is significantly low, during solidifying, MnS is generated in a central portion thereof, and low-temperature impact toughness due to segregation defects may not be secured, and when the amount thereof is excessive, there is a problem that the refractory reacts with Al_2O_3 and accelerates the dissolution of the refractory, making it difficult to secure the stability of the operation. Accordingly, considering the above-mentioned problems, the Ca input amount may be 0.015 to 0.15 kg/ton, preferably 0.015 to 0.10 kg/ton, and more preferably 0.050 to 0.10 kg/ton.

(2) Clean Bubbling

[0106] After inputting Ca, clean bubbling may be performed for 5 to 40 minutes so that the inert gas blowing amount in the ladle becomes 10 to 50 liter/min. The number of inert gas blowing points in the ladle may be two.

[0107] When the amount of inert gas blew into the ladle is significantly low, the amount of Al_2O_3 clusters removed by being attached to the inert gas and the composite inclusions including Ca and Al at the same time are low, resulting in poor cleanliness and a problem in that the HAZ impact toughness may not be secured. On the other hand, when the amount is excessive, stirring force may be strong, causing a slag be mixed, simultaneously with causing a surface of the molten steel to be exposed, which may result in poor cleanliness. Accordingly, the inert gas blowing amount may be 10 to 50 liter/min, preferably 15 to 40 liter/min, and more preferably 20 to 30 liter/min.

[0108] On the other hand, when there is only one inert gas blowing point in the ladle, there may be an uneven region in the molten steel, which may result in poor removal of Al_2O_3 Cluster and complex inclusions including Ca and Al at the same time, and when there are three or more inert gas blowing points, during blowing of gas, the stirring force may be strong due to the occurrence of overlapping parts, cause a slag to be mixed, simultaneously with causing the surface of the molten steel to be exposed, which may result in poor cleanliness.

[0109] When the time for applying clean bubbling is significantly short despite limiting the amount of inert gas blew into the ladle, the amount of Al_2O_3 Cluster removed by being attached to the inert gas and complex inclusions including Ca and Al at the same time may be low, which may result in poor cleanliness and may make it impossible to secure toughness. On the other hand, when the time is excessive, a temperature drop in the molten steel may be large, and a temperature gradient may occur in the ladle, which may result in poor cleanliness. The clean bubbling time may be 5 to 40 minutes, preferably 7 to 17 minutes, and more preferably 10 to 15 minutes.

Heating of Steel Slab

[0110] The steel slab may be heated to a temperature range of 1050 to 1300°C.

[0111] The heating is performed by re-dissolving carbonitrides of Ti or Nb or coarse TiNb(C,N) crystallites formed during casting, and heating and holding austenite after sizing rolling to a temperature higher than the recrystallization temperature, so that a slab heating temperature is preferably 1150°C or higher to maximize the austenite grain size. On the other hand, if the temperature is excessively high, problems may occur due to oxide scale at high temperatures, and the grains may grow excessively to deteriorate the low-temperature impact toughness, so that an upper limit thereof may be 1300°C.

Hot Rolling

[0112] The heated steel slab may be hot rolled at a finishing hot rolling temperature of 830 to 1050°C.

[0113] The 830°C corresponds to a range equal or to higher than a recrystallization temperature. The composite inclusions generated during the refining process should accommodate deformation due to rolling as the strength of the steel sheet increases as the rolling temperature decreases, and as a result, the composite inclusions may be crushed or segmented into small-sized inclusions or inclusions such as MnS may be elongated. Since such small-sized inclusions crushed or segmented or elongated inclusions act as direct causes of the initiation and propagation of low-temperature impact toughness, finishing hot rolling may be preferably performed at 830°C or higher, which is a recrystallization temperature at which no work hardening occurs. However, when the temperature exceeds 1050°C, austenite grain growth continues to occur even after the end of rolling, which may reduce the impact toughness due to the increase in Ductile-Brittle Transition Temperature (DBTT).

[0114] A thickness of the steel sheet after the finishing hot rolling may be 5 to 100mm, more preferably 5 to 70mm, and more preferably 5 to 50mm.

[0115] The steel sheet manufactured by the hot rolling may be air-cooled to room temperature. After the completion of the hot rolling, air-cooling is in principle performed, but accelerated cooling to an appropriate temperature may be performed after the end of rolling for the purpose of suppressing precipitate growth and shortening the process time.

[0116] In the present disclosure, when manufacturing a slab, when the dissolved hydrogen content in the molten steel is 1.3ppm or more, an operation of multistage cooling from a temperature of 200°C or higher to room temperature based on the surface temperature after hot rolling before the reheating heat treatment may be further included. When cooling in a multistage manner, the hydrogen dissolved in the steel may be released, which may more effectively suppress internal microcracks caused by hydrogen, and may ultimately improve the low-temperature impact toughness of the parent material and the weld heat-affected zone.

