(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 633 060 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
08.04.2020 Bulletin 2020/15

(21) Application number: **18922100.5**

(22) Date of filing: **20.08.2018**

(51) Int Cl.:
C22C 38/00 $^{(2006.01)}$ ***C21D 8/02*** $^{(2006.01)}$
C22C 38/54 $^{(2006.01)}$

(86) International application number:
PCT/JP2018/030676

(87) International publication number:
WO 2020/039485 (27.02.2020 Gazette 2020/09)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(71) Applicant: **NIPPON STEEL CORPORATION**
Tokyo 100-8071 (JP)

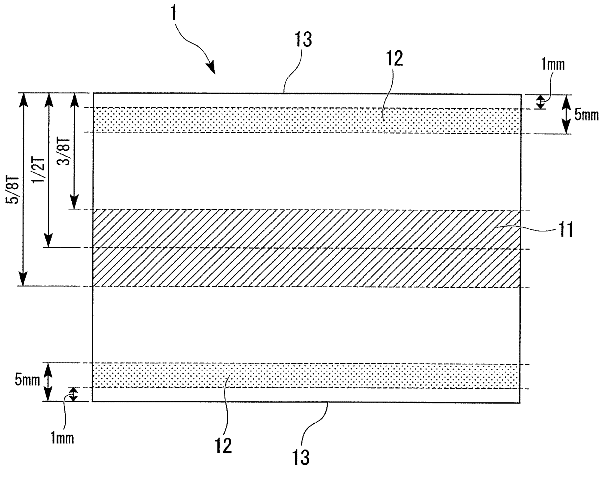
(72) Inventors:
- **TAKAMINE, Fumitoshi**
  Tokyo 100-8071 (JP)
- **FURUYA, Hitoshi**
  Tokyo 100-8071 (JP)
- **KAWABATA, Norimasa**
  Tokyo 100-8071 (JP)
- **MIYAKE, Takumi**
  Tokyo 100-8071 (JP)

(74) Representative: **Vossius & Partner**
Patentanwälte Rechtsanwälte mbB
Siebertstrasse 3
81675 München (DE)

(54) STEEL SHEET AND PRODUCTION METHOD THEREFOR

(57) A steel plate according to an aspect of the present invention has a chemical composition within a predetermined range, in which a total area ratio of martensite and bainite in a thickness middle portion is 99% or more, an average value of a prior austenite grain size in the thickness middle portion is less than 80 μm, Ceq is 0.750% to 0.800%, Al × N is 2.0×10^{-4} or more, Ti/N is 3.4 or less, $4 \times f/g \geq 9.00$ is satisfied, a three-point average of C-direction Charpy at -20°C in the thickness middle portion is 47 J or more, hardnesses of a surface layer and the thickness middle portion are 350 or more by HB, and a plate thickness is more than 200 mm.

FIG. 1



Printed by Jouve, 75001 PARIS (FR)

Description

[Technical Field of the Invention]

[0001] The present invention relates to a steel plate and a method of manufacturing the same.

[Related Art]

[0002] A huge gear (gear) is used in a rotating mechanism of a large industrial machine represented by a rotary kiln. From the viewpoint of the fatigue resistance and durability of the gear, the steel plate, which is to become a material, is required to have hardness and toughness. In recent years, the steel plate which is to become the material is required to have HB 350 or more in the surface layer and in the thickness middle portion and satisfy $vE_{-20^\circ C} \geq 47$ J in the thickness middle portion. This is because the properties of the thickness middle portion are important in order to manufacture a gear by machining the steel to the thickness middle portion.

[0003] Furthermore, in recent years, with the aim of increasing the size of gears, there has been a demand for a steel plate with a plate thickness of more than 200 mm, which has not been achieved in the related art. As the plate thickness is increased, the cooling rate of the thickness middle portion at the time of quenching is decreased. Therefore, with a steel plate having a plate thickness of more than 200 mm, it is difficult to obtain the hardness of the middle portion even after tempering. On the other hand, composition design for the purpose of merely increasing the hardness causes a decrease in toughness. Usually, hardness and toughness are in inverse proportion to each other. Therefore, with an ultra thick material having a plate thickness of more than 200 mm, it is extremely difficult to adjust the composition balance for securing the surface layer hardness and the middle portion hardness and also securing the toughness.

[0004] Furthermore, for the purpose of improving weldability, a demand has arisen to cause a carbon equivalent Ceq to be 0.800% or less by the elements primarily contained. In a case where Ceq exceeds 0.800%, an increase in load on a customer, such as increasing the preheating temperature at the time of welding, is incurred. Since the number of welding passes is very large in a welding operation of the ultra thick material such as the present steel, the increase in welding load is also large. Ceq is represented, for example, by Formula (1). The element symbol included in Formula (1) shows the amount (mass%) of the corresponding element in the chemical composition of the steel.

$$\mathrm{Ceq} = \mathrm{C} + \mathrm{Mn}/6 + (\mathrm{Cu} + \mathrm{Ni})/15 + (\mathrm{Cr} + \mathrm{Mo} + \mathrm{V})/5\text{: Formula (1)}$$

[0005] In the related art, there has been no steel having a plate thickness of more than 200 mm, which secures Ceq ≤ 0.800% and middle portion hardness ≥ HB 350 and guarantees the above-mentioned low temperature toughness at -20°C. Moreover, a steel plate, which is to become a material, has to be tempered at 500°C or more so that the material does not change by stress relief annealing after gear processing. The need for tempering was also a disadvantage for achieving the target hardness of the steel.

[0006] Patent Document 1 aims to provide a thick steel plate having a plate thickness of more than 200 mm and a small hardness difference between the surface layer and the center, as a huge gear material used in a rotating mechanism of a large industrial machine, and a method of manufacturing the same, and provides a thick steel plate in which a three-point average of C-direction Charpy at -20°C is 20 J or more in the thickness middle portion, the hardness of the surface layer is 330 or more by HB, the hardness of the thickness middle portion is 300 or more by HB, and the hardness difference ΔHB between the surface layer and the thickness middle portion is 30 or less. However, Patent Document 1 does not aim to stably cause the hardness of the thickness middle portion to be HB 350 or more.

[Prior Art Document]

[Patent Document]

[0007] [Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2017-186592

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0008] Under such circumstances, the present invention provides a steel plate in which the plate thickness exceeds 200 mm, Ceq shown by the following Formula is 0.800% or less, and Ceq is 0.750% or more for the purpose of securing the hardness of the thickness middle portion, the hardness of the surface layer and the thickness middle portion is HB

350 or more, the absorbed energy of the thickness middle portion at -20°C is 47 J or more, and a method of manufacturing the same.

[Means for Solving the Problem]

[0009] The gist of the present invention is as follows.

(I) According to an aspect of the present invention, a steel plate includes, as a chemical composition, by mass%: C: 0.16% to 0.20%; Si: 0.50% to 1.00%; Mn: 0.90% to 1.50%; P: 0.010% or less; S: 0.0020% or less; Cu: 0% to 0.40%; Ni: 0.20% to 1.00%; Cr: 0.60% to 0.99%; Mo: 0.60% to 1.00%; V: 0% to 0.050%; Al: 0.050% to 0.085%; N: 0.0020% to 0.0070%; B: 0.0005% to 0.0020%; Nb: 0% to 0.050%; Ti: 0% to 0.020%; Ca: 0% to 0.0030%; Mg: 0% to 0.0030%; REM: 0% to 0.0030%; and a remainder including Fe and impurities, in which a total area ratio of martensite and bainite in a thickness middle portion is 99% or more, an average value of a prior austenite grain size in the thickness middle portion is less than 80 μm, Ceq represented by Formula (1) is 0.750% to 0.800%, Al × N is 2.0×10^{-4} or more, Ti/N is 3.4 or less, a value f represented by Formula (2) and a value g represented by Formula (3) satisfy $4 \times f/g \geq 9.00$, a -20°C Charpy absorbed energy measured in a C direction in the thickness middle portion is 47 J or more, hardnesses of a surface layer and the thickness middle portion are HB 350 or more, and a plate thickness of the steel plate is more than 200 mm,

$$\mathrm{Ceq} = \mathrm{C} + \mathrm{Mn}/6 + (\mathrm{Cu} + \mathrm{Ni})/15 + (\mathrm{Cr} + \mathrm{Mo} + \mathrm{V})/5\text{: Formula (1)}$$

$$f = 4 \times \mathrm{C} + \mathrm{Si} + 2 \times \mathrm{Mn} + \mathrm{Ni} + 2 \times \mathrm{Cr} + 5 \times \mathrm{Mo}\text{: Formula (2)}$$

$$g = 2 \times \mathrm{Cr} + 3 \times \mathrm{Mo} + 5 \times \mathrm{V}\text{: Formula (3)}$$

where each element symbol described in each of the Formulas means an amount of an element corresponding to the element symbol in unit mass%.

(II) According to another aspect of the present invention, a method of manufacturing the steel plate according to (I), includes: heating a slab; hot rolling the slab to obtain a steel plate having a plate thickness of more than 200 mm; cooling the steel plate; performing a precipitation treatment on the steel plate; quenching the steel plate; and tempering the steel plate, in which the slab includes, as a chemical composition, by unit mass%, C: 0.16% to 0.20%, Si: 0.50% to 1.00%, Mn: 0.90% to 1.50%, P: 0.010 % or less, S: 0.0020% or less, Cu: 0% to 0.40%, Ni: 0.20% to 1.00%, Cr: 0.60% to 0.99%, Mo: 0.60% to 1. 00%, V: 0% to 0.050%, Al: 0.050% to 0.085%, N: 0.0020% to 0.0070%, B: 0.0005% to 0.0020%, Nb: 0% to 0.050%, Ti: 0% to 0.020%, Ca: 0% to 0.0030%, Mg: 0% to 0.0030%, REM: 0% to 0.0030%, and a remainder including Fe and impurities, Ceq represented by Formula (1) of the slab is 0.750% to 0.800%, Al × N of the slab is 2.0×10^{-4} or more, Ti/N of the slab is 3.4 or less, and a value f of the slab represented by Formula (2) and a value g of the slab represented by Formula (3) satisfy $4 \times f/g \geq 9.00$, a slab heating temperature in the heating the slab is equal to or more than an AlN solid solution temperature Ts (°C) calculated by Formula (4), the precipitation treatment is performed on the steel plate by heating the steel plate to a precipitation treatment temperature Tp (°C) of more than 550°C and less than Ac1 and retaining the steel plate at this temperature for a precipitation treatment time tp (hour), the precipitation treatment temperature Tp (°C) and the precipitation treatment time tp (hour) satisfy Formula (5), the Ac1 is represented by Formula (7), the quenching is performed on the steel plate by heating the steel plate to a quenching retention temperature Tq (°C) of 900°C to 950°C, retaining the steel plate at this temperature for a quenching retention time tq (minute) or more represented by Formula (6), and water cooling the steel plate, and the tempering is performed on the steel plate by heating the steel plate to a tempering temperature of 500°C to 550°C and cooling the steel plate to 150°C or less,

$$\mathrm{Ceq} = \mathrm{C} + \mathrm{Mn}/6 + (\mathrm{Cu} + \mathrm{Ni})/15 + (\mathrm{Cr} + \mathrm{Mo} + \mathrm{V})/5\text{: Formula (1)}$$

$$f = 4 \times \mathrm{C} + \mathrm{Si} + 2 \times \mathrm{Mn} + \mathrm{Ni} + 2 \times \mathrm{Cr} + 5 \times \mathrm{Mo}\text{: Formula (2)}$$

$$g = 2 \times \mathrm{Cr} + 3 \times \mathrm{Mo} + 5 \times \mathrm{V}\text{: Formula (3)}$$

$$Ts = 7400 / (1.95 - \log_{10}(Al \times N)) - 273\text{: Formula (4)}$$

$$\mathrm{Log}_{10}(tp) + 0.012 \times Tp \geq 8.7\text{: Formula (5)}$$

$$tq = 0.033 \times (950 - Tq)^2 + (1.5 \times f)^2/10\text{: Formula (6)}$$

$$Ac1 = 750 - 25 \times C + 22 \times Si - 40 \times Mn - 30 \times Ni + 20 \times Cr + 25 \times Mo\text{: Formula (7)}$$

where each element symbol described in each of the Formulas means an amount of an element corresponding to the element symbol in unit mass%.

(III) In the method of manufacturing the steel plate according to (II), a cooling finishing temperature in the cooling the steel plate may be 150°C or less.

[Effects of the Invention]

[0010] According to the present invention, it is possible to provide a steel plate which is excellent in hardness of a surface layer and a thickness middle portion and impact absorbed energy performance of the thickness middle portion and suppresses Ceq to 0.800% or less even in a steel plate having a plate thickness of more than 200 mm, and the steel plate is applicable to a rotating mechanism of a large industrial machine represented by a rotary kiln.

[Brief Description of the Drawings]

[0011]

FIG. 1 is a schematic view of a cross section of a steel plate according to an embodiment, perpendicular to a rolling direction.

FIG. 2 is a diagram showing the relationship between the amount of C and a thickness middle portion hardness, and the relationship between the amount of C and thickness middle portion toughness ($vE_{-20°C}$).

FIG. 3 is a diagram showing the relationship between Ceq and the middle portion hardness.

FIG. 4 is a diagram showing the relationship between 4 × f/g and the thickness middle portion toughness.

FIG. 5 is a graph showing the relationship between a precipitation treatment temperature Tp and a precipitation treatment time Log_{10} (tp) tested by using composition A4 of Examples.

FIG. 6A is a graph showing the relationship between a quenching retention temperature Tq, a quenching retention time tq, and the middle portion hardness obtained by conducting experiments using composition A6 of the Examples.

FIG. 6B is a view showing the relationship between the quenching retention temperature Tq, the quenching retention time tq, and the middle portion hardness obtained by conducting experiments using composition A2 of the Examples.

FIG. 7 is a flowchart showing a method of manufacturing the steel plate according to the embodiment.

