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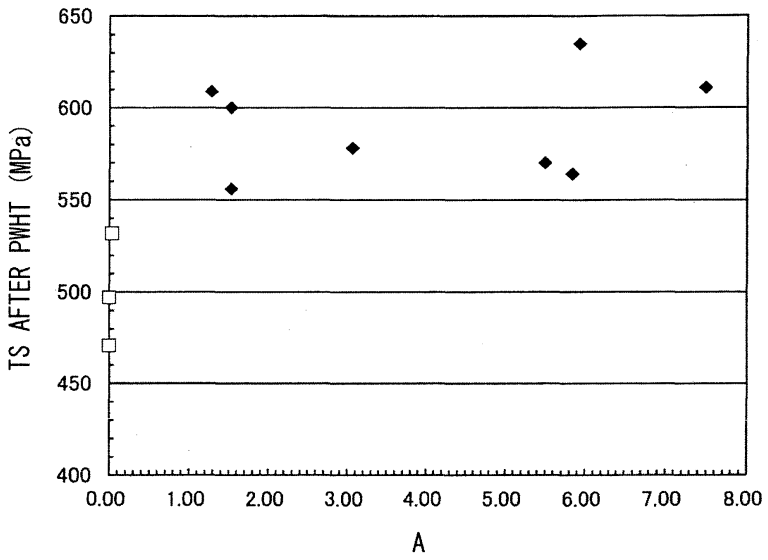
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(54) HIGH STRENGTH STEEL SHEET

(57) Provided is a high strength steel sheet capable of securing high strength before and even after PWHT is performed for a long period, for example, of 15 hours or more. The high strength steel sheet comprises a predetermined component composition, an estimated precipitation amount P_0 is 1.50 or more which is obtained from amounts of Nb, Mo and C, and a metallographic structure satisfies a proportion of ferrite: 60 area% or more; and bainite: 4 area% or more, relative to an entire structure,

Fig. 1



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Description

Technical Field

[0001] The present invention relates to a steel sheet suitably used for the production of a reserve tank, an offshore structure and the like. In detail, the present invention relates to a high strength steel sheet capable of securing a strength of 550 MPa or more before and even after a post welding heat treatment performed to reduce residual stress at a welded part after welding.

Background Art

[0002] When welded structures are produced, such as a reserve tank for crude oil, ethylene, liquefied petroleum gas (LPG) and the like, and an offshore structure, a post weld heat treatment (hereinafter sometimes referred to as PWHT) of holding a welded steel sheet at around 600°C for several hours is sometimes performed to reduce residual stress at a welded part after welding of a steel sheet. In PWHT, an object is held at a high temperature for a long period, so that the metallographic structure of the steel sheet changes to decrease the strength of the steel sheet in some cases.

[0003] Patent Literature 1 discloses a technique for securing the strength after PWHT at high level. The steel sheet disclosed in Patent Literature 1 is characterized in that the amounts of particularly Nb, V, Mo and C in component composition are adjusted to satisfy a predetermined relationship, and the steel sheet has a metallographic structure in which the bainite fraction is 90 area% or more. Further, Patent Literature 1 describes that a carbide of Nb and Mo is formed in the steel sheet before PWHT to suppress a decrease in the strength after PWHT. Further, in order to obtain a bainite structure with an extremely low amount of C, Cr is contained as an essential component in the range of 0.5 to 2.0%. In examples of Patent Literature 1, PWHT of holding the steel sheet at 600°C for a period of sheet thickness (inch) x 1 hour is performed twice, and the holding period is about 8 hours at a maximum.

Prior Art Document

Patent Document

[0004] Patent Literature 1: JP 2007-321228 A

Summary of the Invention

Problems to be Solved by the Invention

[0005] Along with the growth in size of a welded structure, the thickness of a steel sheet used as a material has been increased. An increased thickness of the steel sheet prolongs the period required for a temperature rise to a prescribed temperature according to the position of a welded structure when a heat treatment is performed. Further, when adjustment or the like is necessary after welding, PWHT is required again, further prolonging the heat treatment period. On the other hand, when PWHT is performed at a high temperature or for a long period, the strength of the steel sheet is significantly decreased. Therefore, the steel sheet is required to secure predetermined strength even when PWHT is performed for a long period. Specifically, it is desired to secure high strength even when PWHT is performed for 15 hours or more.

[0006] In the examples of Patent Literature 1, however, only the margin of change in tensile strength between before and after the heat treatment is measured for steel sheets held for about 8 hours at a maximum, and the margin of change in tensile strength is not measured for a steel sheet when PWHT is performed for 15 hours or more as described above. Therefore, it is possible that the steel sheets decrease in the strength not to secure the predetermined strength when prolonged PWHT is performed.

[0007] The present invention has been made with focused attention on the above-described circumstances, and an object of the present invention is to provide a high strength steel sheet capable of securing high strength before and even after PWHT is performed for a long period, for example, of 15 hours or more.

Means for Solving the Problems

[0008] A high strength steel sheet according to the present invention that has been capable of achieving the object contains, as chemical components, by mass: C: 0.02 to 0.07%; Si: 0.1 to 0.4%; Mn: 1.2 to 2%; P: more than 0% and 0.02% or less; S: more than 0% and 0.005% or less; Cu: 0.1 to 0.7%; Al: 0.01 to 0.08%; Ni: 0.45 to 0.85%; Mo: 0.01 to 0.25%; Nb: 0.015 to 0.05%; Ti: 0.005 to 0.025%; Ca: 0.0005 to 0.003%; and N: 0.001 to 0.01%, with the balance being iron and inevitable impurities. Further, in the high strength steel sheet, an estimated precipitation amount Po is 1.50 or

more which is obtained from amounts of Nb, Mo and C and is represented by formula (1) below, and a metallographic structure satisfies a proportion of: ferrite: 60 area% or more and bainite: 4 area% or more, relative to an entire structure.

$$P_0 = 340 \times (0.6 \times [Mo] + 22 \times [Nb]) \times C_1 \ldots (1)$$

[0009] In the formula (1), C_1 is obtained by formulae (2) or (3) below, and [] represents a content of each element by mass% in the formulae (1) to (3),
when $[C] \geq 12/95 \times ([Mo] + [Nb])$

$$C_1 = 12/95 \times ([Mo] + [Nb]) \ldots (2),$$

when $[C] < 12/95 \times ([Mo] + [Nb])$

$$C_1 = [C] \ldots (3).$$

[0010] The high strength steel sheet may further contain, as another element, at least one selected from the group consisting of: Cr: more than 0% and 0.2% or less; V: more than 0% and 0.02% or less; and B: more than 0% and 0.001% or less.

