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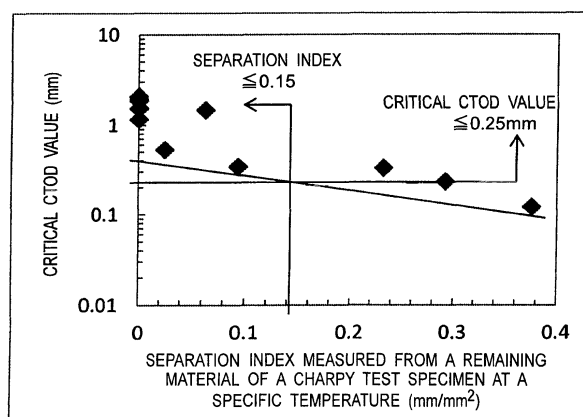
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(54) **STEEL SHEET FOR HIGH STRENGTH LINE PIPE WITH EXCELLENT LOW TEMPERATURE TOUGHNESS AND STEEL PIPE FOR HIGH STRENGTH LINE PIPE**

(57) To provide a high strength line pipe that is excellent in the low temperature toughness, particularly, in both the CTOD properties and DWTT properties. The steel sheet contains oxide particles with a circle equivalent diameter of 2 μm or more at a density of 10 particles/ mm^2 or less in a $t/2$ position where t is a sheet thickness of the steel sheet, and the steel sheet satisfies that in the $t/2$ position, an average circle equivalent diameter

of crystal grains enclosed by high angle grain boundaries in each of which a misorientation between two adjacent crystals is 15° or more is 10 μm or less, and that in the $t/2$ position, a fraction of a hard phase is 5 area% or less, while a separation index SI measured from a fracture surface of a Charpy impact test specimen of the steel sheet at a specific temperature is 0.15 mm/mm^2 or less.

Fig.2



Description

Technical Field

[0001] The present invention relates to a steel sheet for a high strength line pipe with excellent low temperature toughness and to a steel pipe for a high strength line pipe manufactured from the above-mentioned steel sheet for a high strength line pipe. In detail, the present invention relates to a steel sheet for a high strength line pipe and a steel pipe for a high strength line pipe that are excellent in both crack tip opening displacement (CTOD) properties and drop weight tear test (DWTT) properties.

Background Art

[0002] Line pipes used for transportation of natural gas and crude oil tend to undergo high pressure as an operating pressure for the purpose of improving the transportation efficiency. Steel for such line pipes is required to have higher strength. Additionally, in terms of safety, the steel is required to have a excellent CTOD property and a DWTT property as the brittle-fracture prevention properties, which serve as one of assessment indexes of fracture toughness.

[0003] From the perspective of enhancing the strength of steel material, there are proposed some strengthening mechanisms of the steel material, including solid-solution strengthening, precipitation hardening, transformation hardening, and dislocation strengthening. Among them, the dislocation strengthening involves enhancing the strength of material by increasing the dislocation density. The effect of this dislocation strengthening can be exhibited by increasing a cumulative rolling reduction in the so-called two-phase temperature range where part of an austenite single-phase microstructure is transformed into and precipitated as ferrite in a rolling step during a manufacturing process of the steel sheet. Thus, the dislocation strengthening is the strengthening mechanism to be applied more easily, compared to other strengthening mechanisms.

[0004] However, increasing the cumulative rolling reduction in the two-phase temperature range causes the rotation of a crystal orientation together with the increase in dislocation density, thus developing a crystal texture. Such development of the crystal texture leads to a large difference in the toughness of the steel between the rolling surface direction and the sheet thickness direction. This causes the generation of fine openings in the sheet thickness direction, called a "separation", at a fracture surface of a test specimen, when performing a Charpy impact test or COTD test using the test specimen taken in the rolling surface direction. Thus, the separation occurs due to the large difference in toughness between the rolling surface direction and the sheet thickness direction. For this reason, in addition to the influence of the crystal texture, the presence of S in the steel can also generate the separation because of the formation of MnS mainly extending in the rolling surface direction at a center segregation part, which is located at the center of the steel in the thickness direction.

[0005] If the aforesaid separation occurs before a brittle crack is generated during the CTOD test, the opening might be judged wrongly to be stably formed only up to a position where the separation occurs. Consequently, the critical CTOD value as the index of the CTOD properties would be reduced, compared to an intrinsic value. Because of this, in the material that causes such separation, for example, only the improvement of the toughness of a base metal, which is assessed by a fracture appearance transition temperature $vTrs$, cannot improve the critical CTOD value.

[0006] For this reason, for example, Patent Document 1 discloses a method for controlling a rolling temperature, especially, a rolling end temperature or the like in an austenite non-recrystallization region so that excellent DWTT properties are obtained while separation is suppressed, as well as expensive elements are added to achieve solid-solution strengthening.

Prior Art Document

Patent Document

[0007] Patent Document 1: JP 2013-47393 A

Disclosure of the Invention

Problems to be Solved by the Invention

[0008] The technique shown in the above-mentioned Patent Document 1 needs to adopt the solid-solution strengthening by addition of expensive elements, complicated manufacturing steps incorporating the combination of the water-cooling equipment and the heating equipment on the line, and the special rolling conditions. This leads to an increase in cost and a reduction in productivity.

[0009] The present invention has been made in view of the foregoing circumstance, and it is an object of the present invention to provide a technique capable of easily manufacturing a steel sheet for a high strength line pipe that is excellent in the low temperature toughness, particularly, in both the CTOD properties and DWTT properties, at a low cost.

Means for Solving the Problems

[0010] A steel sheet for a high strength line pipe that can solve the above-mentioned problems according to the present invention includes, in percent by mass: 0.02 to 0.2% of C; 0.02 to 0.5% of Si; 0.6 to 2.5% of Mn; more than 0% and 0.03% or less of P; more than 0% and 0.01% or less of S; 0.010 to 0.08% of Al; 0.001 to 0.1% of Nb; 0.003 to 0.03% of Ti; 0.0003 to 0.006% of Ca; 0.001 to 0.01% of N; more than 0% and 0.0045% or less of O; 0.0001 to 0.005% of REM; and 0.0001 to 0.005% of Zr, with the balance being iron and inevitable impurities, wherein the steel sheet contains oxide particles with a circle equivalent diameter of 2 μm or more at a density of 10 particles/ mm^2 or less in a $t/2$ position where t is a sheet thickness of the steel sheet, and the steel sheet satisfies that in the $t/2$ position, an average circle equivalent diameter of crystal grains enclosed by high angle grain boundaries in each of which a misorientation between two adjacent crystals is 15° or more is 10 μm or less, and that in the $t/2$ position, a fraction of a hard phase is 5 area% or less, while a separation index SI measured from a fracture surface of a Charpy impact test specimen of the steel sheet at a specific temperature is 0.15 mm/ mm^2 or less.

[0011] In a preferred embodiment of the present invention, the steel sheet further includes, in percent by mass, at least one element selected from the group consisting of: more than 0% and 1.5% or less of Cu; more than 0% and 1.5% or less of Ni; more than 0% and 1.5% or less of Cr; more than 0% and 1.0% or less of Mo; more than 0% and 0.2% or less of V; and more than 0% and 0.0003% or less of B.

[0012] The present invention encompasses a steel pipe for a high strength line pipe with excellent low temperature toughness, manufactured by using the above-mentioned steel sheet for a high strength line pipe.

Effects of the Invention

[0013] According to the present invention, the number density of coarse oxide particles with the circle equivalent diameter of 2 μm or more in the $t/2$ position where t is a sheet thickness and the separation index SI measured from the fracture surface of the Charpy test specimen at the specific temperature are set within respective appropriate ranges, thereby making it possible to improve the CTOD properties of the steel sheet. Concurrently, in the $t/2$ position, the average circle equivalent diameter of crystal grains enclosed by the high-angle grain boundaries in each of which the misorientation between the two adjacent crystals is 15° or more and the fraction of the hard phase are controlled appropriately, thereby making it possible to improve the DWTT properties. Therefore, the present invention can achieve the steel sheet for a high strength line pipe with excellent low temperature toughness that has a tensile strength of 520 MPa or more and is excellent in both the CTOD properties and the DWTT properties without using any expensive alloy element.