[Embodiments of the Invention]

[0012] In a steel plate according to the present embodiment, the mechanical properties of both the thickness middle portion of the steel plate (sometimes simply referred to as "middle portion") and the surface layer of the steel plate (sometimes simply referred to as "surface layer") are controlled. As shown in FIG. 1, a thickness middle portion 11 of a steel plate 1 is a region between a plane at a depth of 3/8 of a plate thickness T of the steel plate 1 from a rolled surface 13, which is the outermost surface of the steel plate 1, and a plane at a depth of 5/8 of the plate thickness T of the steel plate 1 from the rolled surface 13. The center surface of the thickness middle portion 11 of the steel plate 1 and the center surface of the steel plate 1 are coincident with each other. The surface layer 12 of the steel plate 1 is a region between a plane at a depth of 1 mm and a plane at a depth of 5 mm from the rolled surface 13 of the steel plate 1. The region from the outermost surface of the steel plate 1 to the depth of 1 mm is excluded from the surface layer 12 of the steel plate 1 in the present embodiment. This is because the area corresponds to a decarburized layer and a portion to be removed during processing. In addition, in principle, test pieces for a mechanical test, microstructure observation, and the like are to be collected from portions separated from the end portions of the steel plate in the length direction and the width direction by the plate thickness or more.

[0013] In the steel plate according to the present embodiment, the following (1) to (7) have important meanings. As a requirement for achieving both the hardness of HB 350 grade and $vE_{-20°C} \geq 47$ J in the thickness middle portion of a steel plate having a chemical composition satisfying $Ceq \leq 0.800\%$, Composition Parameter Formula (3) and a precipitation treatment (5) are particularly important.

(1) Restriction of Upper and Lower Limits of Amount of C for Achieving Both Middle Portion Hardness and Middle Portion Toughness (under Conditions Described Later)
In general, in a case where the middle portion hardness is HB 350 or more, and it can be secured HB 350 or more in the surface layer.
(2) Ceq Lower Limit for Securing Middle Portion Hardness
(3) Lower Limit of Parameter Formula 4 × f/g for Securing Middle Portion Toughness
(4) Lower limit of Parameter Formula Al × N for Securing Middle Portion Toughness
(5) Solutionizing Treatment and Precipitation Treatment (Temperature and Time) before Quenching for Securing Middle Portion Hardness and Toughness
(6) Quenching Conditions (Temperature and Time) for Securing Middle Portion Hardness
(7) Restriction of Upper and Lower Limits of Tempering Temperature for Securing Hardness and Toughness of Middle Portion

[0014] The details will be described below.

(1) Restriction of Upper and Lower Limits of Amount Of C for Achieving Both Middle Portion Hardness and Middle Portion Toughness (under Conditions Described Later)

[0015] As a first item, in order to increase both the hardness and toughness of the thickness middle portion under the conditions described later, the amount of C needs to satisfy 0.16% to 0.20% as a composition (mass%) of the steel. In order to secure both the toughness and the hardness at the thickness middle portion of the steel plate having a plate thickness of more than 200 mm, it is necessary to suppress the formation of carbides, which become the brittle fracture origin. In order to suppress the formation of carbides and to achieve $vE_{-20°C}$ (ave.) ≥ 47 J at the thickness middle portion, as shown in FIG. 2, the amount of C has to be 0.20% or less. On the other hand, a decrease in the amount of C greatly reduces the hardness of the steel. Therefore, in order to cause the hardness of the middle portion to be HB 350 or more after tempering at 500°C or more, the amount of C needs to be 0.16% or more as shown in FIG. 2.

(2) Defining of Ceq Lower Limit for Securing Middle Portion Hardness

[0016] As a second item, in order to secure the hardness of the middle portion in the steel plate having a plate thickness of 200 mm or more, sufficient hardenability is required. Therefore, Ceq calculated by Formula (1) needs to satisfy 0.750% or more after a precipitation treatment, which will be described later, is performed. This is to avoid the formation of ferrite, which is a soft structure, during quenching and to form a structure primarily containing bainite and martensite. From the viewpoint of achieving both the hardness and toughness of the middle portion, it is not necessary to determine the upper limit of Ceq. However, an increase in Ceq tends to cause weld cracking. In a case where the Ceq exceeds 0.800%, the welding operation efficiency is significantly deteriorated because it becomes necessary to raise the preheating temperature before welding in order to avoid weld cracking. Therefore, Ceq in the steel plate according to the present embodiment is 0.800% or less. Ceq may be 0.790% or less, 0.785% or less, or 0.780% or less.

$$Ceq = C + Mn/6 + (Cu + Ni)/15 + (Cr + Mo + V)/5\text{: Formula (1)}$$

[0017] The element symbol included in Formula (1) shows the amount (mass%) of the corresponding element in the chemical composition of the steel plate.

[0018] As shown in FIG. 3, the present inventors found that in the steel plate having a plate thickness of more than 200 mm, in a case where Ceq is less than 0.750%, the hardness of the thickness middle portion becomes less than HB 350 even if the precipitation treatment is performed. It is considered that the reason way the hardness of the thickness middle portion is insufficient in the case where Ceq is less than 0.750% that ferrite which is a soft structure is formed. Ceq may be 0.755% or more, 0.760% or more, or 0.770% or more. In addition, the steel in which the hardness of the thickness middle portion is insufficient even if Ceq is 0.750% or more is plotted in FIG. 3. The reason why the hardness of the thickness middle portion in this steel is insufficient is that the precipitation treatment is not performed.

(3) Lower Limit of Parameter Formula "4 × f/g" for Securing Middle Portion Toughness

[0019] As a third item, in the steel plate having a plate thickness of more than 200 mm, in order to secure the hardness of the middle portion ≥ HB 350 while achieving Ceq ≤ 0.800%, and to achieve a toughness of $vE_{-20°C} \geq 47J$ at the thickness middle portion, the parameter f defined by Formula (2) and the parameter g defined by Formula (3) need to satisfy a relationship in which 4 × f/g is 9.00 or more.

$$f = 4 \times C + Si + 2 \times Mn + Ni + 2 \times Cr + 5 \times Mo\text{: Formula (2)}$$

$$g = 2 \times Cr + 3 \times Mo + 5 \times V\text{: Formula (3)}$$

[0020] The element symbol included in Formula (2) and Formula (3) shows the amount (mass%) of the corresponding element in the chemical composition of the steel plate.

[0021] As shown in FIG. 4, the present inventors found that in the steel plate in which the plate thickness is more than 200 mm, Ceq ≤ 0.800% is satisfied, and the hardness of the thickness middle portion is HB 350 or more, the toughness of the thickness middle portion cannot be secured in a case where 4 × f/g is less than 9.00. The element related to the parameter f is an element that improves the hardenability of the steel plate by being solutionized in the matrix during quenching. On the other hand, the element related to the parameter g is an element that reduces the toughness of the steel plate by forming precipitates during tempering. That is, while these elements improve the hardenability, they reduce the toughness by the formation of precipitates during tempering. A large 4 × f/g indicates that the hardenability is increased while reducing the elements precipitated during tempering.

[0022] In the steel plate according to the present embodiment, Cr precipitates, Mo precipitates, and V precipitates at the time of tempering are fine to such an extent that the precipitates cannot be observed without a transmission electron microscope. Therefore, it is industrially unpractical to define the distribution state of the above-mentioned precipitates themselves. From this, it is possible to understand the usefulness of controlling the precipitates by the parameter Formula 4 × f/g.

[0023] 4 × f/g may be 9.20 or more, 9.50 or more, or 9.80 or more. The upper limit of 4 × f/g need not be particularly defined, but may be, for example, 11.00, 10.70, 10.50, 10.00, or 9.90.

(4) Lower limit of Parameter Formula Al × N for Securing Middle Portion Toughness

[0024] In order to secure both the hardness and low temperature toughness in the middle portion of the steel plate having a plate thickness of more than 200 mm, the Al content needs to be 0.050% or more, and Al × N (the product of the Al content (mass%) and the N content (mass%) of the steel plate) needs to be 2.0×10^{-4} or more. This is a requirement for utilizing the austenite pinning effect of AlN, which contributes to the refinement of the structure of the steel plate. In a case where the amount of Al is less than 0.050% or Al × N is less than 2.0×10^{-4}, the prior austenite grain size is coarsened, and the low temperature toughness of the middle portion of the steel plate is deteriorated. It is considered that this is because the total amount of AlN is insufficient.

[0025] In addition, AlN which acts as austenite pinning particles in the steel plate according to the present is too fine to be observed. Therefore, it is industrially unpractical to define the distribution state of AlN itself acting as the austenite pinning particles. From this, it is possible to understand the usefulness of controlling AlN acting as the austenite pinning particles by the parameter Al × N.

[0026] Al × N may be 2.2×10^{-4} or more, 2.5×10^{-4} or more, or 3.0×10^{-4} or more. The upper limit of Al × N need not be particularly defined, but 5.95×10^{-4} which is the product of the upper limits of the Al content and the N content, which will be described later, may be used as the upper limit of Al × N. Al × N may be 5.7×10^{-4} or less, 5.5×10^{-4} or less, 5.2×10^{-4} or less, or 4.8×10^{-4} or less.

(5) Solutionizing Treatment and Precipitation Treatment (Temperature and Time) before Quenching for Securing Middle Portion Hardness and Toughness

[0027] As process requirements for obtaining the austenite pinning effect of AlN, there are solutionizing and precipitation treatments. In the solutionizing treatment, a slab is heated to the AlN solid solution temperature Ts or more calculated by Formula (4). Hot rolling is performed after the solutionizing treatment. In the precipitation treatment, in order to cause Al and N solutionized in the matrix by the solutionizing to finely precipitate as AlN, after hot rolling or before quenching, a hot rolled steel plate is heated to a precipitation treatment temperature Tp, which is a temperature of more than 550°C and less than Ac1, and is retained at the precipitation treatment temperature Tp for a precipitation treatment time tp.

Here, it is necessary to perform the precipitation treatment such that the precipitation treatment temperature Tp and the precipitation treatment time tp satisfy Formula (5).

$$Ts = 7400 / (1.95 - \log_{10}(Al \times N)) - 273\text{: Formula (4)}$$

$$\text{Log}_{10}(tp) + 0.012 \times Tp \geq 8.7\text{: Formula (5)}$$

[0028] Here, Ts in Formula (4) is the solid solution temperature (°C) of AlN, and "Al" and "N" are the Al content and the N content, respectively. "Tp" in the Formula (5) is the precipitation treatment temperature (°C), and "tp" is the precipitation treatment time (hour).

[0029] In addition, slight temperature fluctuations are allowed during the temperature retention of the precipitation treatment. In addition, there are cases where temperature fluctuations occur in actual operation. Therefore, the precipitation treatment temperature Tp is defined as the average temperature of the steel plate of the thickness middle portion after the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the precipitation treatment - 40°C" until the steel plate is extracted from a heat treatment furnace. Specifically, the precipitation treatment temperature Tp is a value calculated by Formula (8).

$$Tp = \{\int[t_A \rightarrow t_B]T(t)dt\} / (t_B - t_A)\text{: Formula (8)}$$

tA: Time at which the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the precipitation treatment - 40°C"
t_B: Time at which the steel plate is extracted from the heat treatment furnace
T(t): Change in the temperature of the thickness middle portion of the steel plate with respect to time (time history of temperature)
$\int[t_A \rightarrow t_B]T(t)dt$: Integral value from t_A to t_B of the change in the thickness middle portion of the steel plate with respect to time

[0030] In addition, the precipitation treatment time tp is defined as the time (that is, "t_B-t_A") after the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the precipitation treatment - 40°C" until the steel plate is extracted from the heat treatment furnace. If the precipitation treatment temperature Tp obtained by applying the time history of the temperature during the precipitation treatment of the thickness middle portion of the steel plate to Formula (8) described above is more than 550°C and less than Ac1, and the precipitation treatment temperature Tp and the precipitation treatment time tp satisfy Formula (5), it is determined that a suitable precipitation treatment has been performed.

[0031] In a case where the solutionizing treatment is not performed before hot rolling, coarse AlN formed during casting of the steel remains in the steel, and the total amount of AlN in the steel is decreased. Therefore, fine AlN obtained by the precipitation treatment is reduced, and the austenite pinning effect cannot be obtained.

[0032] The present inventors measured $vE_{-20°C}$ of a steel plate manufactured by applying various precipitation treatment times tp and precipitation treatment temperatures Tp to a steel having composition A4 of the Examples described below. The results are shown in FIG. 5. It can be seen from FIG. 5 that in order to obtain the austenite pinning effect of AlN, it is necessary to perform the precipitation treatment at an appropriate precipitation treatment temperature Tp for a precipitation treatment time tp.

[0033] Specifically, FIG. 5 plots steel plates with the horizontal axis representing the precipitation treatment temperature Tp of each of the steel plates and the vertical axis representing $\text{Log}_{10}(tp)$ of each of the steel plates. The unit of tp is time (Hr). In FIG. 5, the steel plates plotted by X marks are those having a $vE_{-20°C}$ of less than 47 J, and the steel plates plotted by O marks are those having a $vE_{-20°C}$ of 47 J or more. It can be seen from FIG. 5 that the toughness cannot be secured under the processing condition of $\text{Log}_{10}(tp) + 0.012 \times T < 8.7$. It is presumed that this is because precipitation of AlN is not sufficiently performed in the precipitation treatment, and the austenite pinning effect cannot be exhibited. On the other hand, it is understood that the toughness cannot be secured even in a case where the precipitation treatment temperature Tp exceeds Ac1. It is presumed that this is because, in a case where the precipitation treatment temperature Tp exceeds Ac1, the precipitation treatment becomes temperature retention in an α-γ dual phase region, so that Al and N are concentrated in the γ region and coarsening of AlN is incurred. The upper limit of the precipitation treatment time tp is not particularly limited from the viewpoint of mechanical properties. However, from the viewpoint of industrial production efficiency, 5 days = 120 hours may be the upper limit of the precipitation treatment time tp.