[0011] In the high strength steel sheet, when a precipitation amount P_1 is calculated, by formula (4) below, from an average interval λ (μm) between carbides containing at least one selected from the group consisting of Nb and Mo, a solid solution equivalent A preferably satisfies a value of 0.50 or more, the solid solution equivalent A obtained from the estimated precipitation amount Po and the precipitation amount P_1 and obtained by formula (5) below:

$$P_1 = 0.7/\lambda \ldots (4)$$

$$A = P_0 - P_1 \ldots (5).$$

[0012] The present invention also encompasses a high strength welded structure obtained by subjecting the high strength steel sheet to a heat treatment.

Effects of the Invention

[0013] According to the present invention, there can be provided a high strength steel that has high strength before and after PWHT, because the component composition and metallographic structure of the steel sheet are appropriately controlled, so that the strength of the steel sheet is unlikely to decrease or is rather improved even when PWHT is performed for a long period, for example, of 15 hours or more.

Brief Description of the Drawing

[0014] Fig. 1 is a graph showing the relationship between the solid solution equivalent A and the tensile strength (TS) after PWHT.

Mode for Carrying Out the Invention

[0015] As disclosed in Patent Literature 1, strengthening by transformation with use of a bainite structure is known as means for securing the strength of a steel sheet. Patent Literature 1, however, is a technique of using dislocations introduced during transformation, and therefore, when PWHT is performed for about 15 hours or more, the dislocations may possibly be integrated and annihilated to decrease the strength of the steel sheet.

[0016] Therefore, the present inventor has studied a method for securing the strength of a steel sheet even when PWHT is performed for a long period, for example, of 15 hours or more while setting ferrite as a main structure of the metallographic structure of the steel sheet. A reason for setting ferrite as a main structure is that the ferrite has less dislocations introduced, and therefore, a decrease in the strength is considered to be avoided which is caused by the

integration and annihilation of the dislocations, even when prolonged PWHT is performed.

[0017] Further, the present inventor has focused on carbide dispersion strengthening by Nb and Mo as means for securing the strength after PWHT. As in Patent Literature 1, however, a method of precipitating a carbide of Nb and Mo in the steel sheet before PWHT to improve the strength, the carbide is coarsened and aggregated when PWHT is performed for a long period, so that the carbide does not contribute to the improvement in the strength, anyhow leading to a decrease in the strength.

[0018] As a result of further various studies conducted by the present inventor, the present inventor has found that high strength can be secured before and after PWHT by setting the ferrite as a main structure of the metallographic structure of the steel sheet, and appropriately adjusting the chemical component composition so that a carbide containing at least one selected from the group consisting of Nb and Mo is estimated to be precipitated in a predetermined amount or more through prolonged PWHT while a predetermined amount or more of bainite has been generated. Thus, the present invention has been completed. Particularly, it has been made clear that when Nb and Mo are solid-solved or are dispersed as extremely fine carbide in a step before PWHT, the carbide can be grown into a size for contributing to the carbide dispersion strengthening by performing PWHT for a long period, and high strength can be secured by the carbide dispersion strengthening. In the present specification, performing PWHT for a long period means performing PWHT for, for example, 15 hours or more.

[0019] Hereinafter, a high strength steel sheet according to the present invention will be described in detail.

[0020] The high strength steel sheet according to the present invention contains, as chemical components, by mass: C: 0.02 to 0.07%; Si: 0.1 to 0.4%; Mn: 1.2 to 2%; P: more than 0% and 0.02% or less; S: more than 0% and 0.005% or less; Cu: 0.1 to 0.7%; Al: 0.01 to 0.08%; Ni: 0.45 to 0.85%; Mo: 0.01 to 0.25%; Nb: 0.015 to 0.05%; Ti: 0.005 to 0.025%; Ca: 0.0005 to 0.003%; and N: 0.001 to 0.01%, with the balance being iron and inevitable impurities. Further, an estimated precipitation amount Po is 1.50 or more which is obtained from the amounts of Nb, Mo and C and is represented by the following formula (1), and the metallographic structure satisfies a proportion of: ferrite: 60 area% or more and bainite: 4 area% or more, relative to the entire structure.

$$P_0 = 340 \times (0.6 \times [Mo] + 22 \times [Nb]) \times C_1 \ldots (1)$$

[0021] In the formula (1), C_1 is obtained by the following formulae (2) or (3),

when $[C] \geq 12/95 \times ([Mo] + [Nb])$

$$C_1 = 12/95 \times ([Mo] + [Nb]) \ldots (2),$$

when $[C] < 12/95 \times ([Mo] + [Nb])$

$$C_1 = [C] \ldots (3).$$

[0022] In the formulae (1) to (3), [] represents the content of each element by mass%.

[0023] First, the high strength steel sheet according to the present invention is described in terms of the metallographic structure. In the present specification, the high strength means a tensile strength of 550 MPa or more.

[0024] The metallographic structure of the high strength steel sheet of the present invention has a proportion of ferrite: 60 area% or more and bainite: 4 area% or more, relative to the entire structure.

[Ferrite: 60 area% or more]

[0025] With the ferrite accounting for 60 area% or more of the entire structure, high strength can be secured even when PWHT is performed for a long period. With the amount of the ferrite decreased and the bainite fraction excessively increased in the entire structure, excessive dislocations are integrated and annihilated by performing PWHT for a long period to largely decrease the strength. Therefore, in the present invention, the ferrite is set to 60 area% or more, preferably 65 area% or more, more preferably 70 area% or more, further preferably 75 area% or more. The upper limit of the ferrite fraction is 96 area% or less to secure 4 area% or more of the bainite as described later. The ferrite fraction is preferably 90 area% or less.

[Bainite: 4 area% or more]

[0026] In the metallographic structure of the steel sheet according to the present invention, the ferrite is 60 area% or more as described above; however, an excessively high ferrite fraction greatly decreases the strength of the steel sheet. Therefore, in the present invention, the bainite fraction in the entire structure is set to 4 area% or more, preferably 5 area% or more, more preferably 10 area% or more, to increase the strength of the steel sheet. With the bainite fraction excessively increased, however, 60 area% or more of the ferrite cannot be secured, and the strength after prolonged PWHT is decreased due to the increased bainite. Therefore, in the present invention, the bainite fraction is 40 area% or less, preferably 30 area% or less, more preferably 20 area% or less.

[0027] The metallographic structure of the steel sheet according to the present invention is basically formed of the ferrite and the bainite, while the metallographic structure may also contain, for example, pearlite, island martensite (M-A) and the like as other structure, as long as the effect of the present invention is not inhibited.

[0028] The fraction of the other structure in the entire structure is preferably 10 area% or less, for example.