Brief Description of the Drawings

[0014]

Fig. 1 is a schematic diagram of a fracture surface of a Charpy test specimen for explaining a measurement method of a separation index SI.

Fig. 2 is a graph showing the relationship between the separation index SI and a critical CTOD value as an index of the CTOD properties.

Fig. 3 is a graph showing the relationship between the fraction of a hard phase in the $t/2$ position and a finish cooling temperature (FCT).

Mode for Carrying Out the Invention

[0015] The inventors have diligently studied to provide a steel sheet for a high strength line pipe that is excellent in both the CTOD properties and the DWTT properties. Specifically, regarding the improvement in the CTOD properties, the inventors have aimed to create a steel sheet for a high strength line pipe that can obtain the excellent critical CTOD value, though the occurrence of separation is allowed to some extent without completely shutting out the occurrence of separation. They have studied about the relationship between the occurrence of the separation and the microstructure of the steel sheet in the CTOD test. The result shows that the critical CTOD value obtained in the CTOD test has a correlation with a separation index SI in the Charpy impact test, which reveals that it is necessary to reduce the separation index SI measured from a fracture surface of the Charpy test specimen at a specific temperature, and also to restrain

the number density of coarse oxide particles with a circle equivalent diameter of 2 μm or more in the $t/2$ position. Meanwhile, regarding the improvement in the DWTT properties, the inventors have found that in the $t/2$ position, it is necessary to reduce an average circle equivalent diameter of crystal grains enclosed by high angle grain boundaries in each of which a misorientation between two adjacent crystals is 15° or more, and also to restrain a fraction of a hard phase. Based on these findings, the present invention has been completed.

[0016] The respective requirements for specifying the steel sheet for a line pipe in the present invention will be described below. The term "t" as used in the present specification means a thickness of the steel sheet unless otherwise specified.

(Average grain size of crystal grains enclosed by the high angle grain boundaries in each of which a misorientation between two adjacent crystals is 15° or more: 10 μm or less in the $t/2$ position)

[0017] To ensure the excellent DWTT properties, it is necessary to ensure the toughness of a base metal by refining crystal grains. Thus, in the present invention, the upper limit of the average circle equivalent diameter of crystal grains enclosed by the high angle grain boundaries, in each of which a misorientation between two adjacent crystals is 15° or more, is set at 10 μm or less in the $t/2$ position. The average grain size is preferably 8.0 μm or less, and more preferably 7.0 μm or less. The smaller the average grain size, the better the properties of the steel sheet become. However, the lower limit of the grain size is approximately 4 μm or more.

[0018] Note that the present invention measures the following: the average circle equivalent diameter of the crystal grains enclosed by the high angle grain boundaries, in each of which the misorientation between the two adjacent crystals is 15° or more; a fraction of a hard phase; and the number density of oxide particles with a circle equivalent diameter of 2 μm or more, to be mentioned later. In the present invention, the measurement position of these properties is set not at $t/4$ as a typical position for evaluating the properties of the steel sheet, but at $t/2$. The reason for setting the measurement position at $t/2$ is to ensure the DWTT properties, which is to be aimed, by improving the toughness of a part of the steel sheet serving as a fracture starting point.

(Separation index SI measured from the fracture surface of Charpy test specimen at specific temperature: 0.15 mm/mm² or less)

[0019] The separation index SI at the fracture surface of the Charpy test specimen caused at the specific temperature is set at 0.15 mm/mm² or less, thereby making it possible to ensure the target critical CTOD value even when separation occurs in the CTOD test. The target critical CTOD value is 0.25 mm or more when a test temperature is set at -10°C . Note that the above-mentioned specific temperature can be determined from the following formula (1). That is, the test temperature (specific temperature) for performing the Charpy impact test varies depending on the sheet thickness of the steel sheet. To evaluate the target critical CTOD value when the test temperature is set at -10°C , it is also necessary to consider this specific temperature (T_1).

$$T_1 = T_2 - 6 \times (t)^{1/2} + 20 \quad (1)$$

where T_1 is a Charpy test temperature ($^\circ\text{C}$); T_2 is a CTOD test temperature ($^\circ\text{C}$), which is -10°C in the present specification; and t is a sheet thickness (mm) of the steel sheet.

[0020] As shown in formula (2) below, the separation index SI can be determined by dividing the total length of the separations occurring in the direction perpendicular to the sheet thickness direction at the fracture surface of the Charpy test specimen by an area (cross-sectional area) of the fracture surface of the test specimen (see Fig. 1 to be mentioned later).

$$SI = \sum(L_n)/S_A \quad (2)$$

where L_n indicates the length (mm) of an n-th separation, and S_A is the cross-sectional area (mm²) of the fracture surface.

[0021] In the steel sheet for a high strength line pipe in the present invention, the separation index SI determined as mentioned above needs to be 0.15 mm/mm² or less. The separation index SI is preferably 0.12 mm/mm² or less and more preferably 0.10 mm/mm² or less. Note that from the viewpoint that even after the occurrence of the separation, the high critical CTOD value is exhibited, the separation index SI is not necessarily 0 mm/mm². From this perspective, the separation index SI is preferably 0.05 mm/mm² or more, and more preferably 0.10 mm/mm² or more.

[0022] For reference, Fig. 2 shows the relationship between the separation index SI and the CTOD properties. This graph shows a plot of the relationship between the separation index SI and the critical CTOD value measured as an

indicator of the CTOD properties, based on the result of Examples to be mentioned later. As can be seen from this graph, when the separation index SI is 0.15 mm/mm² or less, the following formula is satisfied as an acceptability criterion of the CTOD properties: critical CTOD value at -10°C $\geq$ 0.25 mm.

(Density of oxide particles with a circle equivalent diameter of 2 μ m or more in the t/2 position: 10 particles/mm² or less)

[0023] Coarse oxide particle adversely affect the improvement of the CTOD properties. Thus, in the present invention, the number density of oxide particles with the above-mentioned size is set at 10 particles/mm² or less. The smaller the number density of the above-mentioned oxide particles, the better the quality of the steel sheet becomes. The number density of the oxide particles is preferably 8 particles/mm² or less, and more preferably 5 particles/mm² or less. From the above-mentioned viewpoint, the lower limit of the number density is not specifically limited, but is preferably approximately 0.1 particles/mm² or more when taking into account the productivity and the like at the stage of manufacturing a slab.

[0024] Note that the term "oxide" of interest in the present invention means one observed by a method mentioned in Examples to be mentioned later.

(Fraction of a hard phase in the t/2 position: 5 area% or less)

[0025] The hard phase adversely affects the improvement of the DWTT properties. Thus, in the present invention, an area fraction of the hard phase occupying the entire microstructure, observed in the t/2 position, is set at 5% or less. The smaller the area fraction of the hard phase, the better the quality of the steel sheet becomes. The area fraction of the hard phase is preferably 3 area% or less, and more preferably 1 area% or less. Note that the lower limit of the area fraction of the hard phase is not specifically limited from the above-mentioned perspective and may be, for example, 0 area%.

[0026] The hard phase of interest in the present invention is, for example, a martensite island, a martensite, or the like.

[0027] The chemical component composition of the steel sheet for a high strength line pipe in the present invention also needs to be adjusted appropriately. The reasons for setting the content ranges of the respective components in the chemical composition will be described below. Regarding the chemical component composition, the term % as used herein means "% by mass".