Reheating

[0117] After the hot rolling, reheating on the steel sheet may be performed by heating the steel sheet to a temperature of 820 to 950°C and holding the steel sheet for 10 to 40 minutes.

[0118] When the heating temperature is lower than 820°C or the holding time is lower than 10 minutes during the reheating, the carbides or grain boundary segregated impurity elements generated during cooling after rolling may not be re-dissolved smoothly and may remain even after cooling, which may be the main cause of low-temperature impact toughness deterioration. On the other hand, when the heating temperature exceeds 950°C or the holding time exceeds 40 minutes, the austenite grain size may grow excessively due to grain growth, which may be the main cause of toughness deterioration due to increased DBTT. Accordingly, the reheating temperature may preferably be 820 to 950°C, and more preferably 850 to 890°C.

Quenching & Tempering

[0119] Quenching & tempering may be performed on the reheated steel sheet.

[0120] The cooling rate during the quenching process may be considered one of the most important process factors that determine the microstructure of the base material, and in the present disclosure, after reheating the steel sheet, the steel sheet may be cooled at a cooling rate of 3°C/s to 80°C/s based on the temperature at a point of a steel material thickness t/4 (t: thickness, unit: mm) to 300°C or lower. When the cooling rate ends at 300°C or higher, a microstructure of the base material may include a Martensite-Austenite (MA) Constituent due to incomplete cooling transformation, which is not dissolved in subsequent tempering and PWHT processes, which causes the low-temperature impact toughness to deteriorate. Accordingly, the cooling end temperature may preferably be 300°C or less.

[0121] On the other hand, if the cooling rate is less than 3°C/s, the structure of the base material is formed of a mixed structure of ferrite and bainite or a single-phase structure of bainite, not a mixed structure of martensite and

bainite or a single-phase structure of martensite required in the present disclosure. When the bainite structure becomes the main structure, the strength before PWHT and low-temperature impact toughness may be secured, but it is not easy to secure low-temperature impact toughness and CTOD quality due to the formation of grain boundary cementite after the PWHT described above. On the other hand, when the cooling rate exceeds 80°C/s, the microstructure is formed of 100% martensite, and the cross-sectional hardness increases to an extent that may not be controlled by the tempering temperature alone, and there may be a risk of sheet fracture due to the difference in a cooling rate between a surface layer and a center.

[0122] Accordingly, the cooling rate during quenching is preferably 3°C/s or more and 80°C/s or less, and more preferably 5°C/s or more and 30°C/s or less.

[0123] The quenched steel sheet may be heated to a temperature of 550 to 700°C and hold for 5 to 60 minutes to perform a tempering heat treatment. If the tempering temperature is less than 550°C or the holding time is less than 5 minutes, dislocation recovery does not occur properly during quenching. Thus, since the strength of the base material becomes excessively high, sufficient low-temperature impact toughness may not be secured. If the tempering temperature exceeds 700°C or the holding time exceeds 60 minutes, since the grain boundary (cementite) of the weld heat-affected zone may become coarsened, it is difficult to guarantee the toughness after PWHT.

[0124] Meanwhile, in addition to the RQT, the steel material may also be manufactured by a method of direct quenching and tempering after hot rolling (so-called DQT).

[0125] Welding may be performed on the manufactured steel material and post-weld heat treatment may be performed.

Welding

[0126] The steel of the present disclosure may be used by performing a post-weld heat treatment (PWHT) after welding, and the steel material of the present disclosure may secure strength and low-temperature impact toughness for the parent material after the post-weld heat treatment, and may secure low-temperature impact toughness and low-temperature CTOD characteristics of the weld heat-affected zone (HAZ).

[0127] When welding is performed on the steel material, there is a parent material that is not affected, a molten part (weld metal) that is melted and joined, and a weld heat-affected zone (HAZ) that is a part of the parent material affected by the welding heat, and the molten part and the weld heat-affected zone may be collectively referred to as a weld portion. Meanwhile, the weld heat-affected zone may be classified into Coarse-grain HAZ (CGHAZ), Subcritical HAZ (SCHAZ), Intercritical HAZ (ICHAZ), Fine-grain HAZ (FGHAZ) according to the maximum heating temperature and histological characteristics. Thereamong, the CGHAZ is a part in which the prior austenite grain size is the largest in the heat-affected zone (HAZ) during welding and is maintained at a high temperature of 1000°C or higher and then cooled. When the grain size is large, a ductile-brittle transition temperature increases, and since the hardenability increases, the brittle fracture resistance decreases when a hard structure is created. Accordingly, the CGHAZ is a part in which toughness values of the low-temperature impact toughness and the CTOD in the HAZ may be the most deteriorated, and the characteristics of the CGHAZ may be considered to be decisive.

