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(54) **STEEL SHEET AND METHOD FOR PRODUCING SAME**

(57) A high strength steel plate having excellent ammonia SCC resistance and low-temperature toughness for use in storage tanks and the like used to contain liquefied gas in energy transport ships. The steel plate has a defined chemical composition and has hardness properties such that, at a 0.5 mm depth position from the surface of the steel plate, average hardness is 210 HV or less and variation of the average hardness is 50 HV or

less, and a metallic microstructure where, at a 0.5 mm depth position from the surface of the steel plate, a volume fraction of bainitic microstructure is 90 % or more and, at a 1/2 thickness position of the steel plate, a volume fraction of bainitic microstructure is 20 % or more and a total volume fraction of ferritic microstructure and bainitic microstructure is 60 % or more.

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Description

TECHNICAL FIELD

5 **[0001]** The present disclosure relates to a high strength steel plate that has excellent toughness and corrosion resistance, in particular a high strength steel plate that has excellent low-temperature toughness and liquid ammonia stress corrosion cracking resistance, suitable for structural parts such as tanks used at low temperatures and in liquid ammonia environments, and a method of producing same.

10 BACKGROUND

[0002] With the increase in energy demand in recent years, liquefied gas is being increasingly transported by energy transport ships. For efficient operation of energy transport ships, tanks may carry liquid ammonia as well as liquefied petroleum gas (LPG).

15 **[0003]** Liquid ammonia is known to cause stress corrosion cracking (hereinafter also referred to as ammonia SCC) in carbon steel pipes, storage tanks, tank cars, line pipes, and the like that handle liquid ammonia. For this reason, for steel materials used in liquid ammonia environments, steel materials having low ammonia SCC susceptibility have been applied, and engineering measures have been taken to suppress ammonia SCC.

20 **[0004]** For example, occurrence of ammonia SCC is known to be correlated with the strength of the material. When using carbon steel, stress corrosion cracking due to ammonia may be avoided by controlling yield stress (YS) to 440 MPa or less. On the other hand, from the perspective of increasing tank size and reducing the amount of steel material used, in recent years there has been an increasing demand for higher strength steel plates.

[0005] Further, liquefied gases such as LPG and liquid ammonia are transported at low temperatures, and therefore steel plates used for storage tanks for such liquefied gases are required to have excellent low-temperature toughness.

25 **[0006]** Technologies for meeting the low-temperature toughness and strength ranges required for liquefied gas storage tanks such as those mentioned above are described in Patent Literature (PTL) 1 and 2. According to the technologies described therein, high low-temperature toughness and defined strength properties are achieved by heat treatment applied multiple times to a steel plate cooled after hot rolling or by heat treatment applied multiple times to a steel plate water cooled after hot rolling.

30

CITATION LIST

Patent Literature

35 **[0007]**

PTL 1: JP H10-140235 A

PTL 2: JP H10-168516 A

40 SUMMARY

(Technical Problem)

45 **[0008]** However, the methods described in PTL 1 and 2 require multiple heat treatments and therefore have an economic problem in that the cost of the equipment and energy required for these treatments is high.

[0009] It would be helpful to solve the technical problem described above and to provide a high strength steel plate that has excellent ammonia SCC resistance and low-temperature toughness for use in storage tanks and the like used to contain liquefied gas in energy transport ships, and a method of producing same.

50 (Solution to Problem)

[0010] In order to achieve the above, the inventors have conducted extensive studies into various factors affecting low-temperature toughness and strength properties of steel plates using a thermo-mechanical control process (TMCP). As a result, the inventors discovered that adding elements such as C, Si, Mn, and N to a steel plate in defined amounts or more and controlling the metallic structure (microstructure) of a steel plate so that the total volume fraction of ferritic microstructure and bainitic microstructure at a 1/2 thickness position of the steel plate is 60 % or more can effectively contribute to achieving desired low-temperature toughness and strength properties.

[0011] Further, the inventors discovered that by controlling the microstructure so that the volume fraction of bainitic

microstructure at a 0.5 mm depth position from the surface of the steel plate is 90 % or more and the average hardness at a 0.5 mm depth position from the surface of the steel plate is 210 HV or less, and by controlling the variation of the average hardness to 50 HV or less, SCC resistance in liquid ammonia environments can be obtained and costly heat treatment as in conventional technology can be eliminated.

[0012] That is, the present disclosure is based on the above discoveries, and the following is a summary of the present disclosure.

1. A steel plate comprising a chemical composition containing (consisting of), in mass%,

C: 0.010 % to 0.200 %,
Si: 0.01 % to 0.50 %,
Mn: 0.50 % to 2.50 %,
Al: 0.060 % or less,
N: 0.0010 % to 0.0100 %,
P: 0.020 % or less,
S: 0.0100 % or less, and
O: 0.0100 % or less,

with the balance being Fe and inevitable impurity, wherein

the steel plate has hardness properties such that, at a 0.5 mm depth position from the surface of the steel plate, average hardness is 210 HV or less and variation of the average hardness is 50 HV or less, and the steel plate has a metallic microstructure where, at a 0.5 mm depth position from the surface of the steel plate, a volume fraction of bainitic microstructure is 90 % or more and, at a 1/2 thickness position of the steel plate, a volume fraction of bainitic microstructure is 20 % or more and a total volume fraction of ferritic microstructure and bainitic microstructure is 60 % or more.

2. The steel plate according to 1, above, wherein the chemical composition further contains, in mass%, at least one selected from the group consisting of

Cu: 0.01 % to 0.50 %,
Ni: 0.01 % to 2.00 %,
Cr: 0.01 % to 1.00 %,
Sn: 0.01 % to 0.50 %,
Sb: 0.01 % to 0.50 %,
Mo: 0.01 % to 0.50 % and,
W: 0.01 % to 1.00 %.

3. The steel plate according to 1 or 2, above, wherein the chemical composition further contains, in mass%, at least one selected from the group consisting of

V: 0.01 % to 1.00 %,
Ti: 0.005 % to 0.100 %,
Co: 0.01 % to 1.00 %,
Nb: 0.005 % to 0.100 %,
B: 0.0001 % to 0.0100 %,
Ca: 0.0005 % to 0.0200 %,
Mg: 0.0005 % to 0.0200 %, and
REM: 0.0005 % to 0.0200 %.

4. A method of producing a steel plate, the method applied to a steel material comprising a chemical composition containing (consisting of), in mass%,

C: 0.010 % to 0.200 %,
Si: 0.01 % to 0.50 %,
Mn: 0.50 % to 2.50 %,
Al: 0.060 % or less,
N: 0.0010 % to 0.0100 %,
P: 0.020 % or less,
S: 0.0100 % or less, and

O: 0.0100 % or less,
with the balance being Fe and inevitable impurity, the method comprising:

hot rolling with a rolling finish temperature that is Ar_3 transformation temperature or more; followed by primary cooling from a cooling start temperature that is the Ar_3 transformation temperature or more; followed by surface heating by recuperation; and followed by secondary cooling, wherein,
in the primary cooling, cooling rate from 600 °C to 400 °C at a 0.5 mm depth position from the surface of the steel plate is 30 °C/s to 100 °C/s,
the surface heating by recuperation occurs until end-point temperature at a 0.5 mm depth position from the steel plate surface is 500 °C or more, and
in the secondary cooling, at a 1/2 thickness position of the steel plate, cooling rate to a cooling stop temperature of 600 °C or less is 10 °C/s or more.