(C: 0.02 to 0.2%)

[0028] Carbon (C) is an element essential to ensure the strengths of a steel sheet as a base metal and a weld bead. To this end, the C content needs to be 0.02% or more. Further, the C content is preferably 0.03% or more, and more preferably 0.05 % or more. However, any excessive C content is more likely to form a martensite island (MA: Martensite-Austenite constituent), thereby degrading the toughness of a Heat Affected Zone (HAZ) of the steel sheet and also degrading the weldability of the steel sheet. From this perspective, the C content needs to be 0.2% or less. The C content is preferably 0.15% or less, and more preferably 0.12% or less.

(Si: 0.02 to 0.5%)

[0029] Silicon (Si) has a deoxidizing function and is effective in improving the strengths of the steel sheet as the base metal and a weld bead. To exhibit these effects, the Si content is set at 0.02% or more. The Si content is preferably 0.05% or more, and more preferably 0.15% or more. However, any excessive Si content degrades the weldability and toughness. Thus, the Si content needs to be restrained to 0.5% or less. The Si content is preferably 0.45% or less, and more preferably 0.35% or less.

(Mn: 0.6 to 2.5%)

[0030] Manganese (Mn) is an element effective in improving the strengths of a steel sheet as a base metal and a weld bead. To exhibit these effects, the Mn content needs to be 0.6% or more. The Mn content is preferably 1.0% or more and more preferably 1.2% or more. However, any excessive Mn content not only promotes the occurrence of the separation because of the formation of MnS, but also degrades the HAZ toughness and weldability of the steel sheet. Thus, the upper limit of the Mn content is set at 2.5% or less. The Mn content is preferably 2.0% or less, more preferably 1.9% or less, and even more preferably 1.8% or less.

(P: more than 0% and 0.03% or less)

[0031] Phosphorus (P) is an element inevitably contained in a steel. When the P content exceeds 0.03%, the toughness of the base metal and the HAZ toughness of the steel sheet are drastically degraded. Therefore, in the present invention, the P content is restrained to 0.03% or less. The P content is preferably 0.020% or less, more preferably 0.015% or less, and even more preferably 0.010% or less. The P content is preferably reduced as much as possible, but it is difficult to industrially set the P content at 0%.

(S: more than 0% and 0.01% or less)

[0032] Any excessive S content forms MnS to promote the occurrence of separation. Thus, the upper limit of S content is set at 0.01% or less. The S content is preferably 0.008% or less, more preferably 0.006% or less, and even more preferably 0.005% or less. From the perspective of suppressing the occurrence of the separation in this way, the S content is desirably set small, but it is difficult to industrially set the S content at 0%. The lower limit of the S content is preferably approximately 0.0001% or more.

(Al: 0.010 to 0.08%)

[0033] Aluminum (Al) is a strong deoxidizing element. To obtain the deoxidizing effect, the Al content needs to be 0.010% or more. The Al content is preferably 0.02% or more, and more preferably 0.03% or more. Meanwhile, any excessive Al content forms a large amount of AlN to decrease the amount of TiN precipitates, thereby degrading the HAZ toughness. Thus, the Al content needs to be 0.08% or less. The Al content is preferably 0.06% or less, and more preferably 0.05% or less.

(Nb: 0.001 to 0.1%)

[0034] Niobium (Nb) is an element effective in enhancing the strength and the toughness of a base metal in the steel sheet without degrading its weldability. To exhibit these effects, the Nb content needs to be 0.001% or more. The Nb content is preferably 0.005% or more, and more preferably 0.010% or more. However, when the Nb content becomes excessive to exceed 0.1%, the toughness of the base metal and HAZ is degraded. Thus, the upper limit of Nb content is set at 0.1% or less. The Nb content is preferably 0.08% or less, and more preferably 0.05% or less.

(Ti: 0.003 to 0.03%)

[0035] Titanium (Ti) precipitates as TiN in a steel. Thus, Ti is an element required to improve the toughness of the base metal by the suppression of coarsening austenite grains when heating a slab and to improve the HAZ toughness by the coarsening of austenite grains in the HAZ during welding. To exhibit these effects, the Ti content needs to be 0.003% or more. The Ti content is preferably 0.005% or more, and more preferably 0.01% or more. Meanwhile, any excessive Ti content precipitates solid-solution Ti and TiC, thereby degrading the toughnesses of the base metal and HAZ. Thus, the Ti content needs to be 0.03% or less. The Ti content is preferably 0.025% or less, and more preferably 0.020% or less.

(Ca: 0.0003 to 0.006%)

[0036] Calcium (Ca) serves to control the form of a sulfide and has an effect of suppressing the formation of MnS by forming CaS. To obtain such an effect, the Ca content needs to be 0.0003% or more. The Ca content is preferably 0.0005% or more, and more preferably 0.0010% or more. Meanwhile, when the Ca content exceeds 0.006% to become excessive, the toughness of the steel sheet is degraded. The upper limit of the Ca content is 0.006% or less. The Ca content is preferably 0.005% or less, and more preferably 0.004% or less.

(N: 0.001 to 0.01%)

[0037] Nitrogen (N) precipitates as TiN in a steel. Thus, N is an element required to improve the toughness of the base metal by the suppression of coarsening austenite grains when heating a slab and to improve the HAZ toughness by the coarsening of austenite grains in the HAZ during welding. To exhibit these effects, the N content needs to be set at 0.001% or more. The N content is preferably 0.003% or more, and more preferably 0.004% or more. However, any excessive N content degrades the toughness of the HAZ by the presence of the solid-solution N. The N content needs to be 0.01% or less. The N content is preferably 0.008% or less, and more preferably 0.006% or less.

(O: more than 0% and 0.0045% or less)

[0038] An oxygen (O) content is preferably small from the viewpoint of suppressing the formation of coarse oxide particles. From this perspective, in the present invention, the upper limit of O content is set at 0.0045% or less. The O content is preferably 0.0040% or less, and more preferably 0.0035% or less. The O content is preferably reduced as much as possible, but it is difficult to industrially set the O content at 0%.

(REM: 0.0001 to 0.005%)

[0039] A REM (Rare Earth Element) is an element that serves to form an oxide and disperse it finely in the steel, thereby contributing to improving the CTOD properties. To exhibit such an effect, the REM content needs to be 0.0001% or more. The REM content is preferably 0.0003% or more, and more preferably 0.0005% or more. Meanwhile, any excessive REM content forms coarse inclusions, thereby degrading the toughness of the base metal. Thus, the upper limit of the REM content is set at 0.005% or less. Note that in the present invention, REM means 15 lanthanoid elements from La to Lu, scandium Sc, and yttrium Y.

(Zr: 0.0001 to 0.005%)

[0040] Zirconium (Zr) is an element that serves to form an oxide and disperse it finely in the steel, thereby contributing to improving the CTOD properties. To obtain such an effect, the Zr content needs to be 0.0001% or more. The Zr content is preferably 0.0003% or more, and more preferably 0.0005% or more. Meanwhile, any excessive Zr content forms coarse inclusions, thereby degrading the toughness of the base metal. Thus, the Zr content needs to be 0.005% or less. The Zr content is preferably 0.003% or less, more preferably 0.002% or less, and even more preferably 0.001% or less.

[0041] The chemical component composition of the steel sheet for a high strength line pipe in the present invention has been mentioned above. The balance of the steel sheet is substantially iron. Note that inevitable impurities are obviously allowed to be brought and contained in the steel, depending on the situations, including raw materials, construction materials, manufacturing facilities, and the like. Examples of the above-mentioned inevitable impurities can include As, Sb, Sn, H, etc.

[0042] The steel sheet for a line pipe in the present invention further preferably contains one or more elements selected from the group consisting of Cu, Ni, Cr, Mo, V, and B in the following amounts as needed. These elements are elements that enhance the respective strength and toughness of the base metal and the HAZ, and thus may be used alone or in combination. The reasons for setting the ranges of the contents of these components in the steel sheet will be described below.