[0029] The metallographic structure of the steel sheet according to the present invention may be exposed in a cross section at a position of t/4, with the thickness of the steel sheet as t (mm), and subjected to mirror polishing. Then, a test piece may be collected, etched with a nital solution, and then observed with an optical microscope, to measure the ferrite fraction and the bainite fraction by image analysis. With the observation magnification set to 400 times and the number of observation fields set to 5, the average values of the ferrite fractions and the bainite fractions may be obtained which are measured in the fields.

[0030] The ferrite fraction in the metallographic structure may be measured by the image analysis with use of an optical microscope as described above, while a value obtained by deducting the bainite fraction from 100% may be regarded as the ferrite fraction as the ferrite and the bainite are basically generated in the high strength steel sheet of the present invention.

[0031] Next, the estimated precipitation amount Po will be described.

[0032] The estimated precipitation amount Po indicates a maximum amount of precipitate that can be, on the basis of the amounts of Mo, Nb and C included in the steel sheet, estimated to be precipitated as a carbide containing at least one selected from the group consisting of Nb and Mo by, for example, PWHT.

[0033] The estimated precipitation amount Po is a calculated value obtained from the amounts of Nb, Mo and C on the basis of the following formula (1). The estimated precipitation amount Po is to be an index for predicting the strength after PWHT. Such a steel sheet whose value P_0 is appropriately controlled is subjected to prolonged PWHT to precipitate a carbide containing at least one selected from the group consisting of Nb and Mo, so that the strength of the steel sheet can be increased by the carbide dispersion strengthening.

[0034] The carbide containing at least one selected from the group consisting of Nb and Mo is not particularly limited as long as the carbide includes at least Nb or Mo. Examples of the carbide include, in addition to a Nb carbide and a Mo carbide, a composite carbide containing both Nb and Mo. The carbide also includes a carbonitride in which nitrogen is bonded to a carbide, and the composite carbide also includes a composite carbonitride in which nitrogen is bonded to a composite carbide.

$$P_0 = 340 \times (0.6 \times [Mo] + 22 \times [Nb]) \times C_1 \ldots (1)$$

[0035] The details that the estimated precipitation amount Po represented by the formula (1) has been derived are as follows.

[0036] A Mo carbide is represented by MoC and a Nb carbide is represented by NbC, and the precipitation amount of the MoC and the NbC is represented by the following formula (a) on the basis of the mass ratio of each element.

$$X = \alpha \times (\beta \times [Mo] + \gamma \times [Nb]) \times C_1 \ldots (a)$$

[0037] In the formula (a), α,, β and γ represent constant numbers, and [] represents the content of each element (mass%).

[0038] In order to determine the constant numbers, the tensile strength after PWHT has been measured with use of steel sheets obtained by changing only the content of Mo or Nb while the content of the other element is kept the same. The conditions for the measurement of the tensile strength are made the same as in examples described later. A straight line graph has been made with the content of Nb or Mo as a horizontal axis and the tensile strength after PWHT as a vertical axis, α, has been determined as 340, β as 0.6 and γ as 22 from the ratio of the gradient of the straight line to determine a parameter x represented by the following formula (b).

$$x = 340 \times (0.6 \times [Mo] + 22 \times [Nb]) \ldots (b)$$

[0039] Next, in the formula (a), C_1 is a value determined on the basis of the relationship between the amount of C [C] and the total of the amount of Mo [Mo] and the amount of Nb [Nb] included in the steel.

[0040] That is, when $[C] \geq 12/95 \times ([Mo] + [Nb])$, the minimum necessary amount of C for generating the MoC and the NbC is included in the steel, and therefore, C_1 is derived from the following formula (2).

$$C_1 = 12/95 \times ([Mo] + [Nb]) \ldots (2)$$

[0041] On the other hand, when $[C] < 12/95 \times ([Mo] + [Nb])$, the amount of C included in the steel is below the amount of C necessary for generating the MoC and the NbC, and therefore, C_1 is derived from the following formula (3).

$$C_1 = [C] \ldots (3)$$

[0042] Here, 12/95 is a coefficient determined in consideration of the atomic weight of C, Mo and Nb.

[0043] The value P_0 is derived from the formula (1) on the basis of the thus derived parameter x and C_1.

[0044] In the present invention, the value Po is set to 1.50 or more. The threshold 1.50 of the value Po is a value determined on the basis of various experimental results. The value Po is set to preferably 2 or more, more preferably 3 or more. The upper limit of the value Po is 29.75 or less which is determined on the basis of the maximum value of the amount of Mo and the maximum value of the amount of Nb. The value Po is preferably 25 or less, more preferably 20 or less, further preferably 15 or less, particularly preferably 10 or less.

[0045] Further, in the high strength steel sheet according to the present invention, a solid solution equivalent A represented by the following formula (5) preferably satisfies a value of 0.50 or more. Here, when a precipitation amount P_1 is calculated by the following formula (4), from an average interval λ (μm) between carbides containing at least one selected from the group consisting of Nb and Mo, the solid solution equivalent A is obtained from the estimated precipitation amount P_0 and the precipitation amount P_1 by the following formula (5).

$$P_1 = 0.7/\lambda \ldots (4)$$

$$A = P_0 - P_1 \ldots (5)$$

[0046] The solid solution equivalent A indicates the total amount of Mo and Nb solid-solved in the high strength steel sheet, and is an index for predicting the strength of the steel sheet after PWHT. The threshold 0.50 of the solid solution equivalent A is a value determined on the basis of various experimental results. With the solid solution equivalent A set to 0.50 or more, a solid-solved Mo and a solid-solved Nb are precipitated as a carbide when PWHT is performed for a long period, so that the strength of a welded structure can be increased by the carbide dispersion strengthening. On the other hand, with the solid solution equivalent A below 0.50, the amounts of Mo, Nb and C are insufficient or Mo and Nb are already precipitated as a carbide, and therefore, the carbide is coarsened or aggregated when PWHT is performed for a long period, so that the strength of a welded structure is decreased. The solid solution equivalent A is preferably 0.50 or more, more preferably 1 or more, further preferably 2 or more. The upper limit of the solid solution equivalent A is not particularly limited, and is preferably 15 or less, more preferably 10 or less, for example. The solid solution equivalent A also includes a fine Mo carbide and a fine Nb carbide that have a particle diameter of 10 nm or less. The fine carbide having a particle diameter of 10 nm or less exceeds the limits of detection by observation with use of a transmission electron microscope described later, and is considered not to contribute to the carbide dispersion strengthening.

[0047] Here, the details that the solid solution equivalent A represented by the formula (5) has been derived are as follows.