5. The method of producing a steel plate according to 4, above, wherein the chemical composition of the steel material further contains, in mass%, at least one selected from the group consisting of

Cu: 0.01 % to 0.50 %,
Ni: 0.01 % to 2.00 %,
Cr: 0.01 % to 1.00 %,
Sn: 0.01 % to 0.50 %,
Sb: 0.01 % to 0.50 %,
Mo: 0.01 % to 0.50 % and,
W: 0.01 % to 1.00 %.

6. The method of producing a steel plate according to 4 or 5, above, wherein the chemical composition of the steel material further contains, in mass%, at least one selected from the group consisting of

V: 0.01 % to 1.00 %,
Ti: 0.005 % to 0.100 %,
Co: 0.01 % to 1.00 %,
Nb: 0.005 % to 0.100 %,
B: 0.0001 % to 0.0100 %,
Ca: 0.0005 % to 0.0200 %,
Mg: 0.0005 % to 0.0200 %, and
REM: 0.0005 % to 0.0200 %.

(Advantageous Effect)

[0013] According to the present disclosure, a steel plate having low-temperature toughness, that is, excellent anti-crash property and ammonia SCC resistance at low temperatures, and high strength suitable for structural parts such as tanks used at low temperatures and in liquid ammonia environments, can be provided by an inexpensive process.

DETAILED DESCRIPTION

[0014] The following is a description of an embodiment of the present disclosure. Hereinafter, "%" representing the content of a component (element) means "mass%" unless otherwise specified.

(1) Chemical composition

[0015] The following describes composition (chemical composition) of a steel plate.

C: 0.010 % to 0.200 %

[0016] C is the most effective element for increasing the strength of the steel plate produced by cooling according to the present disclosure. To obtain this effect, C content is specified as 0.010 % or more. Further, from the viewpoint of production at lower cost by reducing content of other alloying elements, the C content is preferably 0.013 % or more. However, the C content exceeding 0.200 % leads to deterioration of toughness and weldability of the steel plate. Therefore, the C content is specified as 0.200 % or less. Further, from the viewpoint of toughness and weldability, the C content is

preferably 0.170 % or less.

Si: 0.01 % to 0.50 %

5 **[0017]** Si is added for deoxidation. To obtain this effect, Si content is specified as 0.01 % or more. Further, 0.03 % or more is preferred. However, the Si content exceeding 0.50 % leads to deterioration of toughness and weldability of the steel plate. Therefore, the Si content is specified as 0.50 % or less. Further, from the viewpoint of toughness and weldability, the Si content is preferably 0.40 % or less.

10 Mn: 0.50 % to 2.50 %

[0018] Mn is an element that acts to increase hardenability of steel and is one of the key elements that need to be added to meet high strength requirements as in the present disclosure. To obtain this effect, Mn content is specified as 0.50 % or more. Further, from the viewpoint of producing at lower cost by reducing content of other alloying elements, the Mn content is preferably 0.70 % or more. However, the Mn content exceeding 2.50 % decreases weldability and toughness of the steel plate, and also excessively increases alloy cost. The Mn content is therefore specified as 2.50 % or less. Further, from the viewpoint of further suppressing a decrease in toughness and weldability, the Mn content is preferably 2.30 % or less.

Al: 0.060 % or less

20 **[0019]** Al is an element that acts as a deoxidizer and has an effect of refining crystal grains. To obtain these effects, Al content is preferably 0.001 % or more. However, the Al content exceeding 0.060 % increases oxide-based inclusions, decreases cleanliness, and decreases toughness. The Al content is therefore specified as 0.060 % or less. Further, from the viewpoint of further preventing toughness degradation, the Al content is preferably 0.050 % or less.

25 N: 0.0010 % to 0.0100 %

[0020] N contributes to microstructure refinement and improves toughness of the steel plate. To obtain these effects, N content is specified as 0.0010 % or more. The content is preferably 0.0020 % or more. However, the N content exceeding 0.0100 % instead leads to a reduction in toughness. The N content is therefore specified as 0.0100 % or less. Further, from the viewpoint of further suppressing a decrease in toughness and weldability, the N content is preferably 0.0080 % or less. N can combine with Ti, when present, and precipitate as TiN.

P: 0.020 % or less

35 **[0021]** P has adverse effects such as decreasing toughness and weldability due to segregation at grain boundaries. Accordingly, P content is desirably as low as possible, but 0.020 % or less is allowable. A lower limit of the P content is not particularly limited and may be 0 %. Excessive reduction leads to higher refining costs, and therefore from a cost perspective, the P content is preferably 0.0005 % or more.

40 S: 0.0100 % or less

[0022] S is an element that exists in steel as sulfide inclusions such as MnS and has adverse effects such as decreasing toughness of the steel plate by becoming an initiation point for fractures. Accordingly, S content is desirably as low as possible, but 0.0100 % or less is allowable. A lower limit of the S content is not particularly limited and may be 0 %. Excessive reduction leads to higher refining costs, and therefore from a cost perspective, the S content is preferably 0.0005 % or more.

50 O: 0.0100 % or less

[0023] O is an element that forms oxides and has adverse effects such as becoming an initiation point for fractures and reducing toughness of the steel plate, and is therefore limited to 0.0100 % or less. O content is preferably 0.0050 % or less. The O content is more preferably 0.0030 % or less. A lower limit of the O content is not particularly limited and may be 0 %. Excessive reduction leads to higher refining costs, and therefore from a cost perspective, the O content is preferably 0.0010 % or more.

[0024] In the chemical composition of the steel plate, the balance other than the above components is Fe and inevitable impurity. However, the chemical composition may contain the elements listed below as required.

[0025] At least one selected from the group consisting of Cu: 0.01 % to 0.50 %, Ni: 0.01 % to 2.00 %, Cr: 0.01 % to 1.00 %, and

Sn: 0.01 % to 0.50 %, Sb: 0.01 % to 0.50 %, Mo: 0.01 % to 0.50 %, and W: 0.01 % to 1.00 %

[0026] Cu, Ni, Cr, Sn, Sb, Mo, and W are elements that improve strength and ammonia SCC resistance, and one or more of these elements may be included. To achieve these effects, it is preferable that when Cu is contained, Cu content is 0.01 % or more, when Ni is contained, Ni content is 0.01 % or more, when Cr is contained, Cr content is 0.01 % or more, when Sn is contained, Sn content is 0.01 % or more, when Sb is contained, Sb content is 0.01 % or more, when Mo is contained, Mo content is 0.01 % or more, and when W is contained, W content is 0.01 % or more. However, excessive Ni content leads to deterioration of weldability and higher alloy cost. Further, excessive Cu, Cr, Sn, Sb, Mo, and W degrade weldability and toughness, and are detrimental in view of alloy cost. Accordingly, it is preferable that the Cu content is 0.50 % or less, the Ni content is 2.00 % or less, the Cr content is 1.00 % or less, the Sn content is 0.50 % or less, the Sb content is 0.50 % or less, the Mo content is 0.50 % or less, and the W content is 1.00 % or less. More preferably, the Cu content is 0.40 % or less, the Ni content is 1.50 % or less, the Cr content is 0.80 % or less, the Sn content is 0.40 % or less, the Sb content is 0.40 % or less, the Mo content is 0.40 % or less, and the W content is 0.80 % or less.