(Cu: more than 0% and 1.5% or less)

[0043] Copper (Cu) is an element effective in enhancing the strength of a steel sheet. To obtain such an effect, the Cu content is preferably 0.01% or more. The Cu content is more preferably 0.05% or more, and even more preferably 0.10% or more. However, any excessive Cu content degrades the toughness of the base metal. Thus, the Cu content is set at 1.5% or less. The Cu content is more preferably 1.0% or less, and even more preferably 0.5% or less.

(Ni: more than 0% and 1.5% or less)

[0044] Nickel (Ni) is an element effective in improving the strength and toughness of each of a base metal and a weld bead. To obtain these effects, the Ni content is preferably 0.01% or more. Accordingly, the Ni content is more preferably 0.05% or more, and even more preferably 0.10% or more. However, a large Ni content makes the steel for structures extremely expensive. From the economic point of view, the Ni content is preferably 1.5% or less. Accordingly, the Ni content is more preferably 1.0% or less, and even more preferably 0.5% or less.

(Cr: more than 0% and 1.5% or less)

[0045] Chrome (Cr) is an element effective in improving the strength of a steel sheet. To obtain such an effect, the Cr content is preferably 0.01% or more. The Cr content is more preferably 0.05% or more, and even more preferably 0.10% or more. Meanwhile, when the Cr content exceeds 1.5%, the HAZ toughness of the steel sheet is degraded. Thus, the Cr content is preferably set at 1.5% or less. The Cr content is more preferably 1.0% or less, and even more preferably 0.5% or less.

(Mo: more than 0% and 1.0% or less)

[0046] Molybdenum (Mo) is an element effective in improving the strength and toughness of the base metal. To obtain these effects, the Mo content is preferably 0.01% or more. The Mo content is more preferably 0.05% or more, and even more preferably 0.10% or more. However, when the Mo content exceeds 1.0%, the HAZ toughness and weldability of the steel sheet are degraded. Thus, the Mo content is preferably 1.0% or less and more preferably 0.5% or less.

(V: more than 0% and 0.2% or less)

[0047] Vanadium (V) is an element effective in improving the strength of a steel sheet. To obtain such an effect, the V content is preferably 0.003% or more. The V content is more preferably 0.010% or more. Meanwhile, when the V content exceeds 0.2%, the weldability of the steel sheet and the toughness of the base metal thereof are degraded. Thus, the V content is preferably 0.2% or less, more preferably 0.1% or less, and even more preferably 0.08% or less.

(B: more than 0% and 0.0003% or less)

[0048] Boron (B) has the function of enhancing the hardenability of a steel sheet to thereby enhance the strengths of a base metal and a weld bead. Further, B binds with N while a HAZ area heated in welding is being cooled to thereby precipitate BN, thus promoting transformation to ferrite from the inside of the austenite grains. Thus, B also has the function of improving the HAZ toughness. To obtain these effects, the B content is preferably 0.0001% or more. However, any excessive B content degrades the toughnesses of the base metal and the HAZ area, and also results in degradation in the weldability. Thus, the upper limit of B content is preferably set at 0.0003% or less.

[0049] In manufacturing the steel sheet of the present invention, it is necessary to appropriately control manufacturing steps. The manufacturing steps will be described in order below.

[0050] First, the steel is deoxidized using Mn, Si, and Al. Subsequently, the steel is subjected to an RH reflux process by ensuring an RH reflux time of 10 minutes or more in order to float and separate coarse oxide particles from the steel. As demonstrated in Examples mentioned later, if the RH reflux time is short, the number density of coarse oxide particles with a diameter of 2 μm or more will increase, thus degrading the CTOD properties. The RH reflux time is preferably 15 minutes or more, and more preferably 20 minutes or more. Note that the preferable upper limit of the RH reflux time is not particularly limited from the above-mentioned perspective, but is preferably 60 minutes or less in terms of the productivity or the like.

[0051] Then, the elements Ti, (REM, Zr), and Ca are added to the steel in this order. When these respective elements are added in the order other than the addition order mentioned above, an oxide with an appropriate composition will not be obtained. Consequently, the number density of coarse oxide particles with the diameter of 2 μm or more increases, as demonstrated in Example mentioned later, thereby degrading the CTOD properties. In particular, since Ca has an extremely strong deoxidizing capacity, when Ca is added before addition of REM or Zr, there is no more oxygen left to bind with REM or Zr, thus failing to obtain desired oxides of REM and Zr. Note that the term (REM, Zr) as used herein means that the addition order of REM and Zr is not limited particularly. That is, as long as REM and Zr are added after the addition of Ti and before the addition of Ca, either the addition of REM and Zr in this order or the addition of Zr and REM in this order may be performed. Alternatively, both REM and Zr may be added at the same time.

[0052] In the present invention, it is necessary to ensure the time from the addition of (REM, Zr) to the start of casting for 10 minutes or more. When this time is less than 10 minutes, the number density of coarse oxide particles with a diameter of 2 μm or more will increase as demonstrated in Examples mentioned later, thus degrading the CTOD properties. The time from the addition of (REM, Zr) to the start of casting is preferably 15 minutes or more and more preferably 20 minutes or more. Note that the preferable upper limit of the above-mentioned time is not particularly limited from the aforesaid perspective, but is preferably 90 minutes or less in terms of the productivity or the like.

[0053] For example, after fabricating a cast strip, such as a slab, in the ways mentioned above, the slab is reheated at a heating temperature of 1050 to 1200 $^{\circ}\text{C}$, which is a normal temperature range, followed by predetermined rough rolling. Subsequently, the rolled slab is hot-rolled in a temperature range of an Ar_3 transformation temperature to 950 $^{\circ}\text{C}$ (hereinafter referred to as the " Ar_3 temperature to 950 $^{\circ}\text{C}$ ") in such a manner that a cumulative rolling reduction is 50% or more. By setting the cumulative rolling reduction in the hot-rolling at 50% or more, in the $t/2$ position, the average circle equivalent diameter of crystal grains enclosed by the high angle grain boundaries in each of which the misorientation between two adjacent crystals is 15 $^{\circ}$ or more can be set at 10 μm or less, thereby improving the DWTT properties. The cumulative rolling reduction at this time is preferably 55% or more, and more preferably 60% or more. Note that when the cumulative rolling reduction exceeds 80%, the crystal texture is developed to thereby increase the separation index SI, thus degrading the CTOD properties. Thus, the upper limit of the cumulative rolling reduction is set at 80% or less. The cumulative rolling reduction is preferably 70% or less.

[0054] The above-mentioned "cumulative rolling reduction" is a value determined by calculation from the following

formula (3). The above-mentioned "temperature" is defined as an average temperature determined by calculation from the surface temperature of the slab or steel sheet, taking into consideration the sheet thickness and the like.

$$\text{Cumulative Rolling Reduction} = (t_0 - t_1)/t_2 \times 100 \quad (3)$$

where in the formula (3), t_0 is a rolling start thickness (mm) of the steel sheet obtained when the average temperature is within a rolling temperature range, t_1 is a rolling end thickness (mm) of the steel sheet obtained when the average temperature is within the rolling temperature range, and t_2 is a thickness of the cast strip (for example, slab) before the rolling.

[0055] The above-mentioned Ar_3 temperature for use is a value determined by formula (4) below. The same goes for values shown in Table 1 to be mentioned later.

$$Ar_3(^{\circ}C) = 910 - 310 \times [C] - 80 \times [Mn] - 20 \times [Cu] - 15 \times [Cr] - 55 \times [Ni] - 80 \times [Mo] - 0.35 \times (t-8) \quad (4)$$

where in the formula (4), [C], [Mn], [Cu], [Cr], [Ni], and [Mo] indicate the contents (% by mass) of C, Mn, Cu, Cr, Ni, and Mo, respectively, and t denotes a sheet thickness (mm) when measuring the temperature.