(6) Quenching Conditions (Temperature and Time) for Securing Middle Portion Hardness

[0034] As a sixth item, in order to cause the hardness of the thickness middle portion to be HB 350 or more in the composition range of the steel plate according to the present embodiment, it is necessary to perform quenching under predetermined conditions after sufficient precipitation of AlN caused by the above-mentioned precipitation treatment. Specifically, it is necessary to reheat the hot rolled steel plate to a quenching retention temperature Tq of 900°C or more and 950°C or less, retain the hot rolled steel plate at this temperature for a quenching retention time tq (minute) or more represented by Formula (6), and then performing a quenching treatment by water cooling the hot rolled steel plate.

$$\mathrm{tq} = 0.033 \times (950 - \mathrm{Tq})^2 + (1.5 \times \mathrm{f})^2/10\text{: Formula (6)}$$

[0035] In Formula (6), Tq is the quenching retention temperature (°C), and f is a value obtained by Formula (2) described above. In addition, the quenching retention temperature Tq indicates not the setting temperature of the heat treatment furnace but the temperature of the thickness middle portion of the steel plate.

[0036] Slight temperature fluctuations are allowed during the temperature retention of the quenching. In addition, temperature fluctuations may occur in actual operation. Therefore, the quenching retention temperature Tq is defined as the average temperature of the steel plate of the thickness middle portion after the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the quenching - 40°C" until the steel plate is extracted from a heat treatment furnace. Specifically, the quenching retention temperature Tq is a value calculated by Formula (9).

$$\mathrm{Tq} = \{\textstyle\int[\mathrm{t}_1 \rightarrow \mathrm{t}_2]\mathrm{T(t)dt}\} \;/\; (\mathrm{t}_2 - \mathrm{t}_1)\text{: Formula (9)}$$

t_1: Time at which the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the quenching - 40°C"
t_2: When the steel plate is extracted from the heat treatment furnace
T(t): Change in the temperature of the thickness middle portion of the steel plate with respect to time (time history of temperature)
$\int[t_1 \rightarrow t_2]T(t)dt$: Integral value from t_1 to t_2 of the change in the thickness middle portion of the steel plate with respect to time

[0037] Hereinafter, in order to distinguish from Tq as a target value for an operation described later, there are cases where the value calculated by Formula (8) is described as "actual Tq". In addition, the quenching retention time of the steel plate as an actual value is defined as the time (that is, "t_2-t_1") after the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the quenching - 40°C" until the steel plate is extracted from the heat treatment furnace. There are cases where the quenching retention time of the steel plate as the actual value defined as "t_2-t_1" below is described as "actual tq". Moreover, there are cases where the quenching retention time tq calculated from Formula (6) is described as "necessary tq". It is required as a manufacturing condition of the steel plate according to the present embodiment that the actual tq is equal to or more than the necessary tq.

[0038] The quenching retention temperature Tq may be controlled based on a value measured by inserting a thermocouple into the vicinity of the thickness middle portion of the steel plate, or the like, or this value may be controlled based on an estimated value obtained by heat conduction calculation based on the furnace temperature, the plate thickness, and the like.

[0039] An example of an actual quenching method is described below. For example, before the quenching treatment, a quenching retention temperature (target Tq) and a quenching retention time (target tq) as target values that satisfy Formula (6) are determined in advance. The steel plate is inserted into the heat treatment furnace, the steel plate is heated to a temperature range within a target Tq ± 20°C, and retained at the temperature. After retaining the temperature of the steel plate within the range of the target Tq ± 20°C for at least the target tq, a cooling treatment for quenching is performed. Thereafter, the actual Tq is calculated by applying the time history T(t) of the actual temperature (measured value or estimated value) of the thickness middle portion of the steel plate to Formula (8) described above. In addition, the time elapsed from the time t_1 at which the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the quenching - 40°C" to the time t_2 at which the steel plate is extracted from the heat treatment furnace is regarded as the actual tq. Next, the necessary tq is calculated by substituting the actual Tq into Tq of Formula (6). In a case where the actual tq is not smaller than the necessary tq (that is, in a case of the actual tq $\geq$ the necessary tq), it is determined that an appropriate quenching treatment has been performed.

[0040] In addition, also in the precipitation treatment, the determination in the same procedure is required.

[0041] FIG. 6A shows the results of an experiment using a steel having composition A6 of the Examples described later, and FIG. 6B shows the results of an experiment using a steel having composition A2 of the Examples described later.

[0042] The present inventors manufactured various steel plates by applying various temperature retention times (the time for which the temperature of the middle portion of the hot rolled steel plate is retained isothermally at the quenching retention temperature Tq) and the quenching retention temperature Tq to these steels and measured the middle portion hardness thereof. FIGS. 6A and 6B plot the steel plates with the horizontal axis representing the quenching retention temperature Tq of each of the steel plates and the vertical axis representing the temperature retention time of each of the steel plates. In FIGS. 6A and 6B, the steel plates plotted by X marks are those having a middle portion hardness of less than 350 HB, and the steel plates plotted by O marks are those having a middle portion hardness of 350 HB or more.

[0043] It can be seen from FIGS. 6A and 6B that the steel plates having a temperature retention time shorter than the quenching retention time tq represented by Formula (6) described above (the steel plates plotted below the curves in FIGS. 6A and 6B) have a middle portion hardness of less than HB 350. It is considered that this is because alloys that improve the hardenability were not sufficiently solutionized in the matrix and the hardenability could not be secured. In addition, the quenching retention time tq is a function of f because the larger the amount of alloys, the longer the time necessary for such solutionizing.

[0044] In a case where the quenching retention temperature Tq is less than 900°C, solutionizing of alloying elements is not sufficiently performed. Therefore, the hardenability cannot be secured, and HB 350 cannot be achieved at the middle portion of the steel plate. On the other hand, in a case where the quenching retention temperature Tq exceeds 950°C, AlN is partially solutionized, and liberated N is bonded to B in steel. Accordingly, the hardenability improvement effect of B is inhibited, and HB 350 at the middle portion of the steel plate cannot be achieved.

(7) Restriction of Upper and Lower Limits of Tempering Temperature for Securing Hardness and Toughness of Middle Portion

[0045] As a seventh item, in consideration of the construction requirements of a gear (prevention of deterioration of the material in stress relief annealing), the tempering temperature needs to be 500°C or more. In addition, the tempering temperature needs to be 500°C or more in order to secure the toughness of the steel plate by sufficiently tempering the structure. On the other hand, there is concern that in the steel plate according to the present embodiment, the hardness may be rapidly reduced due to tempering at more than 550°C. From this, the tempering temperature needs to be 550°C or less. After this tempering, the steel plate is cooled to 150°C or less.

[0046] Next, the structure of the steel plate according to the present embodiment will be described. In the steel plate according to the present embodiment, the total area ratio of martensite and bainite is 99% or more. Although the remainder of the structure is not particularly defined, for example, ferrite, pearlite, and retained austenite can be considered. Other structures are acceptable in an amount of less than 1 area%

[0047] The above structure is achieved by quenching under conditions under which ferrite is not formed and tempering at a sufficiently high temperature. Specifically, the structure is achieved by performing quenching on the steel plate having a composition of Ceq ≥ 0.750% under the above conditions after the precipitation treatment under the above conditions and performing tempering thereon under the above conditions.

[0048] Ferrite is a factor that reduces the hardness of steel. In particular, ferrite tends to be formed at the thickness middle portion where the quenching cooling rate is slow. In order to secure the middle portion hardness, the amount of ferrite has to be as low as possible.

[0049] Although pearlite is effective in securing hardness, it becomes a brittle fracture origin because of its hardness. Therefore, the amount of pearlite has to be as low as possible. Pearlite is formed by the concentration of C discharged during ferrite precipitation. Therefore, the formation of pearlite is simultaneously suppressed by the avoidance of ferrite precipitation.

[0050] Retained austenite is a brittle fracture origin and reduces the toughness of steel. Therefore, the amount of retained austenite has to be as low as possible. When tempering is performed at a tempering temperature of 500°C or more, the formation of retained austenite is suppressed.

[0051] As described above, it is necessary to suppress the formation of ferrite, pearlite, retained austenite, and the like, which are harmful structures in the steel plate according to the present embodiment, as much as possible. Also in consideration of microsegregation and production due to operation variation, the structure which is neither of martensite and bainite has to be reduced to less than 1%.

[0052] Next, various composition ranges in the steel plate according to the present embodiment will be described. The unit "%" of the amount of an alloying element means mass%.

C: 0.16% to 0.20%

[0053] C increases the hardness of a hardened structure and is thus an element effective for improving the hardness. Based on the experimental results shown in FIG. 2 described above, 0.16% is set to the lower limit of the C content. On the other hand, an excessive amount of C impairs the toughness of the steel plate and also becomes a factor of the hardness difference between the surface layer and the middle portion. Therefore, similarly based on the experimental results shown by FIG. 2 described above, the upper limit of the C content is set to 0.20%. The C content may be 0.17% or more, 0.18% or more, or 0.19% or more. The C content may be 0.19% or less, 0.18% or less, or 0.17% or less.

Si: 0.50% to 1.00%

[0054] Si has a deoxidizing effect. Moreover, Si is an element also effective for improving the strength of a steel plate, and can improve hardenability without raising Ceq. Therefore, the Si content is 0.50% or more. However, a large amount of Si promotes temper embrittlement and reduces the toughness of the steel plate. Therefore, it is preferable to reduce the Si content, and the upper limit thereof is 1.00%. The Si content may be 0.60% or more, 0.65% or more, or 0.70% or more. The Si content may be 0.90% or less, 0.85% or less, or 0.80% or less.

Mn: 0.90% to 1.50%

[0055] Mn has a deoxidizing effect. In addition, Mn is an element which improves hardenability and is effective in improving the strength of a steel plate. Therefore, the Mn content is 0.90% or more. On the other hand, excessive Mn promotes temper embrittlement and lowers the toughness of the steel plate. Therefore, the upper limit of the Mn content is 1.50%. The Mn content may be 1.00% or more, 1.05% or more, or 1.10% or more. The Mn content may be 1.40% or less, 1.35% or less, or 1.30% or less.

P: 0.010% or Less

[0056] P is an impurity element contained in steel. P is a harmful element that promotes intergranular embrittlement and reduces the toughness of the steel plate. Therefore, the P content is preferably as small as possible. Therefore, the P content is reduced to 0.010% or less. Since P is not required by the steel plate according to the present embodiment, the lower limit of the P content is 0%. However, from the viewpoint of refining cost and productivity, the P content may be defined as 0.001% or more. The P content may be 0.002% or more, 0.003% or more, or 0.005% or more. The P content may be 0.008% or less, 0.007% or less, or 0.006% or less.

S: 0.0020% or Less

[0057] S is an impurity element contained in steel. S is an element that reduces the toughness of a steel plate through segregation and formation of sulfides. Therefore, it is preferable that the S content is as small as possible. Therefore, the S content is reduced to 0.0020% or less. Since S is not required by the steel plate according to the present embodiment, the lower limit of the S content is 0%. However, from the viewpoint of refining cost and productivity, the S content may be 0.0004% or more. The S content may be 0.0005% or more, 0.0006% or more, or 0.0007% or more. The S content may be 0.0018% or less, 0.0015% or less, or 0.0010% or less.

Cu: 0% to 0.40%

[0058] Cu is an element that can increase the strength of steel without impairing low temperature toughness. However, there are cases where a large amount of Cu causes a crack in a steel plate during hot working. Furthermore, there is concern that a large amount of Cu may lower the toughness of the steel plate through the precipitation of metal Cu and the like. Therefore, the upper limit of the Cu content is 0.40%. Although Cu contributes to suppression of ferrite by raising Ceq, since Cu can be substituted with other alloying elements, Cu is not essential for the steel plate according to the present embodiment. Therefore, the lower limit of the Cu content is 0%. However, since a reduction in Cu requires cost, from the viewpoint of the refining cost, the lower limit of the Cu content may be set to 0.01% or 0.02%. The Cu content may be 0.03% or more, 0.05% or more, or 0.10% or more. The Cu content may be 0.35% or less, 0.30% or less, or 0.20% or less.

Ni: 0.20% to 1.00%

[0059] Ni is an element effective in improving the strength and toughness of steel. Therefore, the Ni content is 0.20%

or more. On the other hand, the effect is saturated even if the amount of Ni is excessive, and increasing the amount of Ni, which is an expensive alloy, causes the deterioration of the manufacturing cost. Therefore, the upper limit of the Ni content is 1.00%. The Ni content may be 0.25% or more, 0.30% or more, or 0.40% or more. The Ni content may be 0.90% or less, 0.80% or less, or 0.70% or less.

Cr: 0.60% to 0.99%

Mo: 0.60% to 1.00%

[0060] Cr and Mo have a function of improving hardenability and increasing the middle portion hardness. Moreover, Cr and Mo also have an effect of raising the hardness of the surface layer and the middle portion by precipitation quenching. Therefore, the amount of each of Cr and Mo is 0.60% or more. However, there is concern that excessive amounts of Cr and Mo may lower the toughness due to the formation of alloy carbides. Therefore, the upper limit of the Cr content is 0.99%, and the upper limit of the Mo content is 1.00%. The Cr content may be 0.65% or more, 0.70% or more, or 0.75% or more. The Cr content may be 0.95% or less, 0.90% or less, or 0.80% or less. The Mo content may be 0.65% or more, 0.70% or more, or 0.75% or more. The Mo content may be 0.95% or less, 0.90% or less, or 0.80% or less.

V: 0% to 0.050%

[0061] V improves the base metal strength through the formation of carbides. However, a large amount of V causes a reduction in toughness due to the formation of alloy carbides. Therefore, the upper limit of the V content is 0.050%. Although V contributes to suppression of ferrite by raising Ceq, since V is an expensive alloying element and can be substituted with another alloy, V is not essential for the steel plate according to the present embodiment. Therefore, the lower limit of the V content is 0%. However, from the viewpoint of the refining cost, the lower limit of the V content may be 0.003%. The V content may be 0.005% or more, 0.010% or more, or 0.015% or more. The V content may be 0.045% or less, 0.040% or less, or 0.035% or less.

Al: 0.050% to 0.085%,

[0062] Al is an element effective as a deoxidizing material. Furthermore, Al is bonded to N in steel to form AlN, which contributes to the refinement of the structure. In addition, Al forms AlN in the precipitation treatment and contributes to the decomposition of BN, thereby also having a function of stabilizing the hardenability exhibited by B. Therefore, the Al content is 0.050% or more. However, an excess of Al forms coarse AlN and causes a reduction in toughness and cracking in a cast piece. Therefore, the upper limit of the Al content is 0.085%. The Al content may be 0.055% or more, 0.060% or more, or 0.065% or more. The Al content may be 0.080% or less, 0.075% or less, or 0.070% or less.