V: 0.01 % to 1.00 %

[0027] V is an element that has an effect of improving strength of the steel plate and may be added. To obtain this effect, when V is added, V content is preferably 0.01 % or more. However, the V content exceeding 1.00 % leads to deterioration in weldability and higher alloy cost. Accordingly, when V is added, the V content is preferably 1.00 % or less. The lower limit of the V content is more preferably 0.05 %. The upper limit of the V content is more preferably 0.50 %.

Ti: 0.005 % to 0.100 %

[0028] Ti is an element that has a strong tendency to form nitrides, acting to fix N and reduce solute N, and may be added. Further, Ti can improve toughness of the base metal and welded portion. To obtain these effects, when Ti is added, Ti content is preferably 0.005 % or more. Further, 0.007 % or more is more preferred. However, the Ti content exceeding 0.100 % instead reduces toughness. Accordingly, when Ti is added, the Ti content is preferably 0.100 % or less. Further, the Ti content is more preferably 0.090 % or less.

Co: 0.01 % to 1.00 %

[0029] Co is an element that has an effect of improving strength of the steel plate and may be added. To obtain this effect, when Co is added, Co content is preferably 0.01 % or more. However, the Co content exceeding 1.00 % leads to deterioration in weldability and higher alloy cost. Accordingly, when Co is added, the Co content is preferably 1.00 % or less. The lower limit of the Co content is more preferably 0.05 %. The upper limit of the Co content is more preferably 0.50 %.

Nb: 0.005 % to 0.100 %

[0030] Nb is an element that has an effect of reducing prior austenite grain size and improving toughness by precipitating as carbonitride. To obtain this effect, when Nb is added, Nb content is preferably 0.005 % or more. Further, 0.007 % or more is more preferred. However, the Nb content exceeding 0.100 % leads to a large amount of NbC precipitates and a reduction in toughness. Accordingly, when Nb is added, the Nb content is preferably 0.100 % or less. Further, 0.060 % or less is more preferred.

B: 0.0001 % to 0.0100 %

[0031] B is an element that has an effect of significantly improving hardenability even with an addition of a trace amount. That is, strength of the steel plate can be improved. To achieve this effect, when B is added, B content is preferably 0.0001 % or more. However, B content exceeding 0.0100 % decreases weldability. Accordingly, when B is added, the B content is preferably 0.0100 % or less. The lower limit of the B content is more preferably 0.0010 %. The upper limit of the B content is more preferably 0.0030 %.

Ca: 0.0005 % to 0.0200 %

[0032] Ca is an element that combines with S and has an effect of inhibiting the formation of MnS and the like that extend long in the rolling direction. That is, the addition of Ca can provide morphological control on sulfide inclusions so that the sulfide inclusions may have a spherical shape, improving toughness of a welded portion and the like. To obtain this effect, when Ca is added, Ca content is preferably 0.0005 % or more. However, the Ca content exceeding 0.0200 % decreases

cleanliness of steel. A decrease in cleanliness leads to a decrease in toughness. Accordingly, when Ca is added, the Ca content is preferably 0.0200 % or less. The lower limit of the Ca content is more preferably 0.0020 %. The upper limit of the Ca content is more preferably 0.0100 %.

5 Mg: 0.0005 % to 0.0200 %

[0033] Mg, like Ca, is an element that combines with S and has an effect of inhibiting the formation of MnS and the like that extend long in the rolling direction. That is, the addition of Mg can provide morphological control on sulfide inclusions so that the sulfide inclusions may have a spherical shape, improving toughness of a welded portion and the like. To obtain this effect, when Mg is added, Mg content is preferably 0.0005 % or more. However, the Mg content exceeding 0.0200 % decreases cleanliness of steel. A decrease in cleanliness leads to a decrease in toughness. Accordingly, when Mg is added, the Mg content is preferably 0.0200 % or less. The lower limit of the Mg content is more preferably 0.0020 %. The upper limit of the Mg content is more preferably 0.0100 %.

15 REM: 0.0005 % to 0.0200 %

[0034] Rare earth metals (REM), as with Ca and Mg, are elements that combine with S and have an effect of inhibiting the formation of MnS and the like that extend long in the rolling direction. That is, the addition of REM can provide morphological control on sulfide inclusions so that the sulfide inclusions may have a spherical shape, improving toughness of a welded portion and the like. To obtain this effect, when REM is added, REM content is preferably 0.0005 % or more. However, the REM content exceeding 0.0200 % decreases cleanliness of steel. A decrease in cleanliness leads to a decrease in toughness. Accordingly, when REM is added, the REM content is preferably 0.0200 % or less. The lower limit of the REM content is more preferably 0.0020 %. The upper limit of the REM content is more preferably 0.0100 %.

25 (2) Hardness properties and metallic microstructure

[0035] In addition to having the chemical composition described above, the steel plate has hardness properties such that, at a 0.5 mm depth position from the surface of the steel plate (hereinafter also referred to as a 0.5 mm position), average hardness is 210 HV or less and variation of the average hardness is 50 HV or less.

30 **[0036]** Further, at the 0.5 mm position, the steel plate has a volume fraction of bainitic microstructure (hereinafter also referred to simply as bainite) of 90 % or more. Further, at a 1/2 thickness position of the steel plate (hereinafter meaning a position at 1/2 the depth of the plate thickness, also referred to simply as a 1/2 position or mid-thickness part), the steel plate has a volume fraction of bainite of 20 % or more and a total volume fraction of ferritic microstructure (hereinafter also referred to simply as ferrite) and bainite of 60 % or more.

35 **[0037]** The reasons for limiting the hardness properties and metallic microstructure of the steel plate as described above are explained below.

[At 0.5 mm position, average hardness 210 HV or less and variation of the average hardness 50 HV or less]

40 **[0038]** The average hardness at the 0.5 mm position is 210 HV or less and the variation of the average hardness is 50 HV or less. The presence of a high hardness region in the outermost surface layer of the steel plate, specifically at the 0.5 mm position from the surface of the steel plate, promotes stress corrosion cracking in a liquid ammonia environment. Further, when localized regions of high hardness are present, stress concentration occurs when stress is applied to the steel plate and stress corrosion cracking is promoted. Therefore, in the steel plate of the present disclosure, the average hardness at the 0.5 mm position is 210 HV or less and the variation of the hardness property is adjusted to 50 HV or less, in order to secure excellent ammonia SCC resistance. A lower limit of average hardness at the 0.5 mm position is not particularly limited. The lower limit of average hardness at the 0.5 mm position is preferably about 130 HV. A lower limit of variation of the average hardness may be 0 HV. Industrially, the lower limit of variation of the average hardness is about 10 HV.