[0048] When the precipitation amount P_1 is calculated, by the formula (4), from an average interval λ (μm) between carbides containing at least one selected from the group consisting of Nb and Mo, the solid solution equivalent A is a value obtained by deducting the precipitation amount P_1 from the estimated precipitation amount Po. The precipitation amount P_1 indicates the amounts of a Nb carbide and a Mo carbide that are actually precipitated in the steel sheet. Therefore, the total of amounts of Nb and Mo solid-solved in the steel sheet can be calculated by deducting the precipitation amount P_1 from the estimated precipitation amount P_0. A solid-solved Nb and a solid-solved Mo are precipitated as a

carbide by performing PWHT for a long period, contributing to the improvement in the strength of a welded structure after PWHT by the carbide dispersion strengthening.

[0049] The precipitation amount P_1 can be calculated by the formula (4).

[0050] In the formula (4), λ can be calculated on the basis of the following formula (c).

$$\lambda = (1.25 \times [(\pi/(6 \times f)]^{1/2} - \pi/4) \times d \ldots (c)$$

[0051] In the formula (c), λ represents an average interval (μm) between carbides containing at least one selected from the group consisting of Nb and Mo, and f represents an average volume fraction (volume%) of the carbide, and d represents an average particle diameter (μm) of the metallographic structure.

[0052] The formula (c) is generally known as formula for calculating the average interval λ between carbides and is described in, for example, Iron and Steel, Vol. 91 (2005) No. 11, pp. 796 to 802.

[0053] In the formula (c), the average volume fraction f of the carbide can be calculated on the basis of the area of the carbide and the number of particles of the carbide measured by observing a cross section at a position of t/4, with the thickness of the steel sheet as t (mm), with use of, for example, a transmission electron microscope. The observation magnification may be, for example, 30000 times, and the number of observation fields may be 10.

[0054] In the formula (c), the average particle diameter d of the metallographic structure means the average value of circle equivalent diameters of the metallographic structure that are identified in an observation field. In the observation field, for example, when a ferrite structure is identified, particle diameters of the ferrite may be measured, and when a bainite structure is identified, particle diameters of the bainite may be measured. Then, the average value of the particle diameters may be calculated. The observation magnification may be, for example, 30000 times, and the number of observation fields may be 10.

[0055] The particle diameter d of the metallographic structure is considered to be substantially constant by conducting controlled rolling described later. Thus, the average interval λ between the carbides can be obtained on the basis of the average volume fraction f of the carbide and the average particle diameter d of the metallographic structure by the formula (c).

[0056] On the other hand, the precipitation amount P_1 of a carbide per unit mass can be represented by the following formula (A) with use of the average volume fraction of the carbide, the average volume fraction of the metallographic structure, and the mass per unit volume.

$$P_1 = f \times n_1/(f \times n_1 + F \times n_2) \ldots (A)$$

[0057] Here, f is the average volume fraction (volume%) of the carbide, F is the average volume fraction (volume%) of the metallographic structure, n_1 is specific gravity (kg/m^3) of the carbide, and n_2 is specific gravity (kg/m^3) of the metallographic structure. For the specific gravity n_1 of the carbide, component analysis may be conducted for carbide particles identified in an observation field, the specific gravity of each of the carbide particles is obtained, and the average value of the specific gravity may be substituted. For the specific gravity n_2 of the metallographic structure, the specific gravity of iron may be substituted.

[0058] The average volume fraction F of the metallographic structure is represented by

$$F = 100 - f,$$

and therefore, the formula (A) can be rewritten as the following formula (B).

$$P_1 = f \times n_1/[f \times n_1 + (100 - f) \times n_2] \ldots (B)$$

[0059] The present inventor has prepared steel sheets obtained by variously changing the amounts of Mo and Nb and measured the precipitation amount of a carbide to learn that the formula (B) can be represented by the following formula (4) with use of the interval λ between carbides.

$$P_1 = 0.7/\lambda \ldots (4)$$

[0060] In the high strength steel sheet according to the present invention, the value Po calculated on the basis of the amounts of Mo, Nb and C included in the steel is 1.50 or more, and it is also necessary to appropriately control the chemical component composition. Hereinafter, the chemical components of the high strength steel sheet will be described.

[C: 0.02 to 0.07%]

[0061] C is an element that is necessary for increasing the strength of the steel sheet. Also, C is an element that is necessary for precipitating a carbide to suppress a decrease in the strength after PWHT. In the present invention, the amount of C is 0.02% or more, preferably 0.025% or more, more preferably 0.030% or more. Excessive addition of C, however, is likely to generate the bainite. Excessive generation of the bainite causes integration and annihilation of dislocations by prolonged PWHT to largely decrease the strength. In the present invention, the amount of C is 0.07% or less, preferably 0.065% or less, more preferably 0.06% or less, particularly preferably 0.055% or less.

[Si: 0.1 to 0.4%]

[0062] Si is an element that acts as a deoxidizing agent during smelting of steel and has an effect of increasing the strength of the steel. For exhibition of such an action, Si is contained in an amount of 0.1% or more, preferably 0.15% or more, more preferably 0.2% or more in the present invention. An excessive amount of Si, however, deteriorates HAZ toughness. Therefore, the amount of Si is 0.4% or less, preferably 0.37% or less, more preferably 0.35% or less in the present invention.

[Mn: 1.2 to 2%]

[0063] Mn is an element that effectively acts for increasing the strength of the steel sheet. In the present invention, the amount of Mn is 1.2% or more, preferably 1.3% or more, more preferably 1.4% or more. An excessive amount of Mn, however, excessively generates the bainite to decrease the strength after PWHT is performed for a long period. In the present invention, the amount of Mn is 2% or less, preferably 1.8% or less, more preferably 1.6% or less.

[P: more than 0% and 0.02% or less]

[0064] P is an inevitable impurity and is an element that is segregated in crystal grains and decreases the ductibility and toughness of the steel sheet. In the present invention, the amount of P is 0.02 or less, preferably 0.015% or less, more preferably 0.01% or less, particularly preferably 0.008% or less. It is preferred that the amount of P is as less as possible; however, it is industrially difficult to realize 0% of the amount of P.

[S: more than 0% and 0.005% or less]

[0065] S is an inevitable impurity and is an element that forms various inclusions by bonding to an alloy element in the steel to decrease the ductibility and toughness of the steel sheet. In the present invention, the amount of S is 0.005% or less, preferably 0.004% or less, more preferably 0.003% or less. It is preferred that the amount of S is as less as possible; however, it is industrially difficult to realize 0% of the amount of S.

[Cu: 0.1 to 0.7%]

[0066] Cu is an element that acts for increasing the strength of the steel sheet. In the present invention, the amount of Cu is 0.1% or more, preferably 0.12% or more, more preferably 0.15% or more. An excessive amount of Cu, however, easily causes generation of a crack during hot working. In the present invention, the amount of Cu is 0.7% or less, preferably 0.65% or less, more preferably 0.5% or less.