N: 0.0020% to 0.0070%,

[0063] N forms nitrides and carbonitrides with alloying elements and contributes to the refinement of the structure of a steel plate. Therefore, the lower limit of the N content is set to 0.0020%. On the other hand, in a case where N is excessively solutionized in the steel, and in a case where N forms coarse nitrides, carbonitrides, and the like, the toughness of the steel plate is lowered. Therefore, the upper limit of the N content is set to 0.0070%. The N content may be 0.0025% or more, 0.0030% or more, or 0.0035% or more. The N content may be 0.0065% or less, 0.0060% or less, or 0.0050% or less.

[0064] As described above, Al × N (the product of the Al content and the N content) needs to be 2.0×10^{-4} or more. The purpose is to utilize the austenite pinning effect of AlN, which contributes to the refinement of the structure of the steel plate.

B: 0.0005% to 0.0020%

[0065] B is an element which improves the hardenability of steel and improves the strength. Therefore, the B content is 0.0005% or more. However, in a case where B is excessively contained, B forms carboborides and lowers the hardenability. Therefore, the upper limit of the B content is 0.0020%. The B content may be 0.0007% or more, 0.0008% or more, or 0.0010% or more. The B content may be 0.0018% or less, 0.0016% or less, or 0.0015% or less.

[0066] Further, the amounts of the following elements that affect the toughness are specified as selective elements. However, since the following selective elements are not essential for solving the problems by the steel plate according to the present embodiment, the lower limit of the amount of each of the selective elements is 0%.

Nb: 0% to 0.050%

[0067] Nb is an element that contributes to the refinement of the internal structure of steel by forming carbonitrides, and affects the toughness. Therefore, 0.001% or more of Nb can be contained. However, coarse carbonitrides generated by a large amount of Nb rather lower the toughness. Therefore, the upper limit of the Nb content is 0.050%. The Nb content may be 0.002% or more, 0.005% or more, or 0.008% or more. The Nb content may be 0.045% or less, 0.040% or less, or 0.035% or less.

Ti: 0% to 0.020%

Ti/N ≤ 3.4

[0068] Ti is an element that contributes to the refinement of the structure by forming stable nitrides and affects the toughness. Therefore, 0.001% or more of Ti can be contained. However, an excess of Ti causes a reduction in toughness due to coarse nitrides. Therefore, the upper limit of the Ti content is 0.020%. The Ti content may be 0.002% or more, 0.005% or more, or 0.008% or more. The Ti content may be 0.018% or less, 0.016% or less, or 0.012% or less.

[0069] In a case where the Ti content exceeds the stoichiometric ratio of TiN, specifically, in a case of Ti/N> 3.4, an excess of Ti forms carbides and lowers the toughness. Therefore, it is preferable that Ti/N ≤ 3.4 is satisfied. Ti/N may be 3.3 or less, 3.2 or less, or 3.0 or less. Although it is not necessary to define the lower limit of Ti/N, since the lower limit of the Ti content is 0%, the lower limit of Ti/N may be defined as 0%. Ti/N may be 0.2 or more, 0.5 or more, or 1.0 or more.

Ca: 0% to 0.0030%,

Mg: 0% to 0.0030%,

REM: 0% to 0.0030%,

[0070] All of Ca, Mg, and REM are bonded to harmful impurities such as S to form harmless inclusions. Accordingly, all of Ca, Mg, and REM can improve mechanical properties such as the toughness of steel. Therefore, the amount of each of Ca, Mg, and REM can be 0.0001% or more. However, when the amounts of Ca, Mg, and REM become excessive, not only is the effect saturated, but also the erosion of refractory materials such as casting nozzles is promoted. Therefore, the upper limit of the amount of each of Ca, Mg, and REM is 0.0030%. The amount of each of Ca, Mg, and REM may be 0.0002% or more, 0.0005% or more, or 0.0010% or more. The amount of each of Ca, Mg, and REM may be 0.0025% or less, 0.0020% or less, or 0.0015% or less. The term "REM" refers to a total of 17 elements consisting of Sc, Y, and lanthanoids, and "amount of REM" means the total amount of these 17 elements.

[0071] The remainder of the chemical composition of the steel plate according to the present embodiment contains iron and impurities. Impurities are components which are incorporated due to various factors of the raw material such as ore or scrap, or a manufacturing process in the industrial production of steel.

[0072] The average value of the prior austenite grain size in the thickness middle portion of the steel plate according to the present embodiment is less than 80 μm. In a case where the prior austenite grain size in the thickness middle portion is less than 80 μm, the thickness middle portion has high toughness. The prior austenite grain size of the thickness middle portion may be 76 μm or less, 73 μm or less, 70 μm or less, or 68 μm or less. The refinement of the prior austenite grain size in the thickness middle portion of the steel plate according to the present embodiment is achieved mainly by the austenite pinning effect of fine AlN, as described above.

[0073] The plate thickness of the steel plate according to the present embodiment is more than 200 mm. Since a steel plate having a thickness of more than 200 mm can be used as a material of a huge gear used in a rotating mechanism of a large industrial machine represented by a rotary kiln, the steel plate has high industrial applicability. However, the steel plate according to the present embodiment has good hardness and low temperature toughness even when the plate thickness is 200 mm or less. The thickness of the steel plate may be 205 mm or more, 210 mm or more, or 220 mm or more. The upper limit of the plate thickness of the steel plate is not particularly limited, but the plate thickness may be 250 mm or less, 240 mm or less, or 230 mm or less.

[0074] The -20°C Charpy absorbed energy ($vE_{-20°C}$) measured in the C direction of the thickness middle portion of the steel plate according to the present embodiment is 47 J or more. Here, the Charpy absorbed energy is a three-point average of values measured according to American Society for Testing and Materials (ASTM) A370-2017a. $vE_{-20°C}$ measured in the C direction is $vE_{-20°C}$ obtained using a Charpy impact test piece collected along the C direction (direction perpendicular to the rolling direction and the plate thickness direction). A steel plate that satisfies the above requirements with respect to Charpy absorbed energy has high low temperature toughness even in the thickness middle portion where it is usually difficult to control mechanical properties. The -20°C Charpy absorbed energy measured in the C direction at the thickness middle portion of the steel plate according to the present embodiment may be 50 J or more, 55 J or more, or 60 J or more. Although it is not necessary to define the upper limit of the -20°C Charpy absorbed energy measured in the C direction at the thickness middle portion of the steel plate according to the present embodiment, for example, the upper limit may be defined as 400 J, 380 J, or 350 J.

[0075] The hardness of the surface layer and the thickness middle portion of the steel plate according to the present embodiment is HB 350 or more. Here, the hardness of the steel plate according to the present embodiment is a five-point average of HBW 10/3000 (indenter diameter 10 mm, test force 3000 kgf) defined in JIS Z 2243-1:2018. The steel plate that satisfies the above requirements in terms of hardness does not have excessive hardness at the surface layer while having high hardness in the thickness middle portion where it is usually difficult to secure high hardness, and is thus highly applicable as steel for machine structural use. The hardness of the surface layer of the steel plate according to the present embodiment may be HB 360 or more, HB 370 or more, or HB 380 or more. The hardness of the thickness middle portion of the steel plate according to the present embodiment may be HB 360 or more, HB 370 or more, or HB 380 or more. The upper limit of the hardness of the surface layer of the steel plate according to the present embodiment need not be defined, but may be defined as, for example, HB 450, HB 420, or HB 400. The upper limit of the hardness of the thickness middle portion of the steel plate according to the present embodiment need not be defined, but may be defined as, for example, HB 450, HB 420 or HB 400.

[0076] Next, a method of measuring each of the constituent elements of the steel plate according to the present embodiment will be described below.

[0077] The composition of the steel plate is measured according to a known method at a 1/4T portion of the steel plate (a position at a depth of 1/4 of the thickness T of the steel plate from the rolled surface of the steel plate and the vicinity thereof) in order to exclude the effects of surface layer decarburization and segregation. Based on the measured values, Ceq, Al × N, Ti/N, and 4 × f/g of the steel plate are calculated. If the molten steel analysis value of a slab which is the material of the steel plate is known, the analysis value may be regarded as the chemical composition of the steel plate.

[0078] The -20°C Charpy absorbed energy ($vE_{-20°C}$) measured in the C direction of the thickness middle portion is measured according to ASTM A370-2017a. Test pieces are V-notch test pieces. Three test pieces are collected from the thickness middle portion of the steel plate. During the collection of the test pieces, the longitudinal direction of the test pieces and the C direction of the steel plate (the direction perpendicular to the rolling direction and the plate thickness direction) are caused to be coincident with each other. The average value of $vE_{-20°C}$ of these three test pieces is taken as the -20°C Charpy absorbed energy measured in the C direction at the thickness middle portion of the steel plate.

[0079] The hardness of the surface layer of the steel plate and the hardness of the thickness middle portion of the steel plate are measured based on JIS Z 2243-1:2018. HBW 10/3000 is obtained by setting the indenter diameter to 10 mm and the test force to 3000 kgf. The measurement of the surface layer hardness is performed by pressing an indenter against the surface formed by removing the area from the rolled surface of the steel plate to a depth of at least 1 mm. The average value of the measurement results of the surface layer hardness at five points is taken the hardness of the surface layer of the steel plate. The hardness of the thickness middle portion of the steel plate is measured by pressing an indenter against a portion corresponding to the thickness middle portion in a section formed by cutting the steel plate parallel to the rolled surface. The average value of the measurement results of the hardness of the thickness middle portion at five points is taken as the hardness of the thickness middle portion of the steel plate.

[0080] A method of measuring the area ratios of martensite and bainite in the thickness middle portion is as follows. An observed section is a surface parallel to the rolling direction of the steel plate, and is subjected to polishing and nital etching. The observed section is observed with an optical microscope at a magnification of 500-fold. Based on the optical micrograph, the sum of the area ratios of martensite and bainite can be measured. The total area of the observed visual field is 0.300 mm^2 or more.

[0081] A method of measuring the average value of the prior austenite particle size in the thickness middle portion is as follows. An observed section is a surface parallel to the rolling direction of the steel plate, and is subjected to polishing and picric acid etching. The average section length is measured by a section method, and the average section length is taken as the average prior γ particle size. However, the section length at the time of measurement is 1000 μm (1 mm) or more. Although it is not necessary to particularly determine the upper limit of the section length, it is not necessary to measure a section with a length of more than 2000 μm (2 mm), and the upper limit thereof may be 2000 μm (2 mm).

[0082] Next, a preferable method of manufacturing the steel plate according to the present embodiment will be described. According to the knowledge of the present inventors, the steel plate according to the present embodiment can be obtained according to the manufacturing conditions described below. However, even a steel plate obtained by conditions other than the manufacturing conditions described below corresponds to the steel plate according to the present embodiment as long as the above-described requirements are satisfied.

[0083] The method of manufacturing the steel plate according to the present embodiment includes, as shown in FIG. 7, a step S1 of heating a slab, a step S2 of hot rolling the slab to obtain a steel plate, a step S3 of cooling the steel plate, and a step S4 of performing a precipitation treatment on the steel plate, a step S5 of performing a quenching treatment on the steel plate, and a step S6 of tempering the steel plate. The manufacturing conditions in these steps are as shown in the following table.

[Table 1]

S1	Slab heating	Slab heating temperature: AlN solid solution temperature Ts or more Ts = 7400 / (1.95 - $\log_{10}$(Al × N)) - 273: Formula (4)
S2	hot rolling	Plate thickness after rolling: more than 200 nun
S3	Cooling	Cooling stop temperature: 500°C or less, preferably 150°C or less
S4	Precipitation treatment	Precipitation treatment temperature Tp: more than 550°C and less than Ac1, that is, Formula (5) is satisfied. Precipitation treatment time tp: Formula (5) is satisfied. $\mathrm{Log}_{10}(tp) + 0.012 \times Tp \geq 8.7$: Formula (5) $Ac1 = 750 - 25 \times C + 22 \times Si - 40 \times Mn - 30 \times Ni + 20 \times Cr + 25 \times Mo$: Formula (7)
S5	Quenching	Quenching retention temperature Tq: 900°C or more and 950°C or less Temperature retention time: quenching retention time tq represented by Formula (6) or more $tq = 0.033 \times (950 - Tq)^2 + (1.5 \times f)^2/10$: Formula (6) Cooling method: water cooling
S6	Tempering	Tempering temperature: 500°C or more and 550°C or less Cooling finishing temperature: 150°C or less

[0084] In the step S1 of heating the slab, after casting a slab having the composition of the steel plate according to the present embodiment described above, the slab is heated to a temperature equal to or more than the AlN solid solution temperature Ts calculated by Formula (4) described above. The technical significance of the AlN solid solution temperature Ts is as described above.

[0085] For the composition of the slab, not only be the upper and lower limits of each of the alloying elements satisfied, but also it is necessary, as in the steel plate, Ceq is 0.750% to 0.800%, Al × N is 2.0×10^{-4} or more, Ti/N is 3.4 or less, and 4 × f/g is 9.00 or more. Preferable numerical ranges of the amount of each alloying element, Ceq, Al × N, Ti/N, and 4 × f/g are the same as those of the steel plate. In a case where the molten steel analysis value of the slab is known, that value may be regarded as the chemical composition of the slab.

[0086] The step S2 of hot rolling the heated slab is not particularly limited. Since the present embodiment aims to manufacture a steel plate having a thickness of more than 200 mm, the thickness of the steel plate (hot-rolled steel plate) obtained by the hot rolling is more than 200 mm.

[0087] In the step S3 of cooling the steel plate, it is preferable to complete the transformation from austenite in the structure of the steel plate to other structures by cooling the steel plate to 500°C or less, and preferably 150°C or less.