[0056] After the rolling mentioned above, the rolled sheet is cooled. In the present invention, it is recommended that to ensure the desired low temperature toughness (especially, the DWTT properties), the rolling is performed at an unrecrystallized temperature, and immediately after the end of the rolling, the cooling, such as water-cooling, is performed. Specifically, the average cooling speed is set at 10°C/sec or higher in a temperature range from a temperature (start cooling temperature) of the Ar_3 temperature or higher to a temperature (finish cooling temperature) of 550°C or lower. The cooling condition in the above-mentioned temperature range is controlled in this way, so that the fraction of the hard phase in the $t/2$ position can be controlled within a predetermined range, thereby making it possible to ensure the desired DWTT properties. The upper limit of the above-mentioned start cooling temperature is preferably set at approximately $Ar_3 + 80^{\circ}C$ or lower. The preferable lower limit of the average cooling speed is 15°C/sec or higher. However, when the average cooling speed is extremely high, the strength of the steel sheet is drastically enhanced to degrade its toughness. Thus, the upper limit of the average cooling speed is set at 50°C/sec or lower. The preferable upper limit of the average cooling speed is 45°C/sec or lower.

[0057] In the above-mentioned step, the finish cooling temperature has an intimate relationship with the fraction of the hard phase in the $t/2$ position. Thus, by controlling the finish cooling temperature to be 550 °C or lower, the fraction of the hard phase can be suppressed to 5 area% or less.

[0058] For reference, Fig. 3 shows the relationship between the fraction of the hard phase in the $t/2$ position and the finish cooling temperature (FCT). This graph is obtained by plotting the relationship between the fraction of the hard phase and the finish cooling temperature based on a number of basic experiments executed by the inventors. As can be seen from this graph, the finish cooling temperature is controlled to be 550°C or lower, so that the fraction of the hard phase can be restrained to 5 area% or less. The FCT is preferably 530°C or lower, and more preferably 500°C or lower. Note that when the FCT becomes a low temperature, the strength of the steel sheet is enhanced, thereby degrading the toughness of the steel sheet. Thus, the lower limit of FCT is set at 350°C or higher.

[0059] The sheet thickness of the steel sheet for a high strength line pipe according to the present invention is not specifically limited, but when using the steel sheet as the material for the line pipe, the sheet thickness is preferably at least 6 mm or more, and more preferably 10 mm or more. The upper limit of the sheet thickness of the steel sheet is preferably 30 mm or less, and more preferably 25 mm or less.

[0060] The steel sheet for a high strength line pipe according to the present invention is formed into a steel pipe for a line pipe thereafter. Nevertheless, the obtained steel pipe reflects the properties of the steel sheet as raw material and thus has excellent low temperature toughness.

[0061] The present application claims priority to Japanese Patent Application No. 2015-081206, filed on April 10, 2015, the disclosure of which is incorporated herein by reference in its entirety.

Examples

[0062] The present invention will be more specifically described by way of Examples. The present invention is not limited to the following Examples. Some modifications can be made to these Examples as long as they are adaptable to the above-mentioned and below-mentioned concepts, and all of these modifications are included within the scope of

the present invention.

[0063] Various types of steel materials A to O with the chemical component compositions and the A_{r3} temperatures shown in Table 1 were produced in the following ways. The unit shown in Table 1 is % by mass, and the balance of each steel included iron and inevitable impurities. Note that REM shown in Table 1 was added in the form of misch metal containing La and Ce.

[0064] In a molten-steel process step, first, the steel was deoxidized using Mn, Si, and Al. Then, to float and separate coarse oxides, the RH reflux was performed for a period of time shown in Table 2. Subsequently, as shown in Table 2, Ti, (REM, Zr), and Ca were added in this order to the respective steels, except for one type of steel material N, and thereafter, casting was started. The time from addition of (REM, Zr) to the start of casting was shown in Table 2.

[0065] The slab obtained in this way was reheated at a heating temperature shown in Table 2, and then subjected to rough rolling such that a cumulative rolling reduction was 40% or higher at a surface temperature of the steel sheet of 900°C or higher. Thereafter, the slab was further subjected to hot-rolling at a cumulative rolling reduction shown in Table 2 in a temperature range from the A_{r3} temperature to 950°C, thereby producing a steel sheet with a sheet thickness t (20 mm).

[0066] After the above-mentioned rolling, the steel sheet was cooled at an average cooling speed of 30°C/sec in the temperature range from the SCT (Start Cooling Temperature) to the FCT (Finish Cooling Temperature) as shown in Table 2. Then, the steel sheet was allowed to stand to cool to the room temperature, thereby producing various types of steel sheets.

[0067] Regarding the steel sheets obtained in this way, the following properties were measured in the ways to be mentioned later: the number density of oxide particles with a circle equivalent diameter of 2 μm or more; an average crystal grain size in the $t/2$ position; a fraction of the hard phase in the $t/2$ position; the tensile properties (yield strength, tensile strength); the Charpy property (separation index SI); the CTOD property (critical CTOD value); and the DWTT property (85% ductile fracture appearance transition temperature, 85% shear appearance transition temperature (SATT)).

(Measurement of the number density of oxide particles with a circle equivalent diameter of 2 μm or more)

[0068] The $t/2$ position of each steel sheet on a cross-section (L cross-section) perpendicular to the steel sheet surface and parallel to the rolling direction was set as a measurement position. In the measurement position, inclusions with a diameter of 2 μm or more were observed at an observation magnification of 400 times over an observation field of view of approximately 50 mm², and the component composition of a center part of each inclusion was quantitative-analyzed by a wavelength-dispersive X-ray spectroscopy using EPMA-8705 (trade name), manufactured by SHIMADZU Corporation. Elements to be analyzed were Al, Mn, Si, Mg, Ca, Ti, Zr, S, REM (La, Ce, Nd, Dy, Y), and Nb. First, the relationship between the X-ray intensity and an element concentration of each element was determined as a calibration curve by using a known substance. Then, the element concentration of a target inclusion was determined quantitatively from the calibration curve and an X-ray intensity obtained from the inclusion. From the result obtained quantitatively, oxide particles were defined as the inclusions in which an oxygen content was 5% or more, and then the number density of those oxide particles was determined.

(Measurement of the average circle equivalent diameter of crystal grains enclosed by the high angle grain boundaries in each of which a misorientation between two adjacent crystals is 15° or more, in the $t/2$ position)

[0069] A test specimen taken from each steel sheet was used in which its cross-section (L cross-section) perpendicular to the steel sheet surface and parallel to the rolling direction was polished by a colloidal silica. The grain size was measured by an electron backscatter diffraction (EBSD) method with the $t/2$ position set as the measurement position. Specifically, the crystal grain was defined as an area enclosed by the high angle grain boundaries in each of which the misorientation between two adjacent crystals was 15° or more. The average circle equivalent diameter of such a crystal grain was determined by using a combination of an EBSD device, manufactured by TexSEM Laboratories, Inc., and the SEM. The measurement conditions at this time were as follows: measurement region: 200 μm $\times$ 200 μm (region spreading from the $t/2$ position of the steel sheet as the center toward both sides thereof in the sheet thickness direction, each side by 100 μm); and measurement step: at intervals of 0.5 μm . Measurement points in which a confidence index (CI) indicative of the reliability of the measurement orientation was smaller than 0.1 were excluded from the analysis targets.

(Measurement of fraction of a hard phase in the $t/2$ position)

[0070] A test specimen taken from each steel sheet was used in which its cross-section (L cross-section) perpendicular to the steel sheet surface and parallel to the rolling direction was polished and corroded with a repeller reagent. The hard phase in the $t/2$ position as the measurement position was identified by image analysis based on a microstructure

image taken by an optical microscopy at a magnification of 400 times, and then a fraction of the hard phase was determined.

(Measurement of tensile properties (yield strength, tensile strength))

[0071] Regarding the tensile properties, a yield strength YS and a tensile strength TS were measured using full thickness tensile test specimens of the steel sheets in conformity with API-5L by test methods conforming to the API-5L standard. In this way, the tensile properties of the steel sheets were evaluated.