45 **[0039]** Here, the average hardness can be calculated by measuring Vickers hardness at multiple locations (for example, 100 points) at the 0.5 mm position. Further, the variation of the average hardness means the standard deviation of the Vickers hardness measured to obtain the average hardness.

[Volume fraction of bainite at 0.5 mm position 90 % or more]

55 **[0040]** To satisfy strength properties and ammonia SCC resistance, the microstructure at the 0.5 mm position is required to have a bainite volume fraction of 90 % or more. In the surface layer, when hard phases such as martensitic microstructure, martensite austenite constituent (MA) microstructure, and the like are formed, the surface layer hardness increases, increasing the variation of hardness within the steel plate and hindering material homogeneity. That is, when the

volume fraction of bainite is less than 90 %, the volume fraction of other microstructure, namely ferrite, martensite austenite constituent microstructure, martensitic microstructure, pearlitic microstructure, and austenitic microstructure increases, and sufficient strength and/or ammonia SCC resistance are not obtained.

[0041] Here, bainite includes bainitic ferrite or microstructure referred to as granular ferrite, and tempered microstructure thereof, which transforms during or after cooling, contributing to transformation strengthening.

[0042] Residual microstructure, which accounts for 10 % or less by volume fraction, may include ferrite, pearlitic microstructure and austenitic microstructure, as well as martensitic microstructure. The fraction of each microstructure in the residual microstructure need not be particularly limited. The residual microstructure is preferably pearlitic microstructure.

[Volume fraction of bainite 20 % or more and total volume fraction of ferrite and bainite 60 % or more at 1/2 position]

[0043] The microstructure at the 1/2 position is required to have a volume fraction of bainite of 20 % or more and a total volume fraction of ferrite and bainite of 60 % or more. Excessive ferrite formation leads to a reduction in strength or toughness. Further, when the total volume fraction of ferrite and bainite is less than 60 %, the volume fraction of other microstructure, namely martensite austenite constituent microstructure, martensitic microstructure, pearlitic microstructure, and austenitic microstructure increases, sufficient strength or toughness is not obtained, and mechanical properties are unsatisfactory. The total volume fraction of ferrite and bainite may be 100 %.

[0044] Here, ferrite means ferrite formed during a cooling process before tempering, and bainite means bainite formed during a cooling process before tempering. Further, microstructure at the mid-thickness part is specified because the microstructure at the mid-thickness part affects the strength properties of the mid-thickness part, and the strength properties of the mid-thickness part affects the strength properties of the entire steel plate.

[0045] Residual microstructure, which accounts for 40 % or less by volume fraction, may include pearlitic microstructure and austenitic microstructure, as well as martensitic microstructure. The fraction of each microstructure in the residual microstructure need not be particularly limited. The residual microstructure is preferably pearlitic microstructure.

[0046] The volume fraction of each microstructure can be measured by a method described in the EXAMPLES section below.

(3) Production conditions

[0047] The method of production according to the present disclosure is applied to a steel material comprising a chemical composition containing C: 0.010 % to 0.200 %, Si: 0.01 % to 0.50 %, Mn: 0.50 % to 2.50 %, Al: 0.060 % or less, N: 0.0010 % to 0.0100 %, P: 0.020 % or less, S: 0.0100 % or less, and O: 0.0100 % or less, and further, as required, at least one selected from the group consisting of Cu: 0.01 % to 0.50 %, Ni: 0.01 % to 2.00 %, Cr: 0.01 % to 1.00 %, Sn: 0.01 % to 0.50 %, Sb: 0.01 % to 0.50 %, Mo: 0.01 % to 0.50 %, and W: 0.01 % to 1.00 %, and/or at least one selected from the group consisting of V: 0.01 % to 1.00 %, Ti: 0.005 % to 0.100 %, Co: 0.01 % to 1.00 %, Nb: 0.005 % to 0.100 %, B: 0.0001 % to 0.0100 %, Ca: 0.0005 % to 0.0200 %, Mg: 0.0005 % to 0.0200 %, and REM: 0.0005 % to 0.0200 %, with the balance being Fe and inevitable impurity. The steel material is heated and hot rolled, followed by cooling defined according to the present disclosure. The following explains the reasons for limiting the production conditions of the steel plate.

[0048] First, the conditions for producing the steel material need not be particularly limited. For example, molten steel having the chemical composition described above is preferably melted by a known melting method such as a converter and a known casting method such as continuous casting is preferably used to make steel material such as slabs of defined dimensions. Further, there is no problem in making a slab or other steel material having defined dimensions by ingot casting and blooming.

[0049] The steel material thus obtained is either hot rolled directly without cooling or reheated before hot rolling. The hot rolling is performed with the rolling finish temperature as the Ar_3 transformation point temperature (hereinafter also referred to simply as the Ar_3 transformation temperature) or more. Following hot rolling, primary cooling is performed under defined conditions to cool from a cooling start temperature that is the Ar_3 transformation temperature or more, followed by surface heating by recuperation under defined conditions, followed by secondary cooling under defined conditions.

[0050] The heating temperature of the steel material (the temperature at which the steel material is subjected to hot rolling) is not particularly limited, but when the heating temperature is too low, deformation resistance may increase, increasing the load on the hot rolling mill and making hot rolling difficult. On the other hand, at temperatures exceeding 1300 °C, oxidation becomes more significant, oxidation losses increase, and the risk of a decrease in throughput yield increases. For such reasons, the heating temperature is preferably 950 °C or more and 1300 °C or less.

(Hot rolling)

[Rolling finish temperature: A_{r3} transformation temperature or more]

[0051] According to the present disclosure, hot rolling is started after heating to the temperature described above, and the hot rolling finishes at the A_{r3} transformation temperature or more.

[0052] When the rolling finish temperature is less than the A_{r3} transformation temperature, ferrite is formed, which hinders material homogeneity in the surface layer of the steel plate and increases hardness variation, resulting in deterioration of ammonia SCC resistance. Further, formed ferrite will be affected by machining, and therefore toughness deteriorates. Further, the load on the hot rolling mill increases. Accordingly, the rolling finish temperature in the hot rolling is the A_{r3} transformation temperature or more. More preferably, the rolling finish temperature in the hot rolling is the A_{r3} transformation temperature + 10 °C or more. However, the rolling finish temperature exceeding 950 °C risks coarsening the microstructure and deteriorating toughness, and therefore the rolling finish temperature is preferably 950 °C or less.