[0128] The welding may be performed by a method that may be performed in the technical field to which the present disclosure belongs, and is not necessarily limited. In the present disclosure, a thermal cycle of the welding may be performed by heating up to a maximum temperature of 1250 to 1400°C at a maximum heating rate of 50°C/s, holding the target temperature for 5 to 10 seconds, performing a primary cooling at a cooling rate of 10 to 20°C/s to 500°C, and then performing a second cooling at a cooling rate of 5 to 15°C/s to 200°C. The thermal cycle related to the maximum temperature and the cooling rate may be measured using a thermocouple in a CGHAZ position during actual welding, and may be set as described above based thereon.

[0129] The thermal cycle of the welding is implemented as identically as possible through a thermal cycle temperature measurement of the weld heat affected zone (HAZ) during actual welding such as FCAW and SAW. As a substantial example of the thermal cycle, in the case of a Flux Cored Arc Weld (FCAW) method, a heat input amount may be 1.0 to 2.0 kJ/mm, and a heat input amount of the Submerged Arc Weld (SAW) method may be 2.5 to 4.0 kJ/mm. In this case, a preheating temperature and an interpass temperature may both be 150 to 250°C.

Post-Weld Heat Treatment (PWHT)

[0130] The post-weld heat treatment (PWHT) may be performed by a method that may be performed in the technical field to which the present disclosure belongs, and is not particularly limited. As an example, the PWHT may be performed by holding the temperature at 595°C to 625°C for 180 to 540 minutes (min) according to the ASME Sec. VIII standard. Meanwhile, a total LMP in the tempering heat treatment and the PWHT heat treatment according to the following relational expressions 2 and 3 may preferably be 17.0 to 19.5.

[0131] Specifically, when the tempering temperature and the PWHT temperature are identical to each other, the

LMP is determined by Relational Expression 2, and when the tempering temperature and PWHT temperature are different from each other, the LMP is determined by Relational Expression 3.

[Relational Expression 2]

$$LMP = T_k\ (Log\ t + 20)$$

[0132] Where T_k = Kelvin temperature of tempering and PWHT, t = tempering and PWHT time (hour)

[Relational Expression 3]

$$T(\log t_{eq}+20) = T_i(\log t_i+20)$$

$$Total\ LMP = T_i[\log(t_i+t_{eq})+20]$$

Where T_i: Kelvin temperature of PWHT, t_i: PWHT time (hour), T: tempering Kelvin temperature, t_{eq}: Equivalent tempering time (hour) when converted to a PWHT temperature

[0133] When the LMP is less than 17.0, as described above, the dislocation density does not decrease, so that strength excess failure may occur, or the cross-sectional hardness may be significantly high, which may deteriorate the impact toughness. On the other hand, when the LMP exceeds 19.5, a grain boundary occupancy ratio of cementite after PWHT is significantly high, making it difficult to properly secure impact toughness and CTOD quality. Accordingly, the LMP may preferably be between 17.0 and 19.5, and more preferably between 18.0 and 19.3.

Mode for Invention

[0134] Hereinafter, examples of the present disclosure will be described. It should be understood that the following examples may be modified in various ways without departing from the scope of the present disclosure by those skilled in the art. The following examples are provided for the understanding of the present disclosure, and the scope of the present disclosure should not be limited to the following examples, but should be determined by the claims described below as well as their equivalents.

(Example 1)

[0135] A steel slab was manufactured using molten steel having the alloy components of Table 1 (a content unit of the component elements in Table 1 is wt%, but the units of P, S and Ca are ppm, and the remaining components are Fe and unavoidable impurities) and Ceq of the above-described relational expression 1 under the conditions of Table 2, and then heated and hot rolled to manufacture a hot-rolled steel sheet having a thickness of 50 mm.

[0136] The hot-rolled steel sheet manufactured above was reheated and quenched under the conditions disclosed in Table 3, and then tempered at 610°C for 20 minutes.

[0137] Meanwhile, in order to confirm the excellent strength and low-temperature impact toughness of the steel material after the post-weld heat treatment, a heat treatment process simulating the post-weld heat treatment was performed. In this case, the heat treatment process was performed on the hot-rolled steel sheet subjected to the tempering at 595°C for 180 minutes for 3 cycles.

[0138] A microstructure and physical properties of the parent material were measured for each specimen manufactured as described above, and the results are shown in Tables 4 and 5 below.

[0139] Here, a grain size of the prior austenite and fractions of each phase were measured using Electron Back Scattered Diffraction (EBSD) by collecting the specimens. In this case, precipitates and inclusions were measured using transmission electron microscopy (TEM). Precipitates and inclusions were identified through diffraction patterns and EDX mapping.

[0140] Yield/tensile strength was evaluated through a room temperature tensile test, and 0.2% offset was applied for yield strength. In addition, impact toughness for each specimen used an average of absorbed energy values measured three times at a corresponding temperature through a Charpy V-Notch Test. Brinell hardness was tested according to ISO 6506 part 1.