[Al: 0.01 to 0.08%]

[0067] Al is an element that acts as a deoxidizing agent during smelting of steel. In the present invention, the amount of Al is 0.01% or more, preferably 0.015% or more, more preferably 0.020% or more. An excessive amount of Al, however, inhibits the cleanliness of the steel sheet to decrease the strength. In the present invention, the amount of Al is 0.08% or less, preferably 0.06% or less, more preferably 0.04% or less.

[Ni: 0.45 to 0.85%]

[0068] Ni is an element that is necessary for lowering a ferrite transformation start temperature, accelerating the generation of the bainite, and increasing the strength of the steel sheet. In the present invention, the amount of Ni is 0.45% or more, preferably 0.5% or more. An excessive amount of Ni, however, excessively generates the bainite to suppress the generation of the ferrite, decreasing the strength of the steel sheet after PWHT is performed for a long period. In the present invention, the amount of Ni is 0.85% or less, preferably 0.75% or less, more preferably 0.65% or less.

[Mo: 0.01 to 0.25%]

[0069] Mo is an element that is necessary for generating the bainite. Also, Mo is an important element that precipitates a carbide after PWHT is performed for a long period to contribute to the improvement in the strength of the steel sheet after PWHT. In the present invention, the amount of Mo is 0.01% or more, preferably 0.1% or more, more preferably 0.15% or more. An excessive amount of Mo, however, excessively generates the bainite to suppress the generation of the ferrite, decreasing the strength of the steel sheet after PWHT is performed for a long period. In the present invention, the amount of Mo is 0.25% or less, preferably 0.23% or less, more preferably 0.20% or less.

[Nb: 0.015 to 0.05%]

[0070] As with Mo, Nb is an important element that precipitates a carbide after PWHT is performed for a long period to contribute to the improvement in the strength of the steel sheet after PWHT. In the present invention, the amount of Nb is 0.015% or more, preferably 0.020% or more. An excessive amount of Nb, however, deteriorates HAZ toughness. In the present invention, the amount of Nb is 0.05% or less, preferably 0.048% or less, more preferably 0.045% or less.

[Ti: 0.005 to 0.025%]

[0071] Ti is an element that is likely to form a nitride and is an element that is necessary to precipitate fine TiN, so that crystal grains are refined to increase the toughness of the steel sheet. In the present invention, the amount of Ti is 0.005% or more, preferably 0.007% or more, more preferably 0.009% or more. An excessive amount of Ti, however, decreases HAZ toughness. In the present invention, the amount of Ti is 0.025% or less, preferably 0.02% or less, more preferably 0.015% or less.

[Ca: 0.0005 to 0.003%]

[0072] Ca is an element that is necessary for controlling the morphology of an inclusion in the steel to improve the toughness of the steel sheet. In the present invention, the amount of Ca is 0.0005% or more, preferably 0.0008% or more, more preferably 0.001% or more. An excessive amount of Ca, however, causes coarsening of the inclusion to decrease HAZ toughness. In the present invention, the amount of Ca is 0.003% or less, preferably 0.0027% or less, more preferably 0.0025% or less.

[N: 0.001 to 0.01%]

[0073] N is an element that is necessary to precipitate fine TiN by bonding to Ti, so that crystal grains are refined to increase the toughness of the steel sheet. In the present invention, the amount of N is 0.001% or more, preferably 0.003% or more, more preferably 0.004% or more. An excessive amount of N, however, causes coarsening of the TiN to deteriorate HAZ toughness. In the present invention, the amount of N is 0.01% or less, preferably 0.008% or less, more preferably 0.007% or less.

[0074] The chemical components in the steel sheet of the present invention are as described above, and the balance is iron and inevitable impurities such as O (oxygen).

[0075] The steel sheet of the present invention may contain, in addition to the chemical components described above, the following elements as necessary.

[At least one selected from the group consisting of Cr: more than 0% and 0.2% or less, V: more than 0% and 0.02% or less, and B: more than 0% and 0.0010% or less]

[0076] All of Cr, V and B are elements that precipitate a carbonitride to contribute to the improvement in the strength of the steel sheet. For effective exhibition of such an action, the amount of Cr is preferably 0.001% or more, more preferably 0.005% or more. The amount of V is preferably 0.0001% or more, more preferably 0.0005% or more. The

amount of B is preferably 0.0001% or more, more preferably 0.0005% or more. Excessive addition of Cr or V, however, decreases HAZ toughness. In the present invention, the amount of Cr is preferably 0.2% or less, more preferably 0.1% or less, further preferably 0.05% or less. The amount of V is preferably 0.02% or less, more preferably 0.01% or less, further preferably 0.005% or less. An excessive amount of B excessively generates the bainite to decrease the strength after PWHT is performed for a long period. In the present invention, the amount of B is preferably 0.001% or less, more preferably 0.0005% or less.

[0077] Next, a method for producing a high strength steel sheet according to the present invention will be described.

[0078] In the steel sheet of the present invention, the component composition is appropriately controlled as described above, and the production conditions are not particularly limited, while it is recommended that steel that satisfies the component composition described above be smelted according to a usual method and a resultant steel ingot be subjected to controlled rolling and controlled cooling so that the solid solution equivalent A satisfies the predetermined range. That is, with the solid solution equivalent A satisfying the predetermined range, the precipitation behavior of Mo and Nb can be controlled to secure the high strength. Therefore, it is desirable to effectively make use of the controlled rolling and the controlled cooling. A production technique that combines the controlled rolling with the controlled cooling is referred to as a thermo-mechanical control process (hereinafter, sometimes referred to as a TMCP), and steel that is produced by this production technique is sometimes referred to as a TMCP steel sheet.

[0079] Specifically, the TMCP steel sheet can be produced by rolling at a cumulative rolling reduction of preferably 5 to 60% in the temperature range at a position of t/4 of 900 to 800°C, with the thickness of the steel ingot as t (mm), followed by cooling from a starting temperature at the position of t/4 of preferably higher than 670°C to room temperature.

[0080] With the cumulative rolling reduction in the temperature range at the position of t/4 of 900 to 800°C set to preferably 5% or more, a deformation band which is to be a transformation core of the ferrite can be introduced in austenite grains, so that the generation of the ferrite can be encouraged. The cumulative rolling reduction is more preferably 10% or more, further preferably 15% or more. A cumulative rolling reduction of more than 60%, however, prolongs the time required for the rolling, leading to a decrease in the productivity. In the present invention, the cumulative rolling reduction is preferably 60% or less, more preferably 50% or less, further preferably 45% or less.