[0053] Here, the A_{r3} transformation temperature is obtainable by the following expression.

$$A_{r3} (°C) = 910 - 310 \times C - 80 \times Mn - 20 \times Cu - 15 \times Cr - 55 \times Ni - 80 \times Mo$$

[0054] Here, each element indicates the content (mass%) of the element in the steel.

(Primary cooling)

[Cooling start temperature: A_{r3} transformation temperature or more]

[0055] Next, primary cooling is performed on the steel plate after the hot rolling to cool from the cooling start temperature that is the A_{r3} transformation temperature or more. When the cooling start temperature in primary cooling is less than the A_{r3} transformation temperature, ferrite forms excessively, resulting in insufficient strength and further deterioration of ammonia SCC resistance. The cooling start temperature is therefore the A_{r3} transformation temperature or more.

[Cooling rate from 600 °C to 400 °C at 0.5 mm position: 30 °C/s to 100 °C/s]

[0056] In the primary cooling, the cooling rate in a range from 600 °C to 400 °C at the 0.5 mm position (also sometimes referred to as the primary cooling rate) exceeding 100 °C/s causes the average hardness at the 0.5 mm position to exceed 210 HV and the ammonia SCC resistance to deteriorate. On the other hand, at less than 30 °C/s, ferrite and pearlite may form, leading to degradation of ammonia SCC resistance due to loss of material homogeneity. Further, at less than 30 °C/s, excessive ferrite and pearlite may form, leading to insufficient strength. Therefore, the primary cooling rate is specified as 30 °C/s to 100 °C/s.

[0057] The primary cooling rate can be controlled by controlled cooling with intermittent cooling including cooling stop periods. Further, the temperature at the 0.5 mm depth position from the surface of the steel plate is difficult to physically measure directly. However, the temperature distribution in a thickness cross-section, in particular at the 0.5 mm position, can be determined in real time by performing a differential calculation using a process computer, for example, based on the surface temperature at the start of cooling and the surface temperature at the target cooling stop, as measured by a radiation thermometer.

(Surface heating by recuperation)

[End-point temperature at 0.5 mm position: 500 °C or more]

[0058] After the primary cooling, cooling is temporarily stopped and the steel plate surface is heated by recuperation. The surface heating by recuperation occurs until the end-point temperature at the 0.5 mm depth position from the surface of the steel plate is 500 °C or more. Martensite or bainite microstructure formed in the surface layer is tempered by recuperation from the mid-thickness part due to the cooling stop. When the end-point temperature (recuperative temperature) at the 0.5 mm position is less than 500 °C, the tempering effect is insufficient, resulting in high hardness of the surface layer and deterioration of ammonia SCC resistance due to lack of material homogeneity. An upper limit of the end-point temperature at the 0.5 mm position is not particularly limited, and may be 700 °C or less, for example.

(Secondary cooling)

[Cooling stop temperature at 1/2 position: 600 °C or less]

5 **[0059]** After heating the steel plate surface due to the recuperation described above, cooling is resumed, that is, secondary cooling is performed. The secondary cooling is performed until the temperature at the 1/2 position drops to 600 °C or less. According to the present disclosure, after the hot rolling finishes, the secondary cooling is performed under defined conditions to any cooling stop temperature of 600 °C or less to bring ferrite and bainite microstructure to a defined volume fraction at the mid-thickness part. Here, when the cooling stop temperature exceeds 600 °C, excessive ferritic
10 microstructure and pearlitic microstructure may form, resulting in insufficient strength. Accordingly, the cooling stop temperature is specified as 600 °C or less. A lower limit of the cooling stop temperature is not particularly limited, but when the cooling stop temperature is excessively low, the volume fraction of martensite austenite constituent becomes too high and toughness is reduced. The cooling stop temperature is therefore preferably 200 °C or more.

15 [Cooling rate to cooling stop temperature of 600 °C or less at 1/2 position: 10 °C/s or more]

[0060] As the cooling rate during the secondary cooling, the cooling rate to the cooling stop temperature of 600 °C or less at the 1/2 position (sometimes referred to as the secondary cooling rate) is 10 °C/s or more so that ferrite or bainite reaches a defined volume fraction. When the secondary cooling rate is less than 10 °C/s, excessive ferrite and pearlite may form,
20 resulting in insufficient strength. An upper limit of the secondary cooling rate is not particularly limited, and may be 65 °C/s or less, for example.

[0061] Here, the cooling start temperature in the secondary cooling (cooling start temperature at the 1/2 position) can typically be the temperature at the 1/2 position immediately after heating of the surface due to recuperation.

[0062] The secondary cooling rate can be controlled by controlled cooling by intermittent cooling including cooling stop
25 periods. The temperature at the 1/2 position is difficult to physically measure directly. However, the temperature distribution in a thickness cross-section, in particular at the 1/2 position, can be determined in real time by performing a differential calculation using a process computer, for example, based on the surface temperature at the start of cooling and the surface temperature at the target cooling stop, as measured by a radiation thermometer.

[0063] By producing the steel material having the chemical composition described above and according to the
30 production conditions described above, the steel plate having the chemical composition, hardness properties, and metallic structure according to the present invention is obtainable. The steel plate thus obtained has excellent strength properties and toughness. Here, excellent strength properties are defined as yield stress YS (yield point YP when present, otherwise 0.2 % proof stress $\sigma_{0.2}$): 360 MPa or more and tensile strength (TS): 490 MPa or more. Further, excellent toughness is defined as $vTrs$ of -30 °C or less in accordance with Japanese Industrial Standard JIS Z 2241.

35 **[0064]** In the method of production according to the present disclosure, anything not described herein may be a conventional method.

EXAMPLES

40 **[0065]** Steels having the chemical compositions listed in Table 1 (steel sample IDs A to AH), the balance of each being Fe and inevitable impurity, were made into slabs by a continuous casting method, which were then used to make steel plates (No. 1 to 50) each having a thickness of 25 mm. Then, the hot rolling, the primary cooling, the surface heating by recuperation, and the secondary cooling were sequentially performed to obtain steel plates under the conditions listed in Table 2. The obtained steel plates were each subjected to measurement of the microstructure proportion of the metallic
45 microstructure at the 0.5 mm position from the steel plate surface and at the 1/2 thickness position, evaluation of hardness properties at the 0.5 mm position from the steel plate surface, evaluation of strength properties and toughness, and evaluation of ammonia SCC resistance. Test methods were as follows. Further, results are listed in Table 2.

[Microstructure proportion of metallic structure at 0.5 mm position and 1/2 position]

50 **[0066]** Samples were taken from each steel plate so that the 0.5 mm position or the 1/2 position (mid-thickness part) was the observation plane. The samples were then mirror polished and nital etched, and a scanning electron microscope (SEM) was used to capture images of a 10 mm × 10 mm area at a magnification of 500× to 3000×. The captured images were then analyzed using an image interpretation device to obtain the surface fraction of the microstructure (micro-
55 structure proportion of the metallic structure). When microstructure anisotropy is small, the surface fraction corresponds to the volume fraction, and therefore the surface fraction is considered to be the volume fraction for the present disclosure.