[Table 1]

Steel Type	Alloy Component(wt%)														Relational Expression 1 (Ceq)
	C	Si	Mn	Al	P*	S*	Nb	V	Ti	Cr	Mo	Cu	Ni	Ca *	B	
A	0. 11	0. 25	1. 07	0.03	80	10	0. 00 1	0. 03	0. 00 2	0. 55	0.55	0. 1	2	25	0. 00 25	0.63
B	0. 13	0. 25	1. 1	0.03	75	8	0. 00 2	0. 01 5	0. 01 3	0. 43	0.54	0. 08	2. 2	25	0. 00 2	0.66
C	0. 1	0. 3	1. 3	0.03	90	8	0. 01 5	0. 01 7	0. 01 2	0. 85	0.35	0. 02	2. 4	22	0. 00 21	0.72
D	0. 09	0. 17	1. 2	0.02	88	10	0. 01 3	0. 02	0. 01 2	0. 55	0.29	0. 04	3	21	0. 00 26	0.66
E	0. 13	0. 33	1. 3	0.03	11 0	11	0. 01 2	0. 01 3	0. 01 5	0. 53	0.33	0. 15	1. 9	20	0. 00 2	0.66
F	0. 23	0. 33	1. 05	0.02	80	11	0. 01 2	0. 01 3	0. 00 1	0. 05	0.15	0. 02	3. 5	21	0. 00 27	0.68
G	0. 13	0. 39	1. 17	0.02	83	13	0. 01 4	0. 01 5	0. 00 1	0. 55	0.59	0. 12	3. 6	21	0. 00 27	0.80
H	0. 08	0. 51	0. 85	0.02	90	12	0. 01 3	0. 01	0. 01	0. 07	0.05	0. 2	1. 5	20	0. 00 25	0.36
I	0. 11	0. 23	0. 9	0.03	91	10	0. 02	0. 04	0. 03 7	0. 4	0.3	0. 17	3	29	0. 00 2	0.62
J	0. 12	0. 18	1. 15	0.02	87	10	0. 00 9	0. 02	0. 00 7	0. 39	0.45	0. 05	2. 5	21	0. 00 73	0.65

[Table 2]

Specimen Number	Steel Type	Manufacturing of Slab				Slab Heating / rolling	
		Input of Ca	Clean Bubbling			Slab Heating Temperature °C)	Finishing hot-rolling temperature (°C)
		Input Amount of Ca (kg/ton)	Gas Blowing Amount (liter/m in)	Time (minutes)	Number of Blowing points (points)		
1	A	0.018	13	17	2	1159	908
2	B	0.053	12	19	2	1163	846
3	C	0.08	23	15	2	1193	966
4	D	0.102	26	7	2	1175	983
5	E	0.083	35	16	2	1183	952
6	A	0.195	43	15	2	1160	898
7	A	0.085	84	9	2	1168	810
8	A	0.1	6	16	2	1169	889
9	B	0.085	19	2	2	1183	910
10	B	0.073	18	15	1	1165	835
11	B	0.065	25	13	2	1325	896
12	C	0.076	33	18	2	1295	1153
13	D	0.034	34	11	2	1083	905
14	C	0.052	41	9	2	1153	930
15	D	0.042	19	8	2	1208	925
16	D	0.063	38	11	2	1195	955
17	D	0.078	25	10	2	1125	978
18	E	0.082	28	8	2	1100	980
19	E	0.091	41	7	2	1103	1000
20	E	0.1	35	9	2	1109	890
21	F	0.085	33	15	2	1135	888
22	G	0.071	25	17	2	1153	891
23	H	0.036	29	18	2	1129	890
24	I	0.055	34	19	2	1130	910
25	J	0.065	40	7	2	1098	915

[Table 3]

Specimen Number	Steel Type	Reheating and Quenching Treatment		
		Reheating Temperature (°C)	Reheating Holding Time (minutes)	Quenching Cooling Rate (°C/s)
1	A	910	11	20
2	B	890	15	15
3	C	910	32	23
4	D	915	25	19
5	E	886	23	15
6	A	845	32	33

(continued)

Specimen Number	Steel Type	Reheating and Quenching Treatment		
		Reheating Temperature (°C)	Reheating Holding Time (minutes)	Quenching Cooling Rate (°C/s)
7	A	860	35	25
8	A	865	36	18
9	B	910	15	13
10	B	908	15	12
11	B	911	16	9
12	C	925	18	10
13	D	989	20	15
14	C	940	109	32
15	D	851	31	0.5
16	D	865	35	108
17	D	841	34	18
18	E	839	19	5
19	E	850	18	9
20	E	908	15	15
21	F	925	18	10
22	G	933	19	25
23	H	940	24	21
24	I	915	25	19
25	J	925	26	32

[Table 4]