[0081] The resultant rolled steel sheet is cooled from a starting temperature at the position of t/4 of preferably higher than 670°C to room temperature. With the cooling start temperature set to higher than 670°C, the coarsening of the ferrite can be suppressed. The cooling start temperature may be more preferably higher than 700°C. The upper limit of the cooling start temperature is the same as a rolling finish temperature, for example, 850°C.

[0082] The cooling rate from the cooling start temperature to room temperature is not particularly limited, and for example, the steel sheet may be cooled from the cooling start temperature to the temperature range of higher than 300°C to lower than 500°C at an average cooling rate of 5 to 30°C/sec and air-cooled from the temperature at which the cooling has been stopped to room temperature. For example, the steel sheet may be water-cooled from the cooling start temperature to the temperature range of higher than 300°C to lower than 500°C.

[0083] The thickness of the steel sheet of the present invention is not particularly limited, and the thickness may be, for example, 10 mm or more, further 20 mm or more, particularly 30 mm or more. The upper limit of the thickness of the steel sheet is not also particularly limited, and the thickness may be, for example, 150 mm or less, further 120 mm or less, particularly 100 mm or less.

[0084] The steel sheet according to the present invention has a high tensile strength of, for example, 550 MPa or more.

[0085] The present invention also encompasses a welded structure obtained by welding the steel sheet, and then subjecting the steel sheet to a heat treatment. The welded structure of the present invention is characterized in that the high strength of the steel sheet is retained as it is even after a heat treatment. For example, in a case of a steel sheet having a tensile strength of 550 MPa or more, a welded structure thereof can also retain the high tensile strength.

[0086] The present application claims the benefit of the right of priority based on the Japanese Patent Application No. 2014-223751 filed on October 31, 2014. The entire contents of the specification of the Japanese Patent Application No. 2014-223751 are incorporated herein by reference.

Examples

[0087] Hereinafter, the present invention will be described more specifically with reference to examples. The present invention is not limited by the following examples, and can be naturally carried out by adding appropriate modifications thereto within a range that is suitable for the gist described above and below, and any modifications are included in the technical range of the present invention.

[0088] Steel was smelted which contained the chemical components shown in Table 1 below with the balance being iron and inevitable impurities, and steel ingots were produced according to a usual method. Each of the resultant steel ingots was subjected to controlled rolling and controlled cooling to produce a TMCP steel sheet having a thickness of 64 mm. Specifically, the controlled rolling was performed in the temperature range at a position of t/4 of 900 to 800°C, with the thickness of the steel ingot as t (mm), so that the cumulative rolling reduction was as shown in Table 2 below.

The controlled cooling was performed by, after the rolling, starting to cool a resultant steel sheet from the temperature at the position of t/4 shown in Table 2. The steel sheet was water-cooled from the cooling start temperature to the temperature range of 380 to 430°C at an average cooling rate of about 7°C/sec, and air-cooled from a cooling stop temperature in the temperature range of 380 to 430°C to room temperature.

[0089] On the basis of the amounts of Mo and Nb shown in Table 1, a Z value was calculated by the following formula (e), and the result is shown in Table 2.

$$Z = 12/95 \times ([Mo] + [Nb]) \ldots (e)$$

[0090] The Z value was compared with the amount of C [C] shown in Table 1, and the Z value was set for a value C_1 when $[C] \geq Z$, and [C] was set for the value C_1 when $[C] < Z$. The determined value C_1 is shown in Table 2.

[0091] On the basis of the amounts of Mo and Nb shown in Table 1 below and the above value C_1, a value Po was calculated by the following formula (1). The calculation result is shown in Table 2.

$$P_0 = 340 \times (0.6 \times [Mo] + 22 \times [Nb]) \times C_1 \ldots (1)$$

[0092] Next, the cross section at a position corresponding to 1/4 the thickness of the resultant TMCP steel sheet was observed at an observation magnification of 30000 times with use of a transmission electron microscope. A carbide that was observed in an observation field and contained at least one selected from the group consisting of Nb and Mo was measured in terms of the number of the carbide and the area ratio of the carbide to the area of the observation field. The number of observation fields was 10. In the present specification, the area ratio of the carbide was recognized as a volume fraction f (%) of the carbide.

[0093] Next, the resultant TMCP steel sheet was measured in terms of its metallographic structure.

[0094] The steel sheet was exposed in the cross section at the position corresponding to 1/4 the thickness of the steel sheet and was subjected to mirror polishing. Then, a test piece was collected and etched with a nital solution. After the etching, the test piece was observed at an observation magnification of 400 times with use of an optical microscope, and was subjected to image analysis to measure the bainite fraction. With the area of the observation field as 100%, a value obtained by deducting the bainite fraction from 100% was determined as a ferrite fraction. With the number of observation fields set to 5, the average values of the bainite fractions and the ferrite fractions which were measured in the each observation fields were obtained, respectively. The results are shown in Table 2.

[0095] Further, the particle diameter of the ferrite or the bainite that was identified in the observation field was measured and the average value d (μm) of the particle diameters in the 5 fields was obtained.

[0096] On the basis of the volume fraction f (%) of the carbide and the average value d (μm) of the particle diameters, the interval between the carbides was calculated by the following formula (c).

$$\lambda = (1.25 \times [\pi/(6 \times f)]^{1/2} - \pi/4) \times d \ldots (c)$$

[0097] A value P_1 calculated by dividing 0.7 by λ is also shown in Table 2.

[0098] On the basis of the values Po and P_1, a solid solution equivalent A was obtained by the following formula (5). The results are shown in Table 2.

$$A = P_0 - P_1 \ldots (5)$$

[0099] Next, a test piece for a tensile test defined in ASTM A370 was collected from a position corresponding to 1/4 the thickness of the resultant TMCP steel sheet in a direction orthogonal to the rolling direction, and the tensile test was conducted to measure the tensile strength. The measurement result is shown in Table 2 as the tensile strength before PWHT.

[0100] Next, PWHT heat treatment was performed by heating the test piece to a temperature of 595°C and then holding the test piece for 19 hours. The tensile strength of the test piece after the heat treatment was measured in the same procedure as described above. The measurement result is shown in Table 2 as the tensile strength after PWHT.

[0101] In the present invention, a steel sheet having a tensile strength of 550 MPa or more both before and after the heat treatment was determined to be acceptable, and a steel sheet having a tensile strength of less than 550 MPa even either before or after the heat treatment was determined to be unacceptable.

[0102] Fig. 1 shows the relationship between the solid solution equivalent A calculated on the basis of the formula (5) and the tensile strength (TS) after PWHT. In order to show the significance for specifying the solid solution equivalent A, the results of the steel sheets Nos. 1 to 8 shown as invention examples in Table 2 are plotted in Fig. 1, and only the steel sheets Nos. 9 to 11 among the steel sheets Nos. 9 to 15 shown as comparative examples are plotted in Fig.1, whose solid solution equivalent A fell outside the range recommended in the present invention.