[0067] For the present Examples, when calculating fractions of the metallic structure of the samples, the microstructures were distinguished as follows. In the images captured, polygonal ferrite was distinguished as ferrite (F in Table 2), and

microstructures having elongated, lath-shape ferrite and containing carbides having a circle equivalent diameter of 0.05 μm or more were distinguished as bainite (B in Table 2).

[Hardness properties]

[0068] For a cross-section perpendicular to the rolling direction of each steel plate, Vickers hardness (HV0.1) was measured at 100 points at the 0.5 mm position in accordance with JIS Z 2244, and the average value thereof was obtained. Further, the standard deviation of the Vickers hardness of the 100 points was determined, and used as the variation of the average hardness at the 0.5 mm position. Here, HV0.1 was used instead of HV10, which is typically used for measuring the hardness of steel plates, because the indentation is smaller when measuring at HV0.1, which makes it possible to obtain hardness information closer to the surface and that is more sensitive to microstructure.

[Strength properties]

[0069] From the full thickness of each steel plate, a 1B test piece according to JIS Z 2201 was taken perpendicular to the rolling direction and the thickness direction, and tensile tests were conducted as described in JIS Z 2241 to measure yield stress YS (yield point YP when present, otherwise 0.2 % proof stress $\sigma_{0.2}$) and tensile strength (TS). Steel plates having a yield stress of 360 MPa or more and a tensile strength of 490 MPa or more were evaluated as having excellent strength properties.

[Toughness]

[0070] From a position ground down 1 mm from the surface side of each steel plate, V-notch test pieces according to JIS Z 2202 were taken in the rolling direction, and a Charpy impact tests were conducted according to JIS Z 2242 to measure vTrs (fracture appearance transition temperature). A steel plate having a vTrs of $-30\text{ }^{\circ}\text{C}$ or less was evaluated as having excellent toughness.

[Ammonia SCC resistance]

[0071] Ammonia SCC resistance was evaluated by accelerated testing, in which a 4-point bend test was performed in a test solution and constant potential anodic electrolysis was used to accelerate corrosion.

[0072] Specifically, the following procedure was used:

For each steel plate, a 5 mm thick $\times$ 15 mm $\times$ 115 mm test piece was taken from the surface and subjected to ultrasonic degreasing in acetone for 5 min and stress of 100 % YS of the actual yield stress of each steel plate by 4-point bending. The test piece subjected to the 4-point bending was placed in a test cell, filled with a solution of 12.5 g ammonium carbamate mixed with 1 L liquid ammonia, and then a potentiostat was used to control +2.0 V vs Pt flow to the test piece immersed at room temperature ($25\text{ }^{\circ}\text{C}$). After 168 h of immersion, when no crack was observed, ammonia SCC resistance was judged to be "Good", and when a crack was observed, ammonia SCC resistance was judged to be "Poor".

[Table 1]

Steel sample ID		Chemical composition (mass%)																				Ar ₃ (°C)	Remarks			
		C	Si	Mn	Al	N	P	S	O	Cu	Ni	Cr	Mo	Sn	Sb	W	V	Ti	Co	Nb	B	Ca	Mg	REM		
A		0.039	0.09	2.20	0.004	0.0066	0.001	0.0089	0.0013	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	722	Examples
B		0.097	0.16	1.60	0.008	0.0071	0.019	0.0030	0.0032	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	752	
C		0.057	0.15	0.71	0.046	0.0070	0.020	0.0047	0.0028	0.25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	831	
D		0.067	0.14	1.03	0.007	0.0070	0.007	0.0008	0.0018	-	1.04	-	-	-	-	-	-	-	-	-	-	-	-	-	750	
E		0.104	0.15	0.86	0.046	0.0078	0.017	0.0036	0.0037	-	-	0.46	-	-	-	-	-	-	-	-	-	-	-	-	802	
F		0.091	0.14	1.41	0.042	0.0044	0.010	0.0059	0.0032	-	-	-	0.33	-	-	-	-	-	-	-	-	-	-	-	743	
G		0.157	0.20	2.22	0.037	0.0064	0.005	0.0046	0.0028	-	-	-	-	0.14	-	-	-	-	-	-	-	-	-	-	684	
H		0.090	0.10	1.65	0.014	0.0033	0.003	0.0020	0.0033	-	-	-	-	-	0.05	-	-	-	-	-	-	-	-	-	750	
I		0.054	0.38	1.62	0.011	0.0065	0.018	0.0068	0.0037	0.30	1.38	-	-	-	-	-	-	-	-	-	-	-	-	-	682	
J		0.059	0.05	1.27	0.030	0.0048	0.006	0.0021	0.0028	-	0.10	0.51	-	-	-	-	-	-	-	-	-	-	-	-	777	
K		0.129	0.13	1.18	0.011	0.0055	0.017	0.0008	0.0029	-	-	0.76	0.15	-	-	-	-	-	-	-	-	-	-	-	752	
L		0.075	0.22	0.93	0.001	0.0020	0.010	0.0067	0.0019	-	-	-	0.09	0.17	-	-	-	-	-	-	-	-	-	-	805	
M		0.072	0.16	2.19	0.043	0.0058	0.003	0.0088	0.0023	-	-	-	-	0.33	0.08	-	-	-	-	-	-	-	-	-	712	
N		0.063	0.08	1.59	0.044	0.0069	0.010	0.0081	0.0019	-	-	-	-	-	0.16	0.45	-	-	-	-	-	-	-	-	763	
O		0.044	0.35	1.89	0.044	0.0060	0.013	0.0031	0.0027	0.14	0.82	0.79	0.16	0.19	0.04	0.50	-	-	-	-	-	-	-	-	673	
P		0.018	0.10	0.85	0.024	0.0078	0.003	0.0013	0.0019	0.16	-	0.54	-	-	-	-	0.14	-	-	-	-	-	-	-	825	
Q		0.151	0.11	1.35	0.018	0.0069	0.015	0.0054	0.0006	-	0.13	-	-	0.09	-	-	-	0.021	-	-	-	-	-	-	748	
R		0.092	0.40	1.13	0.008	0.0075	0.017	0.0010	0.0037	-	-	0.23	0.04	-	-	-	-	-	0.48	-	-	-	-	-	784	
S		0.055	0.07	1.33	0.023	0.0073	0.004	0.0084	0.0005	0.07	-	-	-	0.40	-	-	-	-	-	0.039	-	-	-	-	785	
T		0.124	0.23	1.28	0.047	0.0039	0.010	0.0022	0.0021	-	-	0.09	-	-	-	0.22	-	-	-	-	-	0.0058	-	-	768	
U		0.128	0.34	1.18	0.050	0.0050	0.018	0.0016	0.0040	0.19	-	-	-	0.40	0.13	-	-	-	-	-	-	-	0.0055	-	772	
V		0.161	0.03	0.80	0.049	0.0037	0.016	0.0081	0.0039	-	1.28	-	-	-	-	0.44	-	-	-	-	-	-	-	0.0081	726	
W		0.143	0.34	1.14	0.001	0.0028	0.017	0.0053	0.0037	0.13	0.84	0.63	0.13	0.30	0.22	0.32	0.12	0.079	0.49	0.035	0.001	0.0036	0.0084	0.0024	706	Comparative Examples
X		0.009	0.22	1.31	0.018	0.0039	0.002	0.0095	0.0044	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	802	
Y		0.230	0.30	2.08	0.048	0.0064	0.009	0.0057	0.0045	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	672	
Z		0.168	0.55	1.36	0.010	0.0075	0.018	0.0074	0.0005	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	749	
AA		0.149	0.05	0.46	0.026	0.0066	0.002	0.0010	0.0051	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	827	
AB		0.169	0.32	2.58	0.013	0.0074	0.002	0.0047	0.0013	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	651	
AC		0.121	0.22	1.55	0.066	0.0045	0.015	0.0011	0.0033	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	748	
AD		0.055	0.25	0.97	0.035	0.0008	0.005	0.0058	0.0021	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	815	
AE		0.111	0.08	1.08	0.006	0.0121	0.004	0.0068	0.0053	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	789	
AF		0.076	0.37	1.76	0.012	0.0020	0.021	0.0098	0.0038	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	746	
AG		0.147	0.33	1.38	0.022	0.0040	0.011	0.0132	0.0025	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	754	
AH		0.080	0.35	2.19	0.047	0.0078	0.018	0.0098	0.0152	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	710	
* Underlining indicates value outside scope of present disclosure.																										
* Ar ₃ = 910 – 310C – 80Mn – 20Cu – 15Cr – 55Ni – 80Mo (element symbol indicates content (mass%) of each element)																										