[0088] In step S4 of performing the precipitation treatment on the steel plate, the steel plate is heated to the precipitation treatment temperature Tp, and the temperature is retained at this temperature T. The precipitation treatment temperature Tp is a temperature of more than 550°C and less than Ac1, and is regarded as satisfying Formula (5) described above. The precipitation treatment time tp is also regarded as satisfying Formula (5) described above. The technical significance of the precipitation treatment conditions is as described above. After the temperature retention in the step S4 of performing the precipitation treatment, the steel plate may be cooled to 500°C or less, and preferably 150°C or less (for example, room temperature), or may be heated as it is for subsequent quenching.

[0089] In the step S5 of performing quenching treatment on the steel plate, the steel plate is heated to the quenching retention temperature Tq (°C) of 900°C or more and 950°C or less, is subjected to temperature retention for the quenching retention time tq (minute) or more represented by Formula (6), and is then subjected to water cooling. The technical significance of the quenching retention temperature Tq and the quenching retention time tq is as described above. In the quenching treatment, means for cooling the steel plate after the completion of the temperature retention is water cooling or one that can achieve a cooling rate equivalent to this. The quenching finishing temperature is, for example, 150°C or less.

[0090] In the step S6 of tempering the steel plate, it is preferable that the steel plate is tempered at a tempering temperature of 500°C or more and 550°C or less and is then cooled to 150°C or less. The technical significance of the tempering temperature is as described above.

[Examples]

[0091] Slabs obtained by melting steels of A1 to A10 and B1 to B24 having the chemical composition shown in Table 2-1 were heated, rolled, and heat-treated under respective conditions of Present Invention Steels Nos. 1 to 10 shown in Tables 3-1 to 3-3 and Comparative Examples Nos. 11 to 43, whereby steel plates having a plate thickness of 210 mm to 230 mm were manufactured. Manufacturing conditions which are not described in the tables are as follows. All the chemical compositions in Table 2-1 are molten steel analysis values.

Cooling finishing temperature after hot rolling: 150°C or less in all the examples and Comparative Examples
Cooling means in quenching: water cooling (cooling to 150°C or less)
Cooling finishing temperature in tempering: 150°C or less in all the Examples and Comparative Examples

[0092] The hardness of the surface layer of the steel plate and the hardness of the thickness middle portion of the steel plate were measured based on JIS Z 2243-1:2018. HBW 10/3000 was obtained by setting the indenter diameter to 10 mm and the test force to 3000 kgf. The measurement of the surface layer hardness was performed by pressing the indenter against the surface formed by removing the area from the rolled surface of the steel plate to a depth of at least 1 mm. The average value of the measurement results of the surface layer hardness at five points was taken as the hardness of the surface layer of the steel plate (Table 4 "HB surface layer"). The hardness of the thickness middle portion of the steel plate was measured by pressing the indenter against a portion corresponding to the thickness middle portion in a surface formed by cutting the steel plate parallel to the rolled surface. The average value of the measurement results of the thickness middle portion hardness at five points was taken as the hardness of the thickness middle portion of the steel plate (Table 4 "HB middle portion"). In addition, the test pieces of the steel plate were collected from portions separated from the end portions of the steel plate in the length direction and the width direction by the plate thickness or more. The -20°C Charpy absorbed energy ($vE_{-20°C}$) measured in the C direction of the thickness middle portion was measured according to ASTM A370-2017a. Three test pieces were collected from the thickness middle portion of the steel plate. During the collection of the test pieces, the longitudinal direction of the test pieces and the C direction of the steel plate (the direction perpendicular to the rolling direction and the plate thickness direction) were caused to be coincident with each other. The average value of $vE_{-20°C}$ of these three test pieces was taken as the -20°C Charpy absorbed energy measured in the C direction at the thickness middle portion of the steel plate (Table 4 "$vE_{-20°C}$").

[0093] A method of measuring the area ratios of martensite and bainite in the thickness middle portion is as follows. An observed section was a surface parallel to the rolling direction of the steel plate, and was subjected to polishing and nital etching. The observed section is observed with an optical microscope at a magnification of 500-fold. Based on the optical micrograph, the sum of the area ratios of martensite and bainite was measured. The total area of the observed visual field was 0.300 mm^2 or more.

[0094] A method of measuring the average value of the prior-austenite particle size in the thickness middle portion was as follows. An observed section was a surface parallel to the rolling direction of the steel plate, and was subjected to polishing and picric acid etching. The average section length was measured by a section method (section length: 1000 μm or more and 2000 μm or less), and the average section length was taken as the average value of the prior austenite grain size of the thickness middle portion (Table 4 "prior γ grain size").

[0095] Hereinafter, compositions are shown in Tables 2-1 and 2-2, manufacturing methods are shown in Tables 3-1 to 3-3, and materials, evaluation and the like are shown in Table 4. The "precipitation treatment temperature Tp" described in the tables is a value obtained by applying the thermal history at the time of the precipitation treatment to Formula (8). The "precipitation treatment time tp" described in the tables is the time after the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the precipitation treatment - 40°C" until the steel plate is extracted from the heat treatment furnace. The "quenching retention temperature Tq" described in the tables is a value obtained by applying the thermal history at the time of the quenching treatment to Formula (9). The "actual quenching retention time" described in the tables means is the time after the temperature of the thickness middle portion of the steel plate lastly exceeds "the maximum temperature of the thickness middle portion of the steel plate during the quenching - 40°C" until the steel plate is extracted from the heat treatment furnace (that is, actual tq). The "quenching retention time tq" described in the tables is a value obtained by substituting the quenching retention temperature Tq and f described in the tables into the Formula (6) described above. However, in the Al × N column of Table 2-2, for example, 2.2E-04 means 2.2×10^{-4}. In addition, in Table 3-2, it is determined whether or not the precipitation treatment temperature Tp and the precipitation treatment time tp satisfy Formula (5) using a precipitation treatment time threshold obtained using Formula (5') below. When the precipitation treatment time tp is equal to or more than the precipitation treatment time threshold, the precipitation treatment temperature Tp and the precipitation treatment time tp satisfy Formula (5).

$$(\text{Precipitation treatment time threshold}) = 10^{(-0.012 \times \mathrm{Tp} + 8.7)}\text{: Formula (5')}$$

[Table 2-1]

Composition	C	Si	Mn	Cu	Ni	Cr	Mo	V	Al	N	B	P	S	Nb	Ti	Ca	Mg	REM
A1	0.19	0.54	1.02	0.32	0.94	0.74	0.86	0.003	0.060	0.0036	0.0007	0.0082	0.0004					
A2	0.18	0.95	1.39	0.02	0.40	0.90	0.89	0.004	0.072	0.0034	0.0015	0.0027	0.0020			0.0025		
A3	0.16	0.73	1.30	0.06	0.82	0.89	0.90	0.025	0.081	0.0041	0.0006	0.0091	0.0019		0.010			
A4	0.18	0.51	1.42	0.10	0.61	0.76	0.77	0.038	0.056	0.0055	0.0019	0.0092	0.0014			0.0018	0.0011	
A5	0.18	0.89	1.41	0.40	0.30	0.74	0.75	0.015	0.084	0.0050	0.0014	0.0035	0.0016					0.0022
A6	0.19	0.85	0.96	0.26	0.85	0.95	0.73	0.033	0.081	0.0025	0.0019	0.0033	0.0007			0.0028		
A7	0.17	0.51	1.26	0.24	0.74	0.80	0.96	0.004	0.071	0.0036	0.0017	0.0049	0.0013	0.016				
A8	0.19	0.95	1.27	0.33	0.85	0.63	0.88	0.028	0.053	0.0039	0.0007	0.0052	0.0011				0.0009	
A9	0.18	0.62	1.21	0.20	0.50	0.90	0.88	0.015	0.071	0.0037	0.0013	0.0079	0.0011					
A10	0.18	0.71	1.15	0.02	0.71	0.97	0.89	0.026	0.085	0.0067	0.0008	0.0041	0.0018			0.0016		
B1	0.15	0.90	1.39	0.24	0.51	0.70	0.89	0.013	0.068	0.0059	0.0007	0.0070	0.0015					
B2	0.22	0.89	1.25	0.30	0.76	0.68	0.73	0.004	0.059	0.0039	0.0011	0.0055	0.0020					
B3	0.19	0.45	1.27	0.32	0.67	0.75	0.86	0.036	0.073	0.0037	0.0012	0.0034	0.0009					
B4	0.18	1.06	1.20	0.35	0.60	0.77	0.72	0.048	0.067	0.0061	0.0017	0.0024	0.0015					
B5	0.17	0.93	0.83	0.26	0.96	0.91	0.89	0.021	0.081	0.0061	0.0011	0.0086	0.0008					
B6	0.19	0.83	1.61	0.08	0.58	0.68	0.62	0.033	0.069	0.0056	0.0011	0.0061	0.0015					
B7	0.17	0.89	1.03	0.06	0.90	0.85	0.95	0.017	0.074	0.0043	0.0006	0.0110	0.0020					
B8	0.17	0.76	1.15	0.36	0.85	0.87	0.67	0.030	0.076	0.0052	0.0014	0.0051	0.0026					
B9	0.20	0.56	1.38	0.50	0.37	0.76	0.64	0.005	0.062	0.0048	0.0008	0.0056	0.0011					
B10	0.19	0.72	1.45	0.14	0.14	0.81	0.71	0.031	0.065	0.0046	0.0018	0.0080	0.0008					
B11	0.16	0.79	1.41	0.36	0.51	0.52	0.96	0.011	0.056	0.0040	0.0019	0.0061	0.0015					
B12	0.19	0.59	1.04	0.36	0.73	1.06	0.65	0.027	0.067	0.0044	0.0017	0.0093	0.0012					
B13	0.19	0.53	1.39	0.36	0.92	0.66	0.53	0.029	0.062	0.0063	0.0015	0.0070	0.0013					
B14	0.17	0.99	1.10	0.29	0.61	0.77	1.08	0.047	0.074	0.0044	0.0014	0.0094	0.0016					
B15	0.19	0.76	1.41	0.12	0.47	0.80	0.79	0.056	0.058	0.0064	0.0012	0.0073	0.0017					
B16	0.17	0.53	1.42	0.23	0.92	0.65	0.91	0.012	0.042	0.0051	0.0019	0.0048	0.0014					
B17	0.18	0.62	1.39	0.03	0.28	0.64	0.99	0.039	0.092	0.0037	0.0018	0.0090	0.0018					
B18	0.19	0.93	1.19	0.05	0.21	0.88	0.83	0.044	0.078	0.0012	0.0019	0.0082	0.0017					
B19	0.19	0.57	1.22	0.35	0.44	0.76	0.72	0.044	0.083	0.0073	0.0015	0.0079	0.0019					
B20	0.17	0.56	1.04	0.29	0.98	0.81	0.80	0.036	0.085	0.0043	0.0003	0.0068	0.0018					
B21	0.19	1.00	1.47	0.05	0.62	0.61	0.89	0.028	0.062	0.0036	0.0026	0.0081	0.0012					
B22	0.19	0.73	1.21	0.26	0.65	0.73	0.68	0.014	0.072	0.0063	0.0012	0.0079	0.0016					
B23	0.18	0.66	1.05	0.38	0.28	0.90	0.95	0.030	0.065	0.0039	0.0013	0.0063	0.0015					
B24	0.17	0.65	1.12	0.12	0.45	0.91	0.88	0.035	0.064	0.0049	0.0006	0.0051	0.0018					

Remainder of chemical composition consists of iron and impurities.

[Table 2-2]

Composition	Ti/N	f	g	4×f/g	Al×N	Ceq (Formula (1))
A1		10.06	4.08	9.87	2.2E-04	0.765
A2		11.10	4.49	9.89	2.4E-04	0.798
A3	2.4	11.07	4.61	9.62	3.3E-04	0.798
A4		10.05	4.02	10.00	3.1E-04	0.778
A5		9.96	3.81	10.47	4.2E-04	0.763
A6		9.93	4.26	9.33	2.0E-04	0.767
A7		10.85	4.50	9.64	2.6E-04	0.798
A8		10.76	4.04	10.65	2.1E-04	0.788
A9		10.46	4.52	9.27	2.6E-04	0.787
A10		10.83	4.74	9.14	5.7E-04	0.798
B1		10.64	4.14	10.29	4.0E-04	0.752
B2		10.04	3.57	11.25	2.3E-04	0.782
B3		10.22	4.26	9.60	2.7E-04	0.797
B4		9.92	3.94	10.07	4.1E-04	0.751
B5		10.50	4.60	9.14	4.9E-04	0.754
B6		9.85	3.39	11.64	3.9E-04	0.769
B7		10.98	4.64	9.48	3.2E-04	0.769
B8		9.68	3.90	9.93	4.0E-04	0.756
B9		9.21	3.47	10.63	3.0E-04	0.769
B10		9.69	3.91	9.93	3.0E-04	0.761
B11		10.60	3.98	10.67	2.2E-04	0.751
B12		9.53	4.21	9.07	2.9E-04	0.783
B13		8.96	3.06	11.73	3.9E-04	0.751
B14		11.42	5.02	9.11	3.3E-04	0.793
B15		10.36	4.25	9.75	3.7E-04	0.794
B16		10.82	4.09	10.58	2.1E-04	0.798
B17		10.63	4.45	9.57	3.4E-04	0.766
B18		10.19	4.47	9.12	9.4E-05	0.756
B19		9.33	3.90	9.57	6.1E-04	0.751
B20		9.92	4.20	9.45	3.7E-04	0.757
B21		10.99	4.03	10.91	2.2E-04	0.785
B22		9.42	3.57	10.55	4.5E-04	0.737
B23		10.31	4.80	8.59	2.5E-04	0.775
B24		10.24	4.64	8.84	3.1E-04	0.760

Al × N indicates an index based on JIS X 0210-1986.