(Measurement of Charpy property (separation index SI))

[0072] The Charpy property was evaluated by using a 2 mm V notched Charpy test specimen of each steel sheet in conformity with ASTM-A370 standard by a test method conforming to this standard. At this time, the Charpy test specimen was taken from the t/2 position of each steel sheet in such a manner as to be aligned with the direction of the CTOD test specimen. Three tests were performed on each test specimen at a separation index measurement temperature shown in Table 3 below to thereby measure separation indexes. The maximum one of the measurement values was adopted as the separation index SI. Fig. 1 is a schematic diagram of a fracture surface of the Charpy test specimen when measuring the separation index SI. Referring to Fig. 1, reference numeral 1 denotes a separation; 2 denotes a fracture surface; 3 denotes 2 mm V notch; and 4 denotes a sheet thickness direction. The separation index SI of each steel sheet was determined by measuring respective lengths L_1 to L_3 of the separations generated at the fracture surface of the Charpy test specimen and dividing the total length of them by the cross-sectional area of the fracture surface of the test specimen according to the above formula (2).

(Measurement of CTOD property (critical CTOD value))

[0073] The CTOD property was evaluated using a three-point bending CTOD test specimen with B x 2B geometry of each steel sheet in conformity with BS7448 by a test method conforming to this standard. The CTOD test was performed on two specimens of each steel sheet at -10°C. A lower one of two measured CTOD values was adopted as the critical CTOD value. In this example, the steel sheets having a CTOD value at -10 °C of 0.25 mm or more were rated as having excellent CTOD property (pass).

(Measurement of the DWTT property (85% ductile fracture appearance transition temperature))

[0074] The DWTT property was evaluated using a DWTT test specimen chevron-notched in conformity with API5L3 standard by a test method conforming to this standard. The test was performed on two specimens of each steel sheet at respective temperatures. In this example, the lowest temperature (85% ductile fracture appearance transition temperature, 85% SATT) where a ductile fracture surface ratio was 85% was determined. The steel sheets in which this value was -10°C or lower were rated as having excellent DWTT property (pass).

[0075] These results are shown in Table 3. Note that in Table 3, the "average circle equivalent diameter of crystal grains enclosed by the high angle grain boundaries in each of which a misorientation between two adjacent crystals is 15° or more, in the t/2 position" is abbreviated as the "average circle equivalent diameter of the high-angle grains in the t/2 position".

[Table 1]

Steel	C	Si	Mn	P	S	Al	Cu	Ni	Cr	Mo	V	Nb	Ti	B	Ca	N	O	REM	Zr	Ar ₃
A	0.068	0.30	1.47	0.008	0.0014	0.038	0	0.21	0.23	0	0.061	0.031	0.013	0	0.0013	0.0054	0.0015	0.0017	0.0008	752
B	0.040	0.20	1.86	0.005	0.0008	0.031	0.24	0.23	0	0.12	0	0.045	0.014	0	0.0011	0.0047	0.0021	0.0025	0.0011	718
C	0.100	0.30	1.55	0.009	0.0020	0.021	0	0	0	0.04	0.060	0.031	0.004	0	0.0013	0.0039	0.0013	0.0012	0.0013	748
D	0.070	0.22	1.52	0.006	0.0005	0.035	0.29	0.23	0	0.11	0	0.051	0.011	0	0.0018	0.0052	0.0018	0.0015	0.0005	735
E	0.055	0.32	1.13	0.006	0.0005	0.032	0	0	0.26	0.07	0.057	0.028	0.012	0	0.0024	0.0031	0.0025	0.0023	0.0016	789
F	0.037	0.29	1.55	0.005	0.0013	0.033	0.27	0.69	0	0.01	0.002	0.026	0.011	0	0.0016	0.0038	0.0035	0.0013	0.0009	726
G	0.080	0.20	1.54	0.013	0.0032	0.032	0	0	0	0	0	0.014	0.015	0.0003	0.0014	0.0036	0.0027	0.0016	0.0012	758
H	0.120	0.07	1.25	0.007	0.0015	0.030	0	0	0	0	0	0.005	0.008	0	0.0017	0.0042	0.0015	0.0034	0.0025	769
I	0.052	0.22	1.24	0.005	0.0010	0.028	0.15	0.16	0.17	0.13	0.030	0.026	0.011	0	0.0022	0.0042	0.0017	0	0	766
J	0.068	0.29	1.15	0.008	0.0009	0.037	0	0	0.22	0	0.060	0.030	0.013	0	0.0014	0.0051	0.0019	0.0013	0.0009	789
K	0.060	0.32	1.14	0.006	0.0005	0.034	0.16	0.25	0.2	0.11	0	0.030	0.012	0	0.0019	0.0051	0.0023	0.0012	0.0005	767
L	0.069	0.30	1.26	0.009	0.0010	0.034	0	0	0.2	0	0.060	0.029	0.011	0	0.0014	0.0051	0.0016	0.0011	0.0011	781
M	0.062	0.28	1.43	0.007	0.0013	0.031	0	0.27	0.36	0	0	0.027	0.014	0	0.0015	0.0046	0.0037	0.0014	0.0007	752
N	0.043	0.26	1.76	0.006	0.0008	0.026	0.29	0.21	0	0.13	0	0.042	0.009	0	0.0017	0.0033	0.0021	0.0017	0.0013	724
O	0.048	0.21	1.82	0.009	0.0022	0.034	0.26	0.24	0	0.11	0	0.048	0.012	0	0.0021	0.0039	0.0032	0.0012	0.0015	718

[Table 2]

Steel	Sheet thickness (mm)	Heating temperature (°C)	Cumulative rolling reduction (%)	SCT (°C)	FCT (°C)	RH reflux time (minutes)	Order of addition of elements	Time from addition of (REM, Zr) to start of casting (minutes)
A	20	1,135	57	818	519	30	Al→Ti→ (REM, Zr) →Ca	30
B	20	1,161	70	731	530	27	Al→Ti→ (REM, Zr) →Ca	38
C	20	1,133	65	818	519	33	Al→Ti→ (REM, Zr) →Ca	43
D	20	1,156	64	754	464	29	Al→Ti→ (REM, Zr) →Ca	39
E	20	1,172	77	793	445	25	Al→Ti→ (REM, Zr) →Ca	29
F	20	1,125	74	779	503	24	Al→Ti→ (REM, Zr) →Ca	43
G	20	1,095	76	804	548	30	Al→Ti→ (REM, Zr) →Ca	37
H	20	1,083	75	801	509	28	Al→Ti→ (REM, Zr) →Ca	35
I	20	1,128	72	798	527	29	Al→Ti→ (REM, Zr) →Ca	39
J	20	1,131	40	867	463	29	Al→Ti→ (REM, Zr) →Ca	46
K	20	1,136	85	772	452	30	Al→Ti→ (REM, Zr) →Ca	36
L	20	1,132	75	807	553	32	Al→Ti→ (REM, Zr) →Ca	49
M	20	1,137	77	786	541	8	Al→Ti→ (REM, Zr) →Ca	32
N	20	1,123	75	753	520	31	Al→Ti→Ca →(REM, Zr)	26

EP 3 282 028 A1

(continued)

Steel	Sheet thickness (mm)	Heating temperature (°C)	Cumulative rolling reduction (%)	SCT (°C)	FCT (°C)	RH reflux time (minutes)	Order of addition of elements	Time from addition of (REM, Zr) to start of casting (minutes)
O	20	1,128	73	762	493	28	Al→Ti→ (REM, Zr) →Ca	7

[Table 3]