Specimen Number	Steel Type	Composition of Microstructure of Base Material after PWHT						
		Bainite (area %)	Tempered martensite (area %)	Cross-sectional hardness (HB)	Packet size (μm)	VC, VCN Precipitate size (nm)	Maximum size of composite oxide inclusion (μm)	Number of composite oxide inclusions (EA/μm^2)
1	A	35	65	285	15.3	7.5	31	12
2	B	28	72	276	16.9	10.2	22	8
3	C	24	76	286	16.3	14.3	15	7
4	D	41	59	265	13.5	13.5	17	12
5	E	35	65	240	14.9	12.2	18	15
6	A	34	66	269	15.3	10.8	105	93
7	A	41	59	286	14.1	11.5	139	183
8	A	37	63	288	16.2	10.8	98	105
9	B	42	58	265	16.2	11.6	119	99
10	B	34	66	254	14.8	12.5	99	88
11	B	31	69	264	28.3	14.8	13	33

(continued)

Specimen Number	Steel Type	Composition of Microstructure of Base Material after PWHT						
		Bainite (area %)	Tempered martensite (area %)	Cross-sectional hardness (HB)	Packet size (μm)	VC, VCN Precipitate size (nm)	Maximum size of composite oxide inclusion (μm)	Number of composite oxide inclusions (EA/μm^2)
12	C	33	67	277	26.8	8.9	17	25
13	D	23	77	265	25.9	11.3	12	22
14	C	32	68	264	25.8	10.5	15	15
15	D	89	11	215	15.3	12.5	10	8
16	D	0	100	309	15.5	13.4	15	9
17	D	44	56	275	16.9	14.2	13	13
18	E	39	61	285	16.5	10.9	14	17
19	E	40	60	255	14.3	12.5	13	16
20	E	27	73	256	15.3	13.6	26	22
21	F	28	72	277	15.9	11.3	9	25
22	G	0	100	315	15.8	10.8	14	21
23	H	100	0	189	14.3	11.2	13	13
24	I	41	59	266	13.9	13.2	12	15
25	J	98	2	278	14.3	11.5	18	33

[Table 5]

Specimen Number	Steel Type	Properties of parent material after PWHT		
		Yield strength (MPa)	Tensile strength (MPa)	-40°C impact toughness (J)
1	A	785	892	153
2	B	852	815	192
3	C	792	908	265
4	D	792	822	241
5	E	810	892	169
6	A	835	903	8
7	A	811	892	12
8	A	798	892	15
9	B	769	884	8
10	B	782	835	13
11	B	813	908	23
12	C	735	826	15
13	D	731	895	13
14	C	788	866	9
15	D	643	753	10
16	D	865	995	11
17	D	776	887	295

(continued)

Specimen Number	Steel Type	Properties of parent material after PWHT		
		Yield strength (MPa)	Tensile strength (MPa)	-40°C impact toughness (J)
18	E	782	825	182
19	E	738	765	208
20	E	780	862	211
21	F	799	892	11
22	G	886	1053	9
23	H	402	515	225
24	I	728	845	12
25	J	654	744	211

[0141] As may be seen from the Tables 1 to 5, in the case of specimen numbers 1 to 5 and 17 to 20, which satisfied the alloy composition and manufacturing conditions proposed by the present disclosure, all of specimens may secure excellent quality, such as excellent strength of the parent material and excellent low-temperature impact toughness at -40°C, even after excellent post-weld heat treatment. In contrast, it may be seen that specimen numbers 6 to 16, which satisfied the alloy composition proposed by the present disclosure but did not satisfy the manufacturing conditions, found it difficult to secure the characteristics of the parent material proposed by the present disclosure. In addition, specimen numbers 21 to 25, which satisfied the steel material manufacturing conditions proposed by the present disclosure but did not satisfy the alloy composition, found it difficult to secure the characteristics of the parent material proposed by the present disclosure.

(Example 2)

[0142] For the steel material manufactured under the conditions of Table 3 above, welding and post-weld heat treatment were performed to confirm the low-temperature toughness and CTOD characteristics of the CGHAZ in the heat-affected zone (HAZ).

[0143] To this end, for the steel materials manufactured according to Tables 1 to 3, welding simulations were performed under the welding thermal cycle conditions of Table 6, and the post-weld heat treatment process was performed at 595°C for 180 minutes for 3 cycles. In Table 6, LMP was derived by the aforementioned relational expression 3.

[0144] The microstructure and physical properties of the CGHAZ in each specimen manufactured as described above were measured, and the results are shown in Tables 7 and 8 below.

[0145] Here, a phase fraction was measured by collecting the specimens and using Electron Back Scattered Diffraction (EBSD).

[0146] The impact toughness for each specimen used an average of absorbed energy values measured three times at a corresponding temperature through the Charpy V-Notch Test. Brinell hardness was tested according to ISO 6506 part 1, and a CTOD test was performed according to BS5762 (British Standard).