[Table 3-1]

Composition	No.	Slab heating temperature (°C)	AlN solid solution temperature Ts (°C)	Formula (4) evaluation	Plate thickness (mm)
A1	1	1150	1045	SUCCESS	210
A2	2	1150	1058	SUCCESS	220
A3	3	1200	1090	SUCCESS	230
A4	4	1200	1082	SUCCESS	210
A5	5	1250	1116	SUCCESS	210
A6	6	1100	1038	SUCCESS	210
A7	7	1150	1062	SUCCESS	220
A8	8	1150	1040	SUCCESS	210
A9	9	1200	1065	SUCCESS	220
A10	10	1250	1152	SUCCESS	210
B1	11	1250	1111	SUCCESS	210
B2	12	1100	1051	SUCCESS	210
B3	13	1200	1068	SUCCESS	210
B4	14	1150	1113	SUCCESS	210
B5	15	1150	1135	SUCCESS	210
B6	16	1150	1107	SUCCESS	210
B7	17	1150	1085	SUCCESS	210
B8	18	1150	1109	SUCCESS	210
B9	19	1150	1078	SUCCESS	210
B10	20	1150	1079	SUCCESS	210
B11	21	1200	1048	SUCCESS	210
B12	22	1200	1077	SUCCESS	210
B13	23	1150	1108	SUCCESS	210
B14	24	1200	1088	SUCCESS	210
B15	25	1200	1102	SUCCESS	210
B16	26	1150	1044	SUCCESS	210
B17	27	1200	1093	SUCCESS	210
B18	28	1050	965	SUCCESS	210
B19	29	1200	1159	SUCCESS	210
B20	30	1150	1101	SUCCESS	210
B21	31	1200	1048	SUCCESS	210
B22	32	1150	1125	SUCCESS	210
B23	33	1150	1061	SUCCESS	210
B24	34	1200	1084	SUCCESS	210
A10	35	1100	1152	FAILURE	210
A3	36	1200	1090	SUCCESS	230
A4	37	1200	1082	SUCCESS	210
A1	38	1150	1045	SUCCESS	210
A6	39	1100	1038	SUCCESS	210
A7	40	1150	1062	SUCCESS	220
A8	41	1150	1040	SUCCESS	210
A5	42	1250	1116	SUCCESS	210
A9	43	1200	1065	SUCCESS	220

[Table 3-2]

No.	Ac1 (°C)	Precipitation treatment temperature Tp (°C)	Precipitation treatment time tp (hour)	Precipitation treatment time threshold by Formula (5') (hour)	Formula (5) evaluation
1	694	625	20	16	SUCCESS
2	709	600	60	32	SUCCESS
3	696	650	10	8	SUCCESS
4	686	600	50	32	SUCCESS
5	703	625	30	16	SUCCESS
6	707	650	10	8	SUCCESS
7	694	575	80	63	SUCCESS
8	694	600	60	32	SUCCESS
9	706	575	100	63	SUCCESS
10	705	625	80	16	SUCCESS
11	701	575	80	63	SUCCESS
12	693	625	40	16	SUCCESS
13	691	625	40	16	SUCCESS
14	706	650	20	8	SUCCESS
15	715	600	60	32	SUCCESS
16	681	600	60	32	SUCCESS
17	708	650	40	8	SUCCESS
18	695	625	20	16	SUCCESS
19	692	650	10	8	SUCCESS
20	703	650	20	8	SUCCESS
21	696	625	20	16	SUCCESS
22	702	625	40	16	SUCCESS
23	670	575	80	63	SUCCESS
24	718	625	40	16	SUCCESS
25	697	625	20	16	SUCCESS
26	679	600	60	32	SUCCESS
27	703	625	20	16	SUCCESS
28	720	600	40	32	SUCCESS
29	699	600	100	32	SUCCESS
30	693	600	80	32	SUCCESS
31	694	625	100	16	SUCCESS
32	695	625	20	16	SUCCESS
33	721	600	60	32	SUCCESS
34	712	575	80	63	SUCCESS
35	706	625	80	16	SUCCESS
36	696	550	130	126	SUCCESS
37	686	700	30	2	SUCCESS
38	694	600	20	32	FAILURE
39	707	650	10	8	SUCCESS
40	694	575	80	63	SUCCESS
41	694	600	60	32	SUCCESS
42	703	625	30	16	SUCCESS
43	706	575	100	63	SUCCESS

[0096] Precipitation treatment time threshold is a value obtained by $10^{(8.7-0.012\times Tp)}$.

[Table 3-3]

No.	Quenching retention temperature Tq (°C)	Actual quenching retention time (min)	Quenching retention time tq by Formula (6) (min)	Formula (6) evaluation	Tempering temperature (°C)
1	920	60	52	SUCCESS	520
2	930	60	41	SUCCESS	520
3	910	120	80	SUCCESS	550
4	930	60	36	SUCCESS	510
5	910	120	75	SUCCESS	500
6	900	120	105	SUCCESS	550
7	950	40	26	SUCCESS	500
8	940	40	29	SUCCESS	530
9	900	120	107	SUCCESS	500
10	930	40	40	SUCCESS	520
11	940	40	29	SUCCESS	500
12	910	80	75	SUCCESS	550
13	910	80	76	SUCCESS	500
14	940	40	25	SUCCESS	550
15	930	40	38	SUCCESS	500
16	900	120	104	SUCCESS	550
17	930	120	40	SUCCESS	550
18	950	40	21	SUCCESS	550
19	900	120	102	SUCCESS	550
20	930	40	34	SUCCESS	550
21	930	80	38	SUCCESS	500
22	930	40	34	SUCCESS	550
23	910	80	71	SUCCESS	500
24	950	100	29	SUCCESS	550
25	910	80	77	SUCCESS	550
26	910	80	79	SUCCESS	500
27	950	40	25	SUCCESS	550
28	930	80	37	SUCCESS	550
29	930	40	33	SUCCESS	550
30	930	60	35	SUCCESS	500
31	930	60	40	SUCCESS	550
32	950	40	20	SUCCESS	500
33	930	40	37	SUCCESS	550
34	910	100	76	SUCCESS	550
35	930	60	40	SUCCESS	520
36	910	120	80	SUCCESS	520
37	930	60	36	SUCCESS	530
38	920	60	52	SUCCESS	500
39	890	160	141	SUCCESS	540
40	960	40	30	SUCCESS	520
41	910	40	79	FAILURE	530
42	910	120	75	SUCCESS	480
43	900	120	107	SUCCESS	560

[Table 4]

No.	Martensite + Bainite (area%)	Prior γ grain size (μm)	HB surface layer (HB)	HB middle portion (HB)	$vE_{-20^\circ C}$ (J)	Note
1	100	62	371	355	81	Invention Examples
2	100	66	383	369	48	
3	100	51	358	353	102	
4	100	71	363	352	65	
5	100	73	360	356	49	
6	100	72	368	354	80	
7	100	71	361	352	79	
8	100	56	368	363	67	
9	100	59	370	361	50	
10	100	62	375	362	53	
11	100	69	348	341	75	Comparative Examples
12	100	72	378	355	39	
13	100	67	359	348	81	
14	100	59	365	356	41	
15	100	68	363	346	48	
16	100	70	361	358	21	
17	100	64	363	356	39	
18	100	73	371	353	45	
19	100	71	357	352	45	
20	100	72	359	355	37	
21	99	60	369	348	19	
22	100	54	358	353	45	
23	99	63	361	346	42	
24	100	62	359	357	39	
25	100	71	366	359	39	
26	98	90	375	348	32	
27	100	56	360	353	46	
28	100	91	355	350	31	
29	100	77	357	352	45	
30	95	56	372	349	21	
31	100	78	360	353	41	
32	97	75	367	346	31	
33	100	68	358	354	41	
34	100	59	359	356	39	
35	100	85	361	352	39	
36	100	88	358	351	45	
37	100	61	357	350	44	
38	100	89	371	350	46	
39	97	65	361	348	33	
40	100	86	354	350	42	
41	99	55	360	346	43	
42	100	74	372	365	33	
43	100	51	351	343	71	

[0097] Test Nos. 1 to 10 satisfy the chemical composition range of the present invention and suitable manufacturing conditions. The total area ratio of martensite and bainite is 99% or more in all the steels, the average value of the prior austenite grain size in the middle portion is 80 μm or less, and the surface layer hardness, the middle portion hardness, the middle portion impact absorbed energy satisfy the targets.

[0098] In Test Nos. 11 and 12, C deviates from the chemical composition range of the present invention. In Test No. 11, C is insufficient, and the hardness at the time of quenching is insufficient, so that the hardness cannot satisfy the target value even after tempering. On the other hand, Test No. 12 is an example in which C is excessive, and the impact absorbed energy is low due to the influence of precipitation of hard carbides which are fracture origins.

[0099] In Test Nos. 13 and 14, Si deviates from the chemical composition range of the present invention. In Test No. 13, Si is insufficient, and the hardenability cannot be secured, so that the middle portion hardness cannot satisfy the target value. On the other hand, Test No. 14 is an example in which Si is excessive, and although the hardness is sufficient, the impact absorbed energy does not satisfy the target due to the promotion of temper embrittlement by Si.

[0100] In Test Nos. 15 and 16, Mn deviates from the chemical composition range of the present invention. In Test No. 15, Mn is insufficient, and the hardness at the time of quenching is insufficient, so that the middle portion hardness cannot satisfy the target value even after tempering. On the other hand, Test No. 16 is an example in which Mn is excessive, and the impact absorbed energy does not satisfy the target value due to the promotion of temper embrittlement.

[0101] In Test No. 17, the P content is high outside the chemical composition range of the present invention, and although the hardness is sufficient, the impact absorbed energy does not satisfy the target due to the embrittlement caused by P.

[0102] In Test No. 18, the S content is high outside the chemical composition range of the present invention. Therefore, in Test No. 18, the impact absorbed energy cannot satisfy the target due to the formation of MnS, which is a stretched inclusion.

[0103] In Test No. 19, the Cu content was high outside the chemical composition range of the present invention, and the precipitated metal Cu became the brittle fracture origin. Therefore, in Test No. 19, the impact absorbed energy does not satisfy the target.

[0104] In Test No. 20, the Ni content is low outside the chemical composition range of the present invention, and does not satisfy the amount that improves the toughness. Therefore, in Test No. 20, the impact absorbed energy does not satisfy the target.

[0105] Test Nos. 21 and 22 are examples in which Cr deviates from the chemical composition range of the present invention. In test No. 21, Cr is insufficient, and sufficient hardenability and precipitation strengthening action are not obtained. From this, in the test No. 21, the middle portion hardness does not satisfy the target, and furthermore, the impact absorbed energy does not achieve the target. On the other hand, in Test No. 22, Cr was excessive, and the influence of precipitation of coarse Cr carbides was significant. As a result, in Test No. 22, the impact absorbed energy does not satisfy the target.

[0106] Test Nos. 23 and 24 are examples in which Mo deviates from the chemical composition range of the present invention. In Test No. 23, Mo is insufficient, and sufficient hardenability and precipitation strengthening action are not obtained. From this, in Test No. 23, the middle portion hardness does not satisfy the target, and the impact absorbed energy does not achieve the target. On the other hand, in Test No. 24, Mo was excessive, and the influence of precipitation of coarse Mo carbides was significant. Accordingly, in Test No. 24, the impact absorbed energy does not satisfy the target value.

[0107] In Test No. 25, V was high outside the chemical composition range of the present invention, and coarse carbides and nitrides of V and the like became the brittle fracture origin. From this, in Test No. 25, the impact absorbed energy does not satisfy the target.

[0108] Test Nos. 26 and 27 are examples in which Al deviates from the chemical composition range of the present invention. Test No. 26 is an example in which Al is insufficient, AlN effective for austenite pinning could not be secured, and an excess of N was bonded B, so that the effect of improving the hardenability was reduced. For this reason, in Test No. 26, the structures other than martensite and bainite were excessive, and the grain size of retained austenite was coarsened. As a result, in Test No. 26, the middle portion hardness and the impact absorbed energy cannot satisfy the targets. On the other hand, Test No. 27 is an example in which Al is excessive, and AlN was excessively coarsened and became a brittle fracture origin. Therefore, in Test No. 27, the impact absorbed energy cannot satisfy the target.

[0109] Test Nos. 28 and 29 are examples in which N deviates from the chemical composition range of the present invention. Test No. 28 is an example in which N is insufficient and Al × N is less than a predetermined range, and the amount of nitrides, carbonitrides, and the like formed was insufficient, so that the austenite pinning effect was weak and grain coarsening had occurred. As a result, in Test No. 28, the impact absorbed energy cannot satisfy the target. On the other hand, Test No. 29 is an example in which N is excessive, and excessive coarsening of nitrides, carbonitrides, and the like occurs. As a result, in Test No. 29, the impact absorbed energy cannot satisfy the target.

[0110] In Test Nos. 30 and 31, B deviates from the chemical composition range of the present invention. Test No. 30 is an example in which B was insufficient, and the amount of solute B necessary for hardenability could not be secured. As a result, in Test No. 30, the structures other than martensite and bainite are excessive, and the middle portion hardness and impact absorbed energy cannot satisfy the targets. On the other hand, Test No. 31 is an example in which B is excessively contained, and carboborides of metal elements are precipitated, so that the impact absorbed energy cannot satisfy the target.

[0111] In Test No. 32, although the composition range of each alloying element is within the range of the present invention, Ceq is low outside the suitable scope of the present invention. In Test No. 32, as a result of the formation of ferrite in the structure due to the decrease in hardenability, the middle portion hardness and impact absorbed energy cannot satisfy the targets.

[0112] In Test Nos. 33 and 34, although the composition range of each alloying element and Ceq are within the ranges of the present invention, the parameter formula $4 \times f/g$ is low outside the suitable range of the present invention. In Test Nos. 33 and 34, the quenching effect of the precipitated elements was larger than the improvement of the hardenability. Therefore, in Test Nos. 33 and 34, the impact absorbed energy cannot satisfy the target.

[0113] In Test No. 35, although various indexes derived from the composition range of each alloying element and the chemical composition are within the ranges of the present invention, the heating temperature before rolling is less than the solid solution temperature Ts. In Test No. 35, undissolved coarse AlN remained and became a brittle fracture origin. Therefore, in Test No. 35, the prior austenite grain size is coarsened, and the absorbed energy cannot satisfy the target.

[0114] In Test Nos. 36 and 37, although various indexes derived from the composition range of each alloying element and the chemical composition are within the ranges of the present invention, the precipitation treatment temperature deviates from the suitable range of the present invention. Test No. 36 is an example in which the precipitation treatment temperature was low, and AlN was not sufficiently precipitated, so that AlN effective for austenite pinning could not be secured. From this, in Test No. 36, the prior austenite grain size is coarsened, and the absorbed energy cannot satisfy the target. On the other hand, Test No. 37 is an example in which the precipitation treatment temperature exceeded Ac1, and the coarsening of AlN had occurred locally due to the retention in the α-γ dual region. Therefore, in Test No. 37, the absorbed energy cannot satisfy the target.