Sample No.	Steel	Fraction of hard phase in the t/2 position (area%)	Average circle equivalent diameter of high-angle grains in the t/2 position (μm)	Measurement temperature of separation index ($^{\circ}\text{C}$)	Separation index (mm/mm^2)	Number density of oxide particles with a diameter of $2\ \mu\text{m}$ or more in the t/2 position (particles/ cm^2)	YS (MPa)	TS (MPa)	Critical CTOD value (mm)	85% SATT ($^{\circ}\text{C}$)
1	A	2.1	6.2	-17	0	4.5	539	663	1.910	-27
2	B	1.8	7.5	-17	0.05	4.4	596	668	2.060	-22
3	C	0.5	7.5	-17	0	2.9	567	653	1.903	-20
4	D	0.2	6.9	-17	0	3.6	602	683	1.543	-27
5	E	0.5	6.7	-17	0.13	6.2	500	605	0.608	-29
6	F	0.1	7.2	-17	0.08	5.8	522	629	1.260	-24
7	G	2.9	6.8	-17	0.04	4.1	463	568	1.710	-19
8	H	1.1	6.5	-17	0.09	5.2	463	568	1.230	-19
9	I	3.1	5.0	-17	0.07	12.3	497	625	0.172	-24
10	J	0.8	12.0	-17	0	4.8	495	635	0.094	-3
11	K	0.2	4.8	-17	0.37	3.3	502	651	0.120	-32
12	L	7.8	6.7	-17	0.13	2.9	480	599	1.340	-9
13	M	1.6	6.3	-17	0.11	18.2	567	678	0.213	-25
14	N	1.1	5.4	-17	0.05	15.7	579	668	0.153	-28
15	O	0.3	5.9	-17	0.01	10.5	598	673	0.169	-26

[0076] From these results, the following consideration can be made.

[0077] First, the samples Nos. 1 to 8 shown in Table 3 are the inventive examples in which steel sheets were manufactured on the recommended conditions by using steel materials A to H of Table 1 that satisfied the chemical component composition specified by the present invention. These samples satisfied the requirements of the present invention in terms of all the following conditions: the number density of coarse oxide particles with a circle equivalent diameter of 2 μm or more; the average circle equivalent diameter of crystal grains enclosed by high-angle grain boundaries in each of which a misorientation between the two adjacent crystals was 15° or more; the fraction of the hard phase; and the separation index SI, all these conditions being specified by the present invention. Thus, it is found that in the CTOD test performed at a test temperature of -10°C , the critical CTOD values of these samples satisfied the target value, i. e. , 0.25 mm or more. Furthermore, it is also found that 85% SATTs of all these samples were -10°C or lower, and thus, these samples also had excellent DWTT properties.

[0078] In contrast, samples Nos. 9 to 15 shown in Table 3 did not satisfy any one of the requirements specified by the present invention. Thus, in these samples, the critical CTOD value or 85% SATT did not reach a corresponding target value.

[0079] In detail, the sample No. 9 shown in Table 3 is an example using the steel material I, shown in Table 1, in which neither REM nor Zr was added to the steel. Since the composition of an oxide was not appropriate, the number density of the coarse oxide particles increased, so that the critical CTOD value did not reach the target value.

[0080] The sample No. 10 shown in Table 3 used the steel material J of Table 1 that satisfied the chemical component composition specified by the present invention. However, in this sample, since the cumulative rolling reduction in a temperature range from the Ar_3 temperature to 950°C was low, the average circle equivalent diameter of crystal grains enclosed by the high-angle grain boundaries, in each of which a misorientation between two adjacent crystals was 15° or more, became larger, thereby degrading the toughness of the base metal. Consequently, both the critical CTOD value and 85% SATT of this sample did not reach the respective target values.

[0081] The sample No. 11 shown in Table 3 used the steel material K of Table 1 that satisfied the chemical component composition specified by the present invention. However, in this sample, since the cumulative rolling reduction in a temperature range from the Ar_3 temperature to 950°C was high, the separation index SI was increased. Consequently, the critical CTOD value of this sample did not reach the target value.

[0082] The sample No. 12 shown in Table 3 used the steel material L of Table 1 that satisfied the chemical component composition specified by the present invention. However, in this sample, since the finish cooling temperature (FCT) after the rolling was high, the area ratio of the hard phase in the $t/2$ position became large. Consequently, the 85% SATT of this sample did not reach the target value.

[0083] The sample No. 13 shown in Table 3 used the steel material M of Table 1 that satisfied the chemical component composition specified by the present invention. However, in this sample, since the RH reflux time in a molten-steel process step was short, the number density of coarse oxide particles was increased. Consequently, the critical CTOD value of this sample did not reach the target value.

[0084] The sample No. 14 shown in Table 3 used the steel material N of Table 1 that satisfied the chemical component composition specified by the present invention. However, in this sample, since the order of addition of elements in the molten-steel process step was not appropriate, the number density of coarse oxide particles was increased. Consequently, the critical CTOD value of this sample did not reach the target value.

[0085] The sample No. 15 shown in Table 3 used the steel material O of Table 1 that satisfied the chemical component composition specified by the present invention. However, in this sample, since the time from addition of (REM, Zr) to start of casting in the molten-steel process step was short, the number density of coarse oxide particles was increased. Consequently, the critical CTOD value of this sample did not reach the target value.

Claims

1. A steel sheet for a high strength line pipe, comprising, in percent by mass:

0.02 to 0.2% of C;
0.02 to 0.5% of Si;
0.6 to 2.5% of Mn;
more than 0% and 0.03% or less of P;
more than 0% and 0.01% or less of S;
0.010 to 0.08% of Al;
0.001 to 0.1% of Nb;
0.003 to 0.03% of Ti;
0.0003 to 0.006% of Ca;

0.001 to 0.01% of N;

more than 0% and 0.0045% or less of O;

0.0001 to 0.005% of REM; and

0.0001 to 0.005% of Zr, with the balance being iron and inevitable impurities, wherein

the steel sheet contains oxide particles with a circle equivalent diameter of 2 μm or more at a density of 10 particles/ mm^2 or less in a $t/2$ position where t is a sheet thickness of the steel sheet,

and the steel sheet satisfies that in the $t/2$ position, an average circle equivalent diameter of crystal grains enclosed by high angle grain boundaries in each of which a misorientation between two adjacent crystals is 15° or more is 10 μm or less, and that in the $t/2$ position, a fraction of a hard phase is 5 area% or less,

while a separation index SI measured from a fracture surface of a Charpy impact test specimen of the steel sheet at a specific temperature is 0.15 mm/ mm^2 or less.

2. The steel sheet for a high strength line pipe according to claim 1, further comprising, in percent by mass, at least one element selected from the group consisting of:

more than 0% and 1.5% or less of Cu;

more than 0% and 1.5% or less of Ni;

more than 0% and 1.5% or less of Cr;

more than 0% and 1.0% or less of Mo;

more than 0% and 0.2% or less of V; and

more than 0% and 0.0003% or less of B.

3. A steel pipe for a high strength line pipe with excellent low temperature toughness, manufactured by using the steel sheet for a high strength line pipe according to claim 1 or 2.