[0147] In addition, a cementite grain boundary occupancy ratio was measured using transmission electron microscopy (TEM). The cementite grain boundary occupancy ratio measured a ratio of film-like cementite to a total grain boundary length.

[Table 6]

Specimen Number	Steel Type	LMP	Welding Thermal Cycle		
			Maximum Temperature (°C)	Primary Cooling Rate (°C/s)	Secondary Cooling Rate (°C/s)
1	A	18.5	1260	10.5	6.5
2	B	17.9	1275	13	10.5
3	C	18.6	1289	12.9	6.4
4	D	19.5	1255	13.6	5.8

(continued)

Specimen Number	Steel Type	LMP	Welding Thermal Cycle		
			Maximum Temperature (°C)	Primary Cooling Rate (°C/s)	Secondary Cooling Rate (°C/s)
5	E	19.1	1325	14.5	8.5
6	A	18.3	1315	19.2	9.5
7	A	18.2	1259	15.3	7.5
8	A	19	1266	15.4	7
9	B	19.2	1325	11.5	6.9
10	B	17.9	1265	13.6	8.3
11	B	18.1	1295	16.2	9.1
12	C	17.6	1295	15.9	11.5
13	D	19	1307	13.2	13.5
14	C	19.1	1265	13.3	10.9
15	D	19.3	1355	14.5	14.2
16	D	18.6	1308	10.9	13.5
17	D	20.9	1315	11.7	10.9
18	E	19	1156	18.6	12.5
19	E	18.6	1352	36	9.8
20	E	18.5	1344	16.4	0.9
21	F	17.6	1369	11.9	7.8
22	G	17.5	1359	12.6	10.9
23	H	18.3	1357	18.4	13.2
24	I	17.9	1359	15.7	14.2
25	J	18.5	1355	16.6	13.9

[Table 7]

Specimen Number	Steel Type	CGHAZ microstructure after PWHT				
		Bainite (Area %)	Tempered martensite (Area %)	Cementite grain boundary occupancy ratio (%)	Cementite size (μm)	Cross-sectional hardness (HB)
1	A	42	58	7.5	0.56	289
2	B	32	68	7.3	0.56	288
3	C	28	72	6.5	0.62	291
4	D	14	86	5.4	0.54	275
5	E	35	65	1.5	0.69	256
6	A	25	75	2.6	0.85	270
7	A	27	73	2.9	0.62	292
8	A	25	75	3.2	0.35	277
9	B	25	75	3.6	0.54	269
10	B	31	69	7.5	0.36	275
11	B	21	79	3.4	0.64	281

(continued)

Specimen Number	Steel Type	CGHAZ microstructure after PWHT				
		Bainite (Area %)	Tempered martensite (Area %)	Cementite grain boundary occupancy ratio (%)	Cementite size (μm)	Cross-sectional hardness (HB)
12	C	11	89	4.6	0.57	286
13	D	28	72	5.1	0.85	278
14	C	35	65	4.4	0.35	288
15	D	28	72	5.3	0.66	289
16	D	12	88	3.9	0.91	288
17	D	17	83	18.5	2.54	245
18	E	25	75	4.9	0.72	315
19	E	33	67	5.8	0.33	322
20	E	12	88	19.5	0.98	235
21	F	8	92	22.5	1.23	288
22	G	17	83	6.6	0.57	338
23	H	88	12	23	3.38	233
24	I	19	81	5.9	0.85	281
25	J	11	89	18.7	1.25	215

[Table 8]

Specimen Number	Steel Type	CGHAZ properties after PWHT	
		-40°C impact toughness (J)	-35°C CTOD δ (mm)
1	A	125	0.18
2	B	135	0.35
3	C	83	0.34
4	D	152	0.51
5	E	156	0.33
6	A	12	0.01
7	A	11	0.01
8	A	8	0.03
9	B	13	0.02
10	B	12	0.02
11	B	22	0.35
12	C	183	0.33
13	D	132	0.29
14	C	162	0.35
15	D	148	0.41
16	D	156	0.38
17	D	18	0.03

(continued)

Specimen Number	Steel Type	CGHAZ properties after PWHT	
		-40°C impact toughness (J)	-35°C CTOD δ (mm)
18	E	12	0.01
19	E	13	0.03
20	E	15	0.01
21	F	12	0.03
22	G	8	0.01
23	H	13	0.04
24	I	145	0.39
25	J	11	0.02

[0148] As may be seen from Tables 6 to 8 above, in the case of specimen numbers 1 to 5 and 11 to 16 which satisfied the alloy composition and manufacturing conditions proposed by the present disclosure, it may be seen that excellent low-temperature impact toughness as well as good CTOD quality may be secured in CGHAZ. In contrast, specimen numbers 6 to 10 satisfied the alloy composition proposed by the present disclosure but did not satisfy the conditions for manufacturing steel, and specifically, as specimen numbers 6 to 10 is a case in which the size of the complex oxide inclusions was coarse, it may be seen that the properties of CGHAZ were inferior. On the other hand, specimen numbers 17 to 20 satisfied the alloy composition and the manufacturing conditions proposed by the present disclosure but did not satisfy the welding and post-weld heat treatment conditions, and thus, the properties of CGHAZ were not secured.