[0115] Test No. 38 is an example in which, although various indexes derived from the composition range of each alloying element and the chemical composition were within the ranges of the present invention, the temperature and time of the precipitation treatment did not satisfy Formula (5), which is a suitable range of the present invention. In Test No. 38, AlN was not sufficiently precipitated, so that AlN effective for austenite pinning could not be secured. From this, in Test No. 38, the prior austenite grain size is coarsened, and the absorbed energy cannot satisfy the target.

[0116] Test No. 39 is an example in which, although various indexes derived from the composition range of each alloying element and the chemical composition are within the ranges of the present invention, the quenching temperature is less than the suitable range of the present invention. In Test No. 39, solutionizing of the alloying elements was not sufficiently performed, so that the hardenability was low and ferrite was excessively formed. Accordingly, in Test No. 39, the middle portion hardness and the absorbed energy cannot satisfy the targets.

[0117] Test No. 40 is an example in which, although various indexes derived from the composition range of each alloying element and the chemical composition are within the ranges of the present invention, the quenching retention temperature Tq exceeds the suitable range of the present invention. Test No. 40 resulted in excessive coarsening of grains. From this, in Test No. 40, the prior austenite grain size is coarsened, and the absorbed energy cannot satisfy the target.

[0118] Test No. 41 is an example in which, although various indexes derived from the composition range of each alloying element and the chemical composition are within the ranges of the present invention, the actual quenching retention time is less than the quenching retention time tq, which is the suitable range of the present invention, and solutionizing of the alloying elements was not sufficiently performed. From this, in Test No. 41, the hardenability was low and ferrite was excessively formed. As a result, in Test No. 41, the middle portion hardness and the absorbed energy cannot satisfy the targets.

[0119] Test No. 42 is an example in which, although various indexes derived from the composition range of each alloying element and the chemical composition are within the ranges of the present invention, the tempering temperature is less than the suitable range. In Test No. 42, temper embrittlement had occurred. From this, in Test No. 42, the absorbed energy cannot satisfy the target.

[0120] Test No. 43 is an example in which, although various indexes derived from the composition range of each alloying element and the chemical composition are within the ranges of the present invention, the tempering temperature is more than the suitable range. In Test No. 43, the precipitation quenching effect of the alloy carbides was reduced. Therefore, in Test No. 43, the middle portion hardness does not satisfy the target.

[Brief Description of the Reference Symbols]

[0121]

1	steel plate
11	thickness middle portion
12	surface layer
13	rolled surface

Claims

1. A steel plate comprising, as a chemical composition, by mass%:

C: 0.16% to 0.20%;
Si: 0.50% to 1.00%;

Mn: 0.90% to 1.50%;
P: 0.010% or less;
S: 0.0020% or less;
Cu: 0% to 0.40%;
Ni: 0.20% to 1.00%;
Cr: 0.60% to 0.99%;
Mo: 0.60% to 1.00%;
V: 0% to 0.050%;
Al: 0.050% to 0.085%;
N: 0.0020% to 0.0070%;
B: 0.0005% to 0.0020%;
Nb: 0% to 0.050%;
Ti: 0% to 0.020%;
Ca: 0% to 0.0030%;
Mg: 0% to 0.0030%;
REM: 0% to 0.0030%; and
a remainder including Fe and impurities,
wherein a total area ratio of martensite and bainite in a thickness middle portion is 99% or more,
an average value of a prior austenite grain size in the thickness middle portion is less than 80 μm,
Ceq represented by Formula (1) is 0.750% to 0.800%,
Al × N is 2.0×10^{-4} or more,
Ti/N is 3.4 or less,
a value f represented by Formula (2) and a value g represented by Formula (3) satisfy $4 \times f/g \geq 9.00$,
a -20°C Charpy absorbed energy measured in a C direction in the thickness middle portion is 47 J or more,
hardnesses of a surface layer and the thickness middle portion are HB 350 or more, and
a plate thickness of the steel plate is more than 200 mm,

$$Ceq = C + Mn/6 + (Cu + Ni)/15 + (Cr + Mo + V)/5\text{: Formula (1)}$$

$$f = 4 \times C + Si + 2 \times Mn + Ni + 2 \times Cr + 5 \times Mo\text{: Formula (2)}$$

$$g = 2 \times Cr + 3 \times Mo + 5 \times V\text{: Formula (3)}$$

where each element symbol described in each of the formulas means an amount of an element corresponding to the element symbol in unit mass%.

2. A method of manufacturing the steel plate according to claim 1, the method comprising:

heating a slab;
hot rolling the slab to obtain a steel plate having a plate thickness of more than 200 mm;
cooling the steel plate;
performing a precipitation treatment on the steel plate;
quenching the steel plate; and
tempering the steel plate,
wherein the slab includes, as a chemical composition, by unit mass%, C: 0.16% to 0.20%, Si: 0.50% to 1.00%, Mn: 0.90% to 1.50%, P: 0.010 % or less, S: 0.0020% or less, Cu: 0% to 0.40%, Ni: 0.20% to 1.00%, Cr: 0.60% to 0.99%, Mo: 0.60% to 1. 00%, V: 0% to 0.050%, Al: 0.050% to 0.085%, N: 0.0020% to 0.0070%, B: 0.0005% to 0.0020%, Nb: 0% to 0.050%, Ti: 0% to 0.020%, Ca: 0% to 0.0030%, Mg: 0% to 0.0030%, REM: 0% to 0.0030%, and a remainder including Fe and impurities, Ceq represented by Formula (1) of the slab is 0.750% to 0.800%, Al × N of the slab is 2.0×10^{-4} or more, Ti/N of the slab is 3.4 or less, and a value f of the slab represented by Formula (2) and a value g of the slab represented by Formula (3) satisfy $4 \times f/g \geq 9.00$,
a slab heating temperature in the heating the slab is equal to or more than an AlN solid solution temperature Ts (°C) calculated by Formula (4),
the precipitation treatment is performed on the steel plate by heating the steel plate to a precipitation treatment temperature Tp (°C) of more than 550°C and less than Ac1 and retaining the steel plate at this temperature for

a precipitation treatment time tp (hour), the precipitation treatment temperature Tp (°C) and the precipitation treatment time tp (hour) satisfy Formula (5), and the Ac1 is represented by Formula (7),
the quenching is performed on the steel plate by heating the steel plate to a quenching retention temperature Tq (°C) of 900°C to 950°C, retaining the steel plate at this temperature for a quenching retention time tq (minute) or more represented by Formula (6), and water cooling the steel plate, and
the tempering is performed on the steel plate by heating the steel plate to a tempering temperature of 500°C to 550°C and cooling the steel plate to 150°C or less,

$$\mathrm{Ceq} = \mathrm{C} + \mathrm{Mn}/6 + (\mathrm{Cu} + \mathrm{Ni})/15 + (\mathrm{Cr} + \mathrm{Mo} + \mathrm{V})/5\text{: Formula (1)}$$

$$\mathrm{f} = 4 \times \mathrm{C} + \mathrm{Si} + 2 \times \mathrm{Mn} + \mathrm{Ni} + 2 \times \mathrm{Cr} + 5 \times \mathrm{Mo}\text{: Formula (2)}$$

$$\mathrm{g} = 2 \times \mathrm{Cr} + 3 \times \mathrm{Mo} + 5 \times \mathrm{V}\text{: Formula (3)}$$

$$\mathrm{Ts} = 7400 / (1.95 - \log_{10}(\mathrm{Al} \times \mathrm{N})) - 273\text{: Formula (4)}$$

$$\mathrm{Log}_{10}(\mathrm{tp}) + 0.012 \times \mathrm{Tp} \geq 8.7\text{: Formula (5)}$$

$$\mathrm{tq} = 0.033 \times (950 - \mathrm{Tq})^2 + (1.5 \times \mathrm{f})^2/10\text{: Formula (6)}$$

$$\mathrm{Ac1} = 750 - 25 \times \mathrm{C} + 22 \times \mathrm{Si} - 40 \times \mathrm{Mn} - 30 \times \mathrm{Ni} + 20 \times \mathrm{Cr} + 25 \times \mathrm{Mo}\text{: Formula (7)}$$

where an each element symbol described in each of the formulas means an amount of an element corresponding to the element symbol in unit mass%.

3. The method of manufacturing the steel plate according to claim 2,
wherein, a cooling finishing temperature in the cooling the steel plate is 150°C or less.

FIG. 1

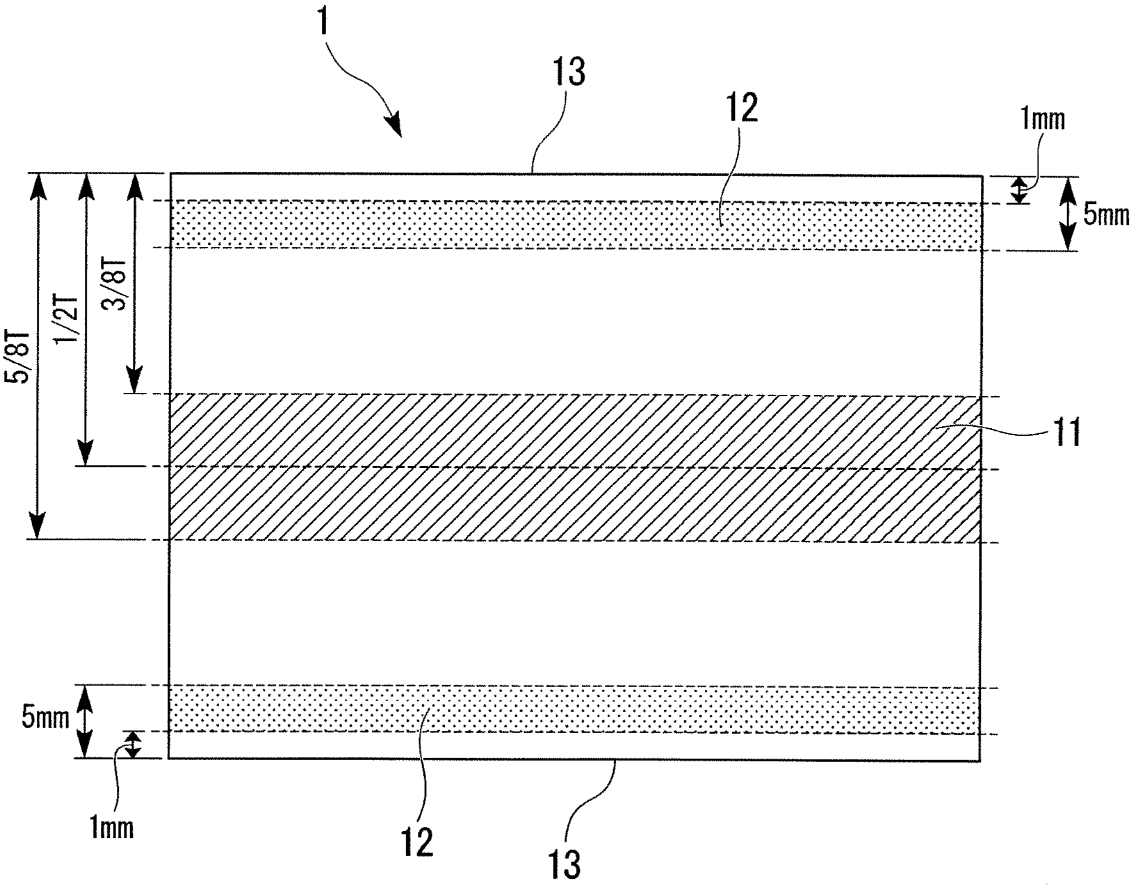


FIG. 2

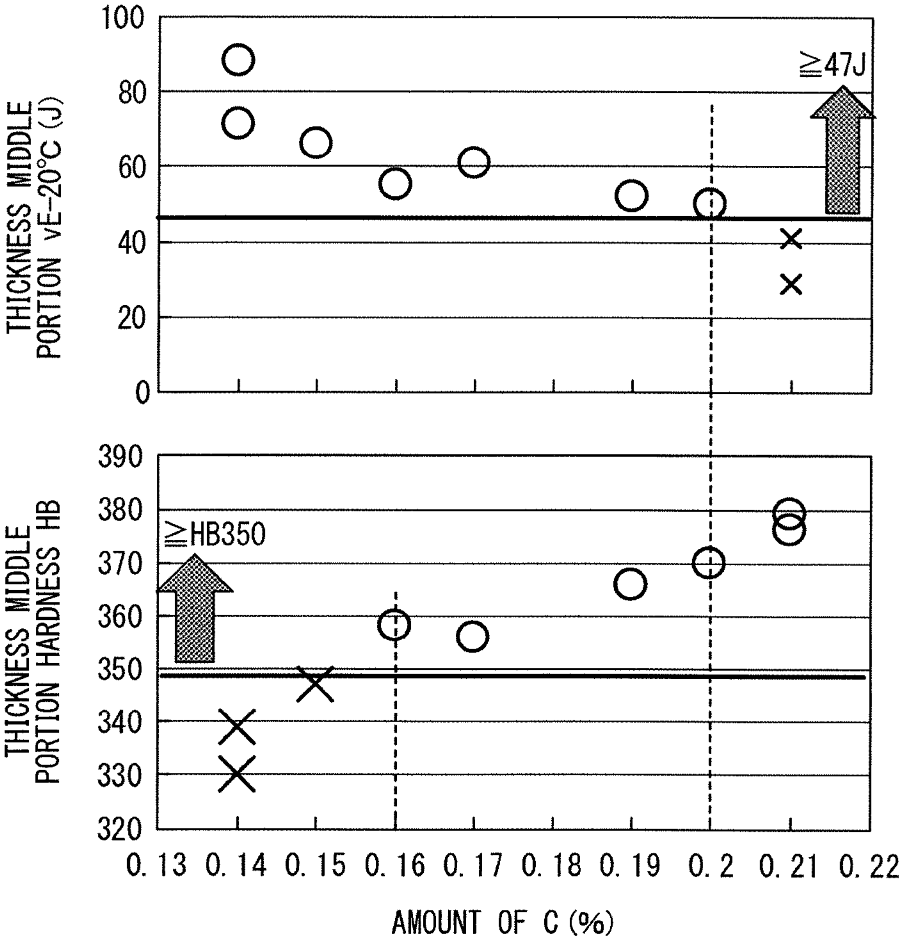

100
80
60
40
20
0
THICKNESS MIDDLE PORTION vE-20°C (J)
≧47J
390
380
370
360
350
340
330
320
THICKNESS MIDDLE PORTION HARDNESS HB
≧HB350
0.13 0.14 0.15 0.16 0.17 0.18 0.19 0.2 0.21 0.22
AMOUNT OF C (%)