[Table 2]

Steel material		Steel plate	Hot rolling	Primary cooling		Recuperation	Secondary cooling		Metallic structure		Hardness properties			Strength properties		Toughness	Remarks
				Start temp. (°C)	Cooling rate (*1) (°C/s)		End-point temp. (*3) (°C)	Cooling rate (*2) (°C/s)			0.5 mm position		Average hardness HV	YS (MPa)	TS (MPa)		
No.	Steel sample ID	Ar ₃ (°C)	Thickness (mm)	Finish temp. (°C)	Cooling rate (*1) (°C/s)	End-point temp. (*3) (°C)	Cooling rate (*2) (°C/s)	Stop temp. (°C)	0.5 mm position		1/2 thickness position		Variation HV	YS (MPa)	TS (MPa)	vTrs (°C)	Ammonia SCC resistance
									B fraction (%)	B fraction (%)	F+B fraction (%)	F+B fraction (%)					
1	A	722	25	750	58	616	57	380	94	55	83	161	23	425	511	-90	Good
2	B	752	25	810	80	590	34	400	95	44	75	193	17	461	595	-83	Good
3	B	752	25	770	78	508	20	510	91	48	91	185	43	428	551	-73	Good
4	B	752	25	790	770	36	580	21	92	49	83	161	44	421	510	-75	Good
5	B	752	25	800	790	98	539	28	94	64	81	205	32	455	636	-83	Good
6	B	752	25	790	770	35	511	58	95	79	94	200	42	418	521	-94	Good
7	B	752	25	820	800	68	561	17	94	57	69	187	33	432	558	-72	Good
8	B	752	25	780	760	48	533	48	96	66	78	183	38	473	581	-48	Good
9	B	752	25	790	770	68	621	30	98	46	71	164	19	426	543	-73	Good
10	C	831	25	870	850	66	615	46	91	41	75	150	23	398	503	-85	Good
11	D	750	25	810	800	64	541	33	93	44	75	159	33	403	493	-84	Good
12	E	802	25	860	840	44	544	18	98	82	98	186	34	445	572	-82	Good
13	F	743	25	810	790	45	618	33	99	41	85	178	26	439	534	-89	Good
14	G	684	25	750	730	58	522	33	95	75	85	207	28	470	665	-78	Good
15	H	750	25	810	800	81	536	18	96	79	96	202	35	442	614	-87	Good
16	I	682	25	710	690	97	572	24	96	60	80	201	31	429	596	-80	Good
17	J	777	25	820	800	67	560	58	92	65	82	188	33	421	575	-88	Good
18	K	752	25	830	810	85	560	40	97	59	96	204	26	503	721	-68	Good
19	L	805	25	880	860	64	631	24	98	42	82	173	20	422	504	-98	Good
20	M	712	25	760	750	96	541	36	95	64	81	194	29	474	645	-81	Good
21	N	763	25	840	820	50	611	59	99	43	99	171	25	426	510	-90	Good
22	O	673	25	730	710	63	662	60	92	42	97	198	17	459	667	-75	Good
23	P	825	25	890	870	93	552	52	97	24	73	188	28	473	653	-76	Good
24	Q	748	25	770	750	49	570	31	99	69	84	163	28	463	502	-58	Good
25	Q	748	25	800	780	53	512	28	96	65	72	208	34	503	624	-38	Good
(*1) Cooling rate from 600 °C to 400 °C at 0.5 mm depth from steel sheet surface																	
(*2) Cooling rate at 1/2 thickness position																	
(*3) 0.5 mm depth from steel sheet surface																	

Table 2 (cont'd)