[0149] Specimen numbers 21 to 25 satisfied the manufacturing conditions proposed by the present disclosure but did not satisfy the alloy composition, and thus, it may be seen that the appropriate quality required by the present disclosure was not satisfied.

[0150] As described above, the detailed description of the present disclosure has described preferred embodiments of the present disclosure, but it is obvious that various modifications are possible within the scope of the present disclosure by those skilled in the technical field to which the present disclosure belongs. Therefore, the scope of the rights of the present disclosure should not be limited to the described embodiments, but should be determined by the claims described below as well as their equivalents.

Claims

1. A steel material, comprising: by wt%, C: 0.05 to 0.20%, Si: 0.05 to 0.50%, Mn: 0.5 to 2.0%, Al: 0.005 to 0.10%, P: 0.010% or less, S: 0.015% or less, Nb: 0.001 to 0.070%, V: 0.001 to 0.30%, Ti: 0.001 to 0.030%, Cr: 0.01 to 1.0%, Mo: 0.01 to 1.0%, Cu: 0.01 to 0.60%, Ni: 1.0 to 4.0%, B: 0.001 to 0.005%, Ca: 0.0005 to 0.0040%, O: 0.001%, and a balance of Fe and other inevitable impurities,

   wherein Ceq defined in the following relational expression 1 satisfies a range of 0.50 to 0.70,
   a microstructure comprises tempered martensite having an area fraction of 50% or more,
   a packet size of the microstructure comprises 17μm or less, and
   a maximum size of a $CaO\text{-}Al_2O_3$-X (where X is at least one of Ti, Mg or S) composite oxidation inclusion observed in an upper layer, which is a region of a surface layer to t/4 (where t is a thickness, unit: mm) in a thickness direction from a surface of the steel material, is 50μm or less, and the number of the inclusions per unit area of $1\mu m^2$ is 50 or less,

   $$Ceq = [C] + [Mn]/6 + ([Cr] + [Mo] + [V])/5 + ([Ni] + [Cu])/15 \quad \text{[Relational Expression 1]}$$

   in Relational Expression 1, [C], [Mn], [Cr], [Mo], [V], [Ni] and [Cu] represent the contents (wt%) of C, Mn, Cr, Mo, V, Ni and Cu included in the steel material, respectively, and when these components are not intentionally added, 0 is substituted.

2. The steel material of claim 1, wherein the microstructure comprises bainite and other inevitable structures.

3. The steel material of claim 1 or 2, wherein when the tempered martensite exceeds 80%, a cross-sectional Brinell hardness of the steel material is 220 to 290 HB.

4. The steel material of claim 1, wherein in the steel material, the number of VC or VCN precipitates having a diameter of 5 to 15 nm, among precipitates observed in a cross-section of the steel material, is at least 5 per 1 μm^2.

5. The steel material of claim 1, wherein the microstructure is observed within an prior austenite grain size having an average grain size of 30 μm or less.

6. The steel material of claim 1, wherein the steel material has a yield strength of 690 MPa or more, a tensile strength of 770 to 940 MPa, and a Charpy impact absorption energy of 50J or more at -40°C.

7. A manufacturing method of a steel material, comprising:

manufacturing a steel slab comprising, by wt%, C: 0.05 to 0.20%, Si: 0.05 to 0.50%, Mn: 0.5 to 2.0%, Al: 0.005 to 0.10%, P: 0.010% or less, S: 0.015% or less, Nb: 0.001 to 0.070%, V: 0.001 to 0.30%, Ti: 0.001 to 0.030%, Cr: 0.01 to 1.0%, Mo: 0.01 to 1.0%, Cu: 0.01 to 0.60%, Ni: 1.0 to 4.0%, B: 0.001 to 0.005%, Ca: 0.0005 to 0.0040%, O: 0.001%, and a balance of Fe and other inevitable impurities, wherein Ceq defined in the following relational expression 1 satisfies a range of 0.50 to 0.70, and a maximum size of a $CaO\text{-}Al_2O_3\text{-}X$ (where X is at least one of Ti, Mg or S) composite oxidation inclusion observed in an upper layer, which is a region of a surface layer to t/4 (where t is a thickness, unit: mm) in a thickness direction from a surface of the steel slab, is 50μm or less, and the number of inclusions per unit area of 1μm^2 is 50 or less;
reheating the steel slab to a temperature range of 1050 to 1300°C;
manufacturing a steel material by hot-rolling the steel slab at a finishing hot-rolling temperature of 830 to 1050°C;
heating the steel material to a temperature range of 820 to 950°C and holding the heated steel material for 10 to 40 minutes, and then cooling the steel material to a temperature of 300°C or less at a cooling rate of 3°C/s to 80°C/s based on a steel thickness t/4 temperature; and
a tempering heat treatment operation of heating the steel material to 550 to 700°C and maintaining the steel material for 5 to 60 minutes after the cooling,