[0103] The following conclusion can be derived from the following Table 2 and Fig. 1.

[0104] Nos. 1 to 8 are invention examples that satisfy the requirements of the present invention. That is, the predetermined metallographic structure is obtained and the estimated precipitation amount Po also satisfies the predetermined range to achieve a high tensile strength of 550 MPa or more. Further, the steel sheets can secure a tensile strength of 550 MPa or more even after prolonged PWHT as long as 19 hours.

[0105] In contrast, Nos. 9 to 15 are comparative examples that do not satisfy any of the requirements specified in the present invention.

[0106] Among the comparative examples, No. 9 is an example that did not contain Mo to excessively generate the ferrite, not securing the bainite fraction, so that the tensile strength of the steel sheet could not be secured. In addition, the steel sheet did not contain Mo and Nb, so that the tensile strength after prolonged PWHT was further smaller than before PWHT.

[0107] No. 10 is an example that did not contain Nb and did not satisfy the predetermined range of the estimated precipitation amount Po. As a result, the tensile strength after prolonged PWHT lowered.

[0108] No. 11 is an example that did not contain Mo to excessively generate the ferrite, not securing the bainite fraction, so that the tensile strength of the steel sheet could not be secured. In addition, the steel sheet did not contain Mo and Nb, so that the tensile strength after prolonged PWHT lowered by performing PWHT for a long period.

[0109] No. 12 was small in the amount of Ni to increase the ferrite transformation start temperature, excessively generating the ferrite. Therefore, the bainite fraction was decreased. As a result, the strength before PWHT was near the lower limit of the strength to be aimed at, and the strength was decreased by performing PWHT for a long period.

[0110] No. 13 was small in the amount of Ni to increase the ferrite transformation start temperature, excessively generating the ferrite. Therefore, the bainite fraction was decreased. As a result, the tensile strength before and after PWHT could not be secured.

[0111] No. 14 is an example in which the amounts of Cu, Ni and Nb were below the ranges specified in the present invention and which excessively contained Mo. Therefore, the ferrite was excessively generated and the bainite was not generated. As a result, the tensile strength was low both before and after PWHT.

[0112] No. 15 is an example in which Ni was below the range specified in the present invention and which excessively contained Mo but did not contain Nb. Therefore, the ferrite was excessively generated and the bainite fraction could not be secured. As a result, the tensile strength after PWHT could not be secured.

[0113] In Nos. 9 to 11, the solid solution equivalent A was below the range recommended in the present invention to decrease the tensile strength after PWHT.

[Table 1]

No.	Component composition (mass%)														
	C	Si	Mn	P	S	Cu	Al	Ni	Cr	Mo	V	Nb	Ti	Ca	N
1	0.034	0.29	1.49	0.003	0.002	0.18	0.026	0.54	0.01	0.22	0.001	0.023	0.011	0.0014	0.0055
2	0.034	0.29	1.49	0.003	0.002	0.18	0.026	0.54	0.01	0.22	0.001	0.023	0.011	0.0014	0.0055
3	0.036	0.31	1.57	0.004	0.002	0.30	0.028	0.56	0.01	0.25	0.001	0.025	0.013	0.0014	0.0052
4	0.040	0.30	1.50	0.005	0.001	0.65	0.030	0.55	-	0.01	-	0.045	0.012	0.0015	0.0055
5	0.034	0.29	1.49	0.003	0.002	0.18	0.026	0.54	0.01	0.22	0.001	0.023	0.011	0.0014	0.0055
6	0.040	0.30	1.50	0.005	0.001	0.20	0.030	0.55	-	0.01	-	0.045	0.012	0.0015	0.0055
7	0.040	0.30	1.50	0.005	0.001	0.65	0.030	0.55	-	0.01	-	0.045	0.012	0.0015	0.0055
8	0.041	0.31	1.56	0.004	0.002	0.32	0.023	0.55	0.01	0.13	-	0.023	0.012	0.0012	0.0050
9	0.036	0.31	1.56	0.004	0.002	0.67	0.027	0.54	-	-	-	-	0.013	0.0012	0.0059
10	0.039	0.31	1.55	0.004	0.003	0.64	0.027	0.55	0.01	0.20	0.001	-	0.013	0.0014	0.0059
11	0.039	0.30	1.50	0.005	0.001	0.67	0.032	0.54	-	-	0.051	-	0.013	0.0012	0.0051
12	0.040	0.31	1.54	0.004	0.002	0.32	0.029	0.40	0.01	0.21	0.001	0.026	0.013	0.0016	0.0060
13	0.041	0.31	1.55	0.004	0.002	0.31	0.030	0.20	0.01	0.20	0.001	0.025	0.012	0.0015	0.0052
14	0.040	0.30	1.56	0.004	0.002	0.01	0.026	0.01	0.01	0.40	0.001	0.001	0.012	0.0018	0.0055
15	0.040	0.31	1.57	0.004	0.002	0.24	0.029	0.25	0.01	0.59	0.001	-	0.013	0.0016	0.0061

[Table 2]

No.	12/95 × ([Mo] + [Nb])	C_1	P_0	λ (μm)	P_1	A	Cumulative rolling reduction (%)	Cooling start temperature (°C)	Structure fraction (area%)		TS(MPa)	
									Ferrite	Bainite	Before PWHT	After PWHT
1	0.031	0.031	6.66	0.95	0.74	5.92	33	733	71	29	632	635
2	0.031	0.031	6.66	0.60	1.17	5.49	60	750	96	4	586	570
3	0.035	0.035	8.27	0.90	0.78	7.49	60	739	81	19	594	611
4	0.007	0.007	2.35	0.85	0.82	1.53	60	728	87	13	596	600
5	0.031	0.031	6.66	0.85	0.82	5.83	42	709	94	6	579	564
6	0.007	0.007	2.35	0.85	0.82	1.53	60	730	96	4	569	556
7	0.007	0.007	2.35	0.65	1.08	1.28	60	731	85	15	586	609
8	0.019	0.019	3.84	0.90	0.78	3.06	60	737	82	18	596	578
9	-	-	-	-	-	-	60	701	99	1	500	471
10	0.025	0.025	1.03	0.70	1.00	0.03	60	739	94	6	575	532
11	-	-	-	-	-	-	60	705	99	1	501	497
12	0.030	0.030	7.07	1.00	0.70	6.37	60	741	98	2	563	518
13	0.028	0.028	6.47	1.05	0.67	5.81	60	740	98	2	542	518
14	0.051	0.040	3.56	1.15	0.61	2.95	60	775	100	0	546	473
15	0.075	0.040	4.81	1.20	0.58	4.23	60	781	97	3	574	536