Fig. 1

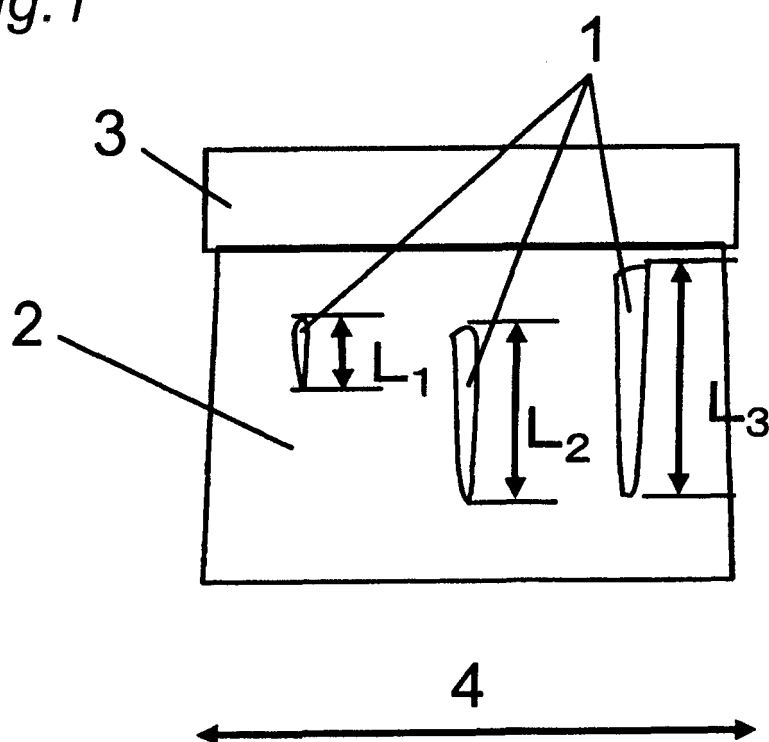


Fig. 2

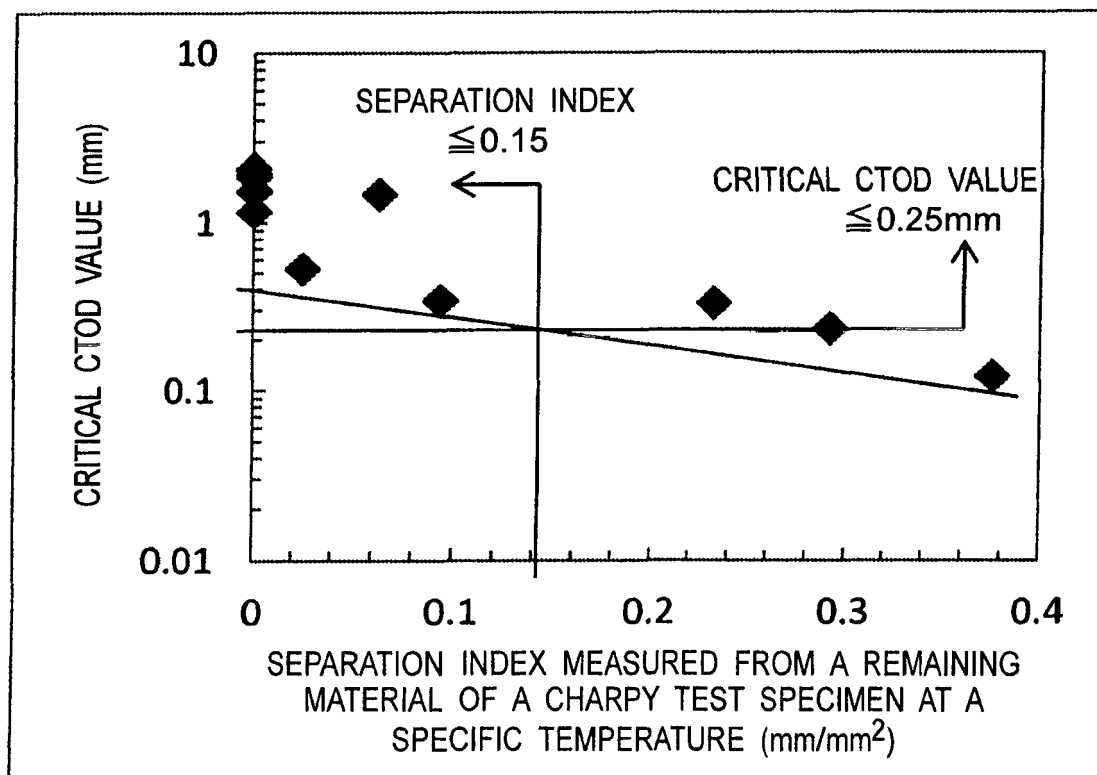
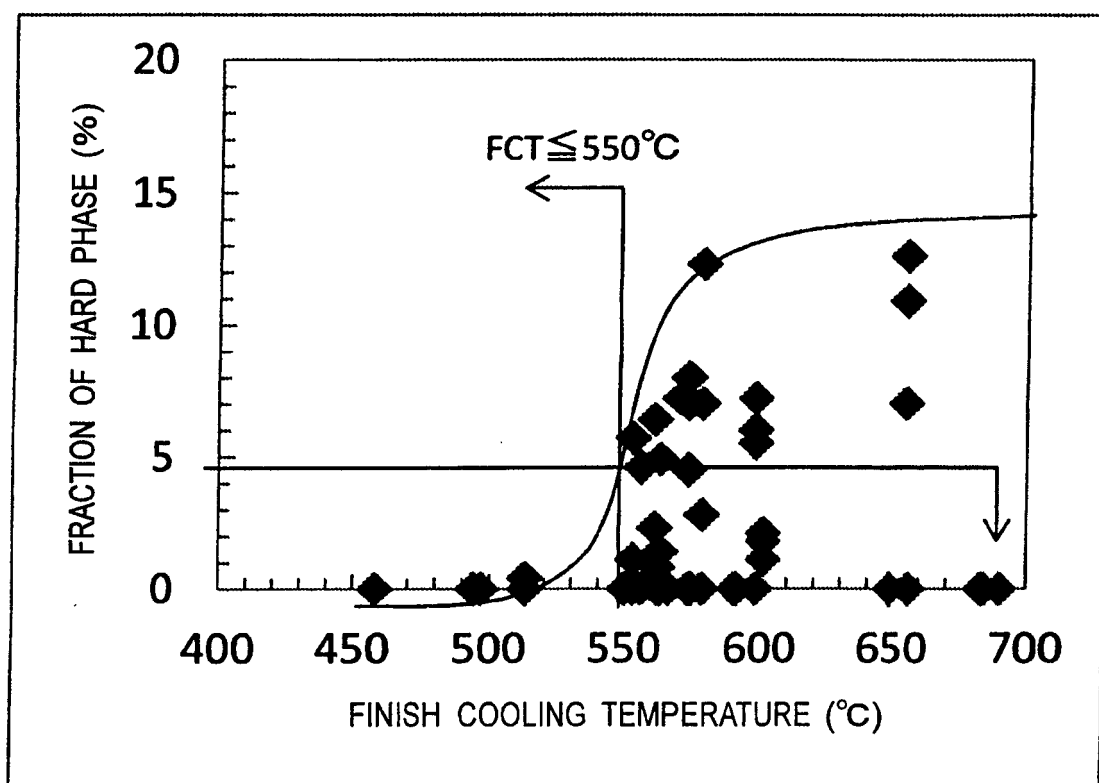


Fig.3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/061381

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C22C38/14(2006.01)i, C22C38/58(2006.01)i, C21C7/04
(2006.01)n, C21D8/02(2006.01)n

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)

C22C38/00-38/60, C21C7/04, C21D8/02

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016
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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/045829 A1 (Kobe Steel, Ltd.), 27 March 2014 (27.03.2014), & JP 2014-58734 A & EP 2899289 A1 & CN 104603314 A	1-3
A	WO 2014/157215 A1 (Kobe Steel, Ltd.), 02 October 2014 (02.10.2014), & JP 2014-208891 A & EP 2980235 A1 & CN 105074036 A & KR 10-2015-0119958 A	1-3
A	WO 2015/022899 A1 (Nippon Steel & Sumitomo Metal Corp.), 19 February 2015 (19.02.2015), & JP 5765497 B1 & CN 105452506 A & KR 10-2015-0140826 A	1-3

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search
04 July 2016 (04.07.16)

Date of mailing of the international search report
12 July 2016 (12.07.16)

Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/061381

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/190975 A1 (Kobe Steel, Ltd.), 27 December 2013 (27.12.2013), & JP 2014-1432 A & EP 2862953 A1 & CN 104411849 A & KR 10-2015-0015506 A	1-3
A	JP 2010-248611 A (Kobe Steel, Ltd.), 04 November 2010 (04.11.2010), & CN 101845590 A & KR 10-2010-0107412 A	1-3
P, A	WO 2015/147055 A1 (Kobe Steel, Ltd.), 01 October 2015 (01.10.2015), & JP 2015-190042 A	1-3

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2013047393 A [0007]
- JP 2015081206 A [0061]