$$Ceq = [C] + [Mn]/6 + ([Cr] + [Mo] + [V])/5 + ([Ni] + [Cu])/15 \quad \text{[Relational Expression 1]}$$

in Relational Expression 1, [C], [Mn], [Cr], [Mo], [V], [Ni] and [Cu] represent the contents (wt%) of C, Mn, Cr, Mo, V, Ni and Cu included in the steel material, respectively, and when these components are not intentionally added, 0 is substituted.

8. The manufacturing method of a steel material of claim 7, wherein the manufacturing a steel slab comprises:

inputting a metal Ca wire into molten steel after secondary refining so that an amount of Ca input is 0.015 to 0.15 kg/ton; and
performing clean bubbling for 5 to 40 minutes so that an inert gas blowing amount in a ladle is 10 to 50 liter/min after the Ca input,
wherein an input velocity of the Ca wire is 100 to 300 meters/min, and the number of inert gas blowing points in the ladle is 2.

9. The manufacturing method of a steel material of claim 7, further comprising:
performing multistage stacking cooling in a temperature range from 200°C to room temperature after the hot rolling.

10. The manufacturing method of a steel material of claim 7, further comprising:
performing a post-weld heat treatment on the steel material.

11. The manufacturing method of a steel material of claim 10, wherein the post-weld heat treatment is performed at

595°C to 625°C for 180 to 540 minutes (min).

12. The manufacturing method of a steel material of claim 11, wherein when temperatures of the tempering heat treatment and the post-weld heat treatment are identical to each other, LMP according to the following relational expression 2 is 17.0 to 19.5,

[Relational Expression 2]

$$LMP = T_k\ (Log\ t + 20)$$

where T_k = Kelvin temperature of tempering and PWHT, and t = tempering and PWHT time (hour).

13. The manufacturing method of a steel material of claim 11, wherein when temperatures of the tempering heat treatment and the post-weld heat treatment are different from each other, the LMP according to the following relationship 3 is 17.0 to 19.5,

[Relational Expression 3]

$$T(\log t_{eq}+20) = T_i(\log t_i+20)$$

$$Total\ LMP = T_i[\log(t_i+t_{eq})+20]$$

where T_i: Kelvin temperature of PWHT, t_i: PWHT time (hour), T: tempering Kelvin temperature, and t_{eq}: Equivalent tempering time (hour) when converted to a PWHT temperature.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2024/019099

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/58(2006.01)i; **C22C 38/44**(2006.01)i; **C22C 38/48**(2006.01)i; **C22C 38/46**(2006.01)i; **C22C 38/50**(2006.01)i; **C22C 38/06**(2006.01)i; **C21D 8/02**(2006.01)i; **C21D 9/50**(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)

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: 용접열영향부(Heat-Affected Zone), 용접후열처리(Post-Weld Heat Treatment), CTOD(Crack Tip Opening Displacement), 탱크(Tank), 저온충격인성(Low-Temperature Impact Toughness), 칼슘(Ca), 니켈(Ni), 보론(B), 템퍼링(Tempering)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-1846759 B1 (JFE STEEL CORPORATION) 06 April 2018 (2018-04-06) See paragraphs [0001] and [0149] and claims 1-2 and 6.	1-13
Y	KR 10-2016-0078669 A (POSCO) 05 July 2016 (2016-07-05) See paragraphs [0063]-[0066] and [0102]-[0104] and claims 1 and 5 and table 2.	1-13
Y	KR 10-2021-0032833 A (POSCO) 25 March 2021 (2021-03-25) See claim 4.	6
Y	KR 10-2022-0089409 A (POSCO) 28 June 2022 (2022-06-28) See claims 7 and 11.	8-9
A	WO 2023-203815 A1 (JFE STEEL CORPORATION) 26 October 2023 (2023-10-26) See claims 1-3.	1-13

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 March 2025	**06 March 2025**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2024/019099

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KR 10-1846759 B1	06 April 2018	CN 105980588 A	28 September 2016
		CN 105980588 B	27 April 2018
		EP 3081662 A1	19 October 2016
		EP 3081662 B1	13 November 2019
		JP 5950045 B2	13 July 2016
		JP WO2015-088040 A1	16 March 2017
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REFERENCES CITED IN THE DESCRIPTION

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- KR 1020227030534 **[0014]**
- CN 202211506158 **[0014]**
- WO 2021255858023761 A **[0014]**