Claims

1. A high strength steel sheet comprising, as chemical components, by mass:

C: 0.02 to 0.07%;
Si: 0.1 to 0.4%;
Mn: 1.2 to 2%;
P: more than 0% and 0.02% or less;
S: more than 0% and 0.005% or less;
Cu: 0.1 to 0.7%;
Al: 0.01 to 0.08%;
Ni: 0.45 to 0.85%;
Mo: 0.01 to 0.25%;
Nb: 0.015 to 0.05%;
Ti: 0.005 to 0.025%;
Ca: 0.0005 to 0.003%; and
N: 0.001 to 0.01%, with the balance being iron and inevitable impurities, wherein,
an estimated precipitation amount Po being 1.50 or more which is obtained from amounts of Nb, Mo and C and is represented by formula (1) below, and
a metallographic structure satisfying a proportion of:

ferrite: 60 area% or more; and
bainite: 4 area% or more, relative to an entire structure,
$Po = 340 \times (0.6 \times [Mo] + 22 \times [Nb]) \times C_1$ ... (1)
in the formula (1), C_1 is obtained by formulae (2) or (3) below, and [] represents a content of each element by mass% in the formulae (1) to (3),
when $[C] \geq 12/95 \times ([Mo] + [Nb])$

$$C_1 = 12/95 \times ([Mo] + [Nb]) \ldots (2),$$

when $[C] < 12/95 \times ([Mo] + [Nb])$

$$C_1 = [C] \ldots (3).$$

2. The high strength steel sheet according to claim 1, further comprising, as another element, at least one selected from the group consisting of:

Cr: more than 0% and 0.2% or less;
V: more than 0% and 0.02% or less; and
B: more than 0% and 0.001% or less.

3. The high strength steel sheet according to claim 1 or 2, wherein
when a precipitation amount P_1 is calculated, by formula (4) below, from an average interval λ (μm) between carbides containing at least one selected from the group consisting of Nb and Mo,
a solid solution equivalent A satisfies a value of 0.50 or more, the solid solution equivalent A obtained from the estimated precipitation amount P_0 and the precipitation amount P_1 and represented by formula (5) below:

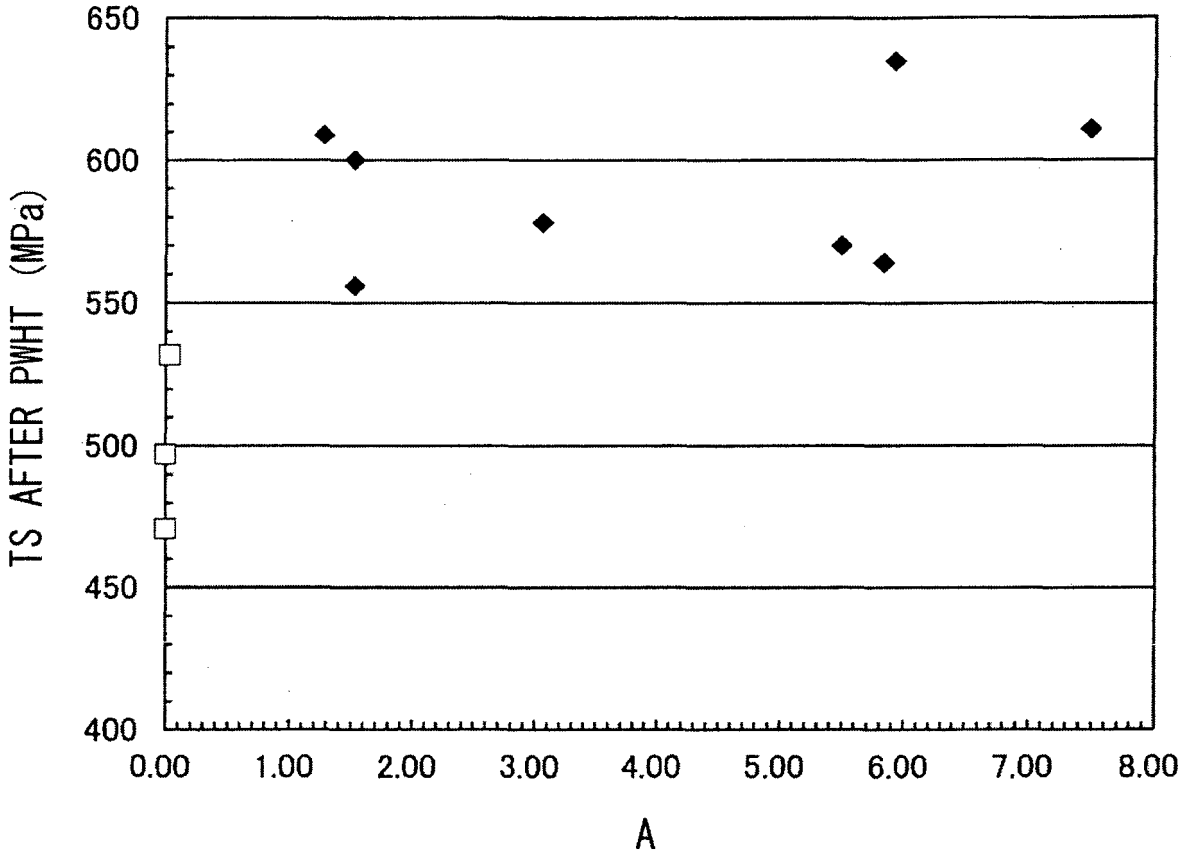
$$P_1 = 0.7/\lambda \ldots (4)$$

$$A = P_0 - P_1 \ldots (5).$$

4. A high strength welded structure obtained by subjecting the high strength steel sheet according to claim 1 or 2 to a heat treatment.

5. A high strength welded structure obtained by subjecting the high strength steel sheet according to claim 3 to a heat treatment.

Fig. 1


650
600
550
500
450
400
TS AFTER PWHT (MPa)
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
A

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/079874

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/16*(2006.01)i, *C22C38/58*(2006.01)i, *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, C21D8/00-8/10

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
Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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	CN 102691007 A (BAOSHAN IRON & STEEL CO., LTD.), 26 September 2012 (26.09.2012), claims (Family: none)	1-5
A	JP 9-256038 A (Nippon Steel Corp.), 30 September 1997 (30.09.1997), claims (Family: none)	1-5

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 January 2016 (08.01.16)	19 January 2016 (19.01.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/079874

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-355038 A (Sumitomo Metal Industries, Ltd.), 25 December 2001 (25.12.2001), claims & US 2002/0026970 A1 & EP 1164204 A1 claims & KR 10-0422408 B1	1-5

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2007321228 A **[0004]**
- JP 2014223751 A **[0086]**