FIG. 3

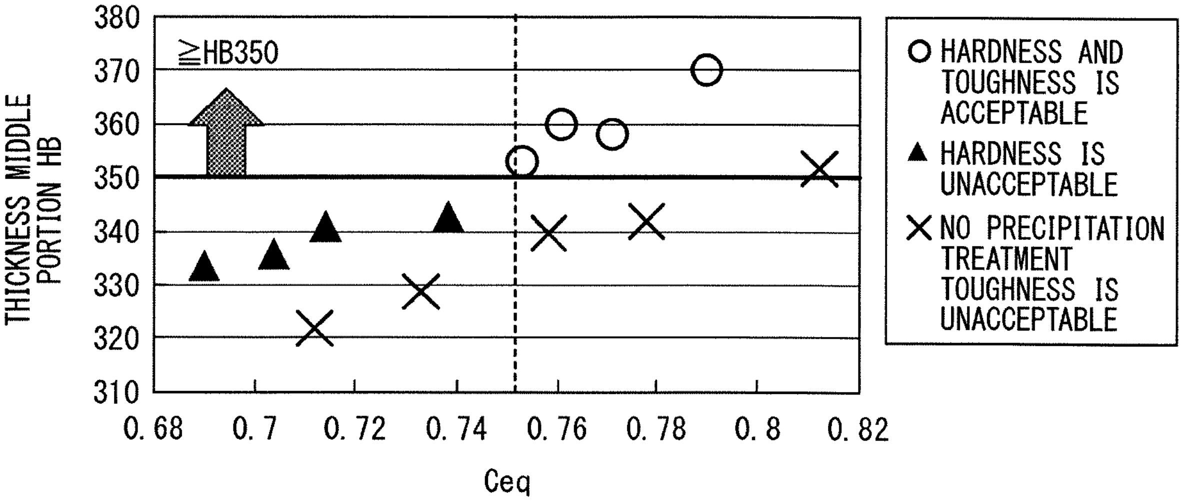

380
370
360
350
340
330
320
310
THICKNESS MIDDLE PORTION HB
≧HB350
0.68 0.7 0.72 0.74 0.76 0.78 0.8 0.82
Ceq
○ HARDNESS AND TOUGHNESS IS ACCEPTABLE
▲ HARDNESS IS UNACCEPTABLE
× NO PRECIPITATION TREATMENT TOUGHNESS IS UNACCEPTABLE

FIG. 4

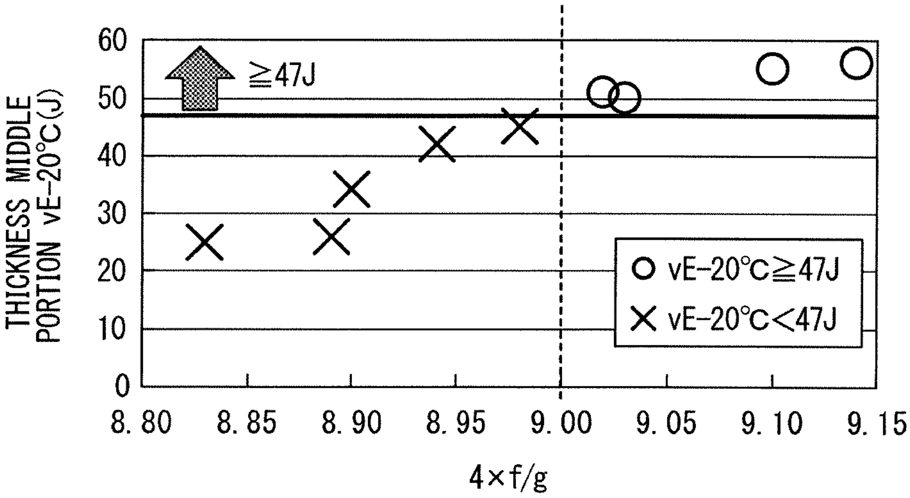

THICKNESS MIDDLE PORTION vE-20°C(J)
60
50
40
30
20
10
0
≧47J
○ vE-20°C≧47J
× vE-20°C<47J
8.80
8.85
8.90
8.95
9.00
9.05
9.10
9.15
4×f/g

FIG. 5

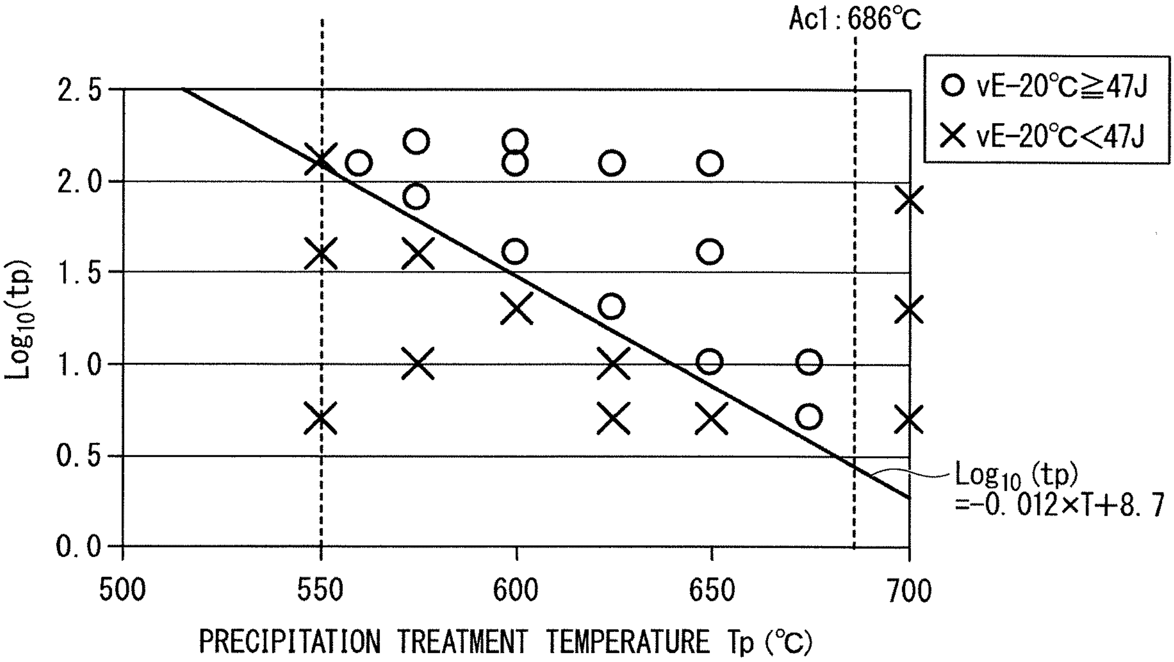

Ac1 : 686°C
○ vE-20°C≧47J
× vE-20°C<47J
Log10(tp)
2.5
2.0
1.5
1.0
0.5
0.0
500
550
600
650
700
Log10 (tp) =-0.012×T+8.7
PRECIPITATION TREATMENT TEMPERATURE Tp (°C)

FIG. 6A

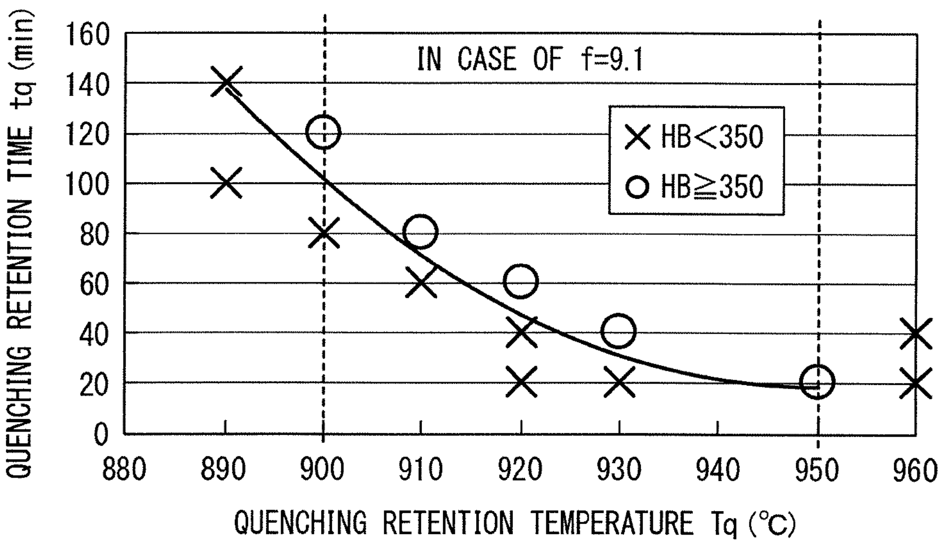

QUENCHING RETENTION TIME tq (min)
160
140
120
100
80
60
40
20
0
880
890
900
910
920
930
940
950
960
QUENCHING RETENTION TEMPERATURE Tq (℃)
IN CASE OF f=9.1
× HB<350
○ HB≧350

FIG. 6B

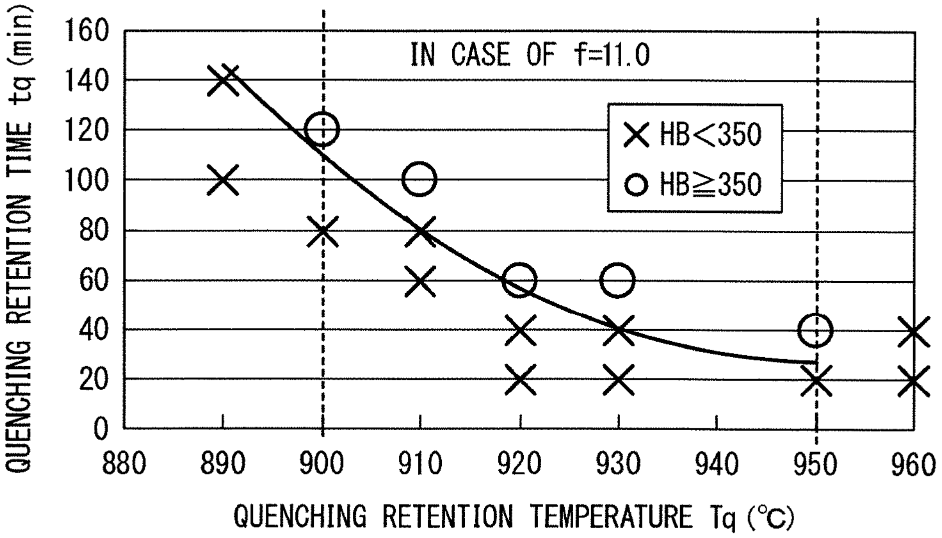
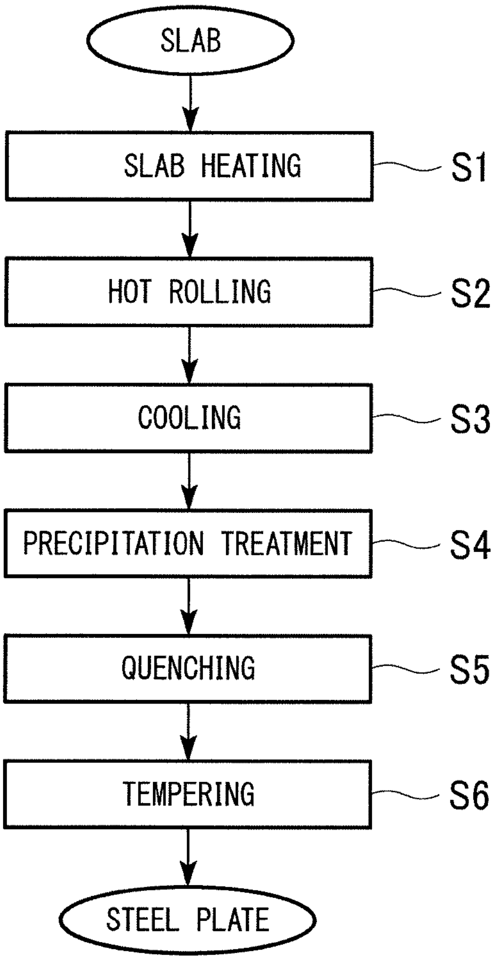

QUENCHING RETENTION TIME tq (min)
160
140
120
100
80
60
40
20
0
880
890
900
910
920
930
940
950
960
QUENCHING RETENTION TEMPERATURE Tq (℃)
IN CASE OF f=11.0
× HB<350
○ HB≧350

FIG. 7


SLAB
SLAB HEATING
S1
HOT ROLLING
S2
COOLING
S3
PRECIPITATION TREATMENT
S4
QUENCHING
S5
TEMPERING
S6
STEEL PLATE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/030676

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl. C22C38/00(2006.01)i, C21D8/02(2006.01)i, C22C38/54(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl. C22C38/00-38/60, C21D8/02

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2017-186592 A (NIPPON STEEL & SUMITOMO METAL CORP.) 12 October 2017 (Family: none)	1-3
A	WO 2016/079978 A1 (JFE STEEL CORP.) 26 May 2016 & US 2018/0155805 A1 & EP 3222744 A1 & KR 10-2017-0066612 A & CN 107109561 A	1-3
A	JP 2016-79425 A (NIPPON STEEL & SUMITOMO METAL CORP.) 16 May 2016 (Family: none)	1-3

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

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

Date of the actual completion of the international search
24.10.2018

Date of mailing of the international search report
06.11.2018

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)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2017186592 A **[0007]**