No.	Steel material		Steel plate	Hot rolling	Primary cooling		Recuperation	Secondary cooling		Metallic structure			Hardness properties			Strength properties		Toughness	Ammonia SCC resistance	Remarks
	Steel sample ID	Ar ₃ (°C)	Thickness (mm)	Finish temp. (°C)	Start temp. (°C)	Cooling rate (*1) (°C/s)	End-point temp. (*3) (°C)	Cooling rate (*2) (°C/s)	Stop temp. (°C)	1/2 thickness position			0.5 mm position			YS (MPa)	TS (MPa)	vTrs (°C)		
										B fraction (%)	B fraction (%)	F+B fraction (%)	Average hardness HV	Variation HV						
26	R	784	25	810	790	49	570	31	540	99	47	84	163	28	463	502	-104	Good	Examples	
27	S	785	25	850	830	43	512	39	490	98	65	98	181	41	433	528	-101	Good		
28	T	768	25	830	820	58	508	25	450	97	75	87	183	43	422	558	-91	Good		
29	U	772	25	820	810	48	636	38	460	98	48	98	169	25	446	525	-82	Good		
30	V	726	25	760	750	85	523	36	520	95	27	79	177	34	449	560	-88	Good		
31	W	706	25	740	720	46	542	39	560	92	27	91	191	41	510	655	-82	Good	Comparative Examples	
32	B	752	25	690	680	42	546	36	370	70	13	73	179	62	453	562	-29	Poor		
33	B	752	25	800	690	44	543	46	410	87	12	83	176	53	344	475	-61	Poor		
34	B	752	25	820	810	21	529	41	390	79	88	99	176	58	341	479	-80	Poor		
35	B	752	25	780	770	116	554	39	530	97	38	80	255	26	443	637	-78	Poor		
36	B	752	25	790	770	58	486	54	420	98	36	89	274	61	438	564	-91	Poor		
37	B	752	25	780	770	58	633	8	310	98	7	56	169	18	334	465	-57	Good		
38	B	752	25	810	800	34	630	40	610	95	9	59	157	30	351	461	-53	Good		
39	Q	748	25	710	690	47	560	34	480	72	18	74	184	69	458	553	-28	Poor		
40	X	802	25	830	810	96	520	49	420	91	55	82	195	37	339	473	-98	Good		
41	Y	672	25	770	750	89	533	56	660	92	74	91	205	33	435	616	-24	Good		
42	Z	749	25	820	810	63	545	41	570	95	63	97	197	35	424	596	-28	Good		
43	AA	827	25	860	850	99	573	44	580	92	35	79	206	24	341	469	-73	Good		
44	AB	651	25	690	670	63	530	57	410	99	32	74	209	36	464	638	-28	Good		
45	AC	748	25	820	810	37	571	36	370	98	60	78	186	33	433	526	-27	Good		
46	AD	815	25	840	830	52	531	32	330	96	84	98	140	39	421	505	-25	Good		
47	AE	789	25	850	830	65	621	56	400	91	53	80	162	22	437	536	-26	Good		
48	AF	746	25	790	770	82	519	59	560	97	47	84	194	39	432	589	-13	Good		
49	AG	754	25	780	760	63	618	33	380	93	36	96	175	27	413	544	-7	Good		
50	AH	710	25	750	740	70	502	54	470	95	66	85	208	41	465	622	-23	Good		

(*1) Cooling rate from 600 °C to 400 °C at 0.5 mm depth from steel sheet surface
(*2) Cooling rate at 1/2 thickness position
(*3) 0.5 mm depth from steel sheet surface

(*1) Cooling rate from 600 °C to 400 °C at 0.5 mm depth from steel sheet surface

(*2) Cooling rate at 1/2 thickness position

(*3) 0.5 mm depth from steel sheet surface

[0073] As can be seen in Tables 1 and 2, for the Examples (No. 1 to No. 31) all obtained steel plates had a yield stress YS of 360 MPa or more, a tensile strength TS of 490 MPa or more, vTrs of -30 °C or less, excellent toughness at low temperature, and excellent ammonia SCC resistance.

[0074] In contrast, although the chemical compositions of No. 32 to No. 39 were within the scope of the present disclosure, the method of production was in each case outside the scope of the present disclosure, and therefore the

desired metallic structure and/or hardness properties were not obtained. As a result, at least one of yield stress YS, tensile strength TS, toughness at low temperatures, or ammonia SCC resistance was poor.

[0075] Further, the chemical compositions of No. 40 to No. 50 were outside the scope of the present disclosure, and therefore at least one of yield stress YS, tensile strength TS, toughness at low temperatures, or ammonia SCC resistance was poor. Hereinafter, the chemical composition of the steel may be considered to be the chemical composition of the steel plate.

Claims

1. A steel plate comprising a chemical composition containing, in mass%,

C: 0.010 % to 0.200 %,

Si: 0.01 % to 0.50 %,

Mn: 0.50 % to 2.50 %,

Al: 0.060 % or less,

N: 0.0010 % to 0.0100 %,

P: 0.020 % or less,

S: 0.0100 % or less, and

O: 0.0100 % or less,

with the balance being Fe and inevitable impurity, wherein

the steel plate has hardness properties such that, at a 0.5 mm depth position from the surface of the steel plate, average hardness is 210 HV or less and variation of the average hardness is 50 HV or less, and

the steel plate has a metallic microstructure where, at a 0.5 mm depth position from the surface of the steel plate, a volume fraction of bainitic microstructure is 90 % or more and, at a 1/2 thickness position of the steel plate, a volume fraction of bainitic microstructure is 20 % or more and a total volume fraction of ferritic microstructure and bainitic microstructure is 60 % or more.

2. The steel plate according to claim 1, wherein the chemical composition further contains, in mass%, at least one selected from the group consisting of

Cu: 0.01 % to 0.50 %,

Ni: 0.01 % to 2.00 %,

Cr: 0.01 % to 1.00 %,

Sn: 0.01 % to 0.50 %,

Sb: 0.01 % to 0.50 %,

Mo: 0.01 % to 0.50 % and,

W: 0.01 % to 1.00 %.

3. The steel plate according to claim 1 or 2, wherein the chemical composition further contains, in mass%, at least one selected from the group consisting of

V: 0.01 % to 1.00 %,

Ti: 0.005 % to 0.100 %,

Co: 0.01 % to 1.00 %,

Nb: 0.005 % to 0.100 %,

B: 0.0001 % to 0.0100 %,

Ca: 0.0005 % to 0.0200 %,

Mg: 0.0005 % to 0.0200 %, and

REM: 0.0005 % to 0.0200 %.

4. A method of producing a steel plate, the method applied to a steel material comprising a chemical composition containing, in mass%,

C: 0.010 % to 0.200 %,

Si: 0.01 % to 0.50 %,

Mn: 0.50 % to 2.50 %,

Al: 0.060 % or less,

N: 0.0010 % to 0.0100 %,
P: 0.020 % or less,
S: 0.0100 % or less, and
O: 0.0100 % or less,

with the balance being Fe and inevitable impurity, the method comprising:

hot rolling with a rolling finish temperature that is Ar_3 transformation temperature or more; followed by primary cooling from a cooling start temperature that is the Ar_3 transformation temperature or more; followed by surface heating by recuperation; and followed by secondary cooling, wherein,
in the primary cooling, cooling rate from 600 °C to 400 °C at a 0.5 mm depth position from the surface of the steel plate is 30 °C/s to 100 °C/s,
the surface heating by recuperation occurs until end-point temperature at a 0.5 mm depth position from the steel plate surface is 500 °C or more, and
in the secondary cooling, at a 1/2 thickness position of the steel plate, cooling rate to a cooling stop temperature of 600 °C or less is 10 °C/s or more.

5. The method of producing a steel plate according to claim 4, wherein the chemical composition of the steel material further contains, in mass%, at least one selected from the group consisting of

Cu: 0.01 % to 0.50 %,
Ni: 0.01 % to 2.00 %,
Cr: 0.01 % to 1.00 %,
Sn: 0.01 % to 0.50 %,
Sb: 0.01 % to 0.50 %,
Mo: 0.01 % to 0.50 % and,
W: 0.01 % to 1.00 %.

6. The method of producing a steel plate according to claim 4 or 5, wherein the chemical composition of the steel material further contains, in mass%, at least one selected from the group consisting of

V: 0.01 % to 1.00 %,
Ti: 0.005 % to 0.100 %,
Co: 0.01 % to 1.00 %,
Nb: 0.005 % to 0.100 %,
B: 0.0001 % to 0.0100 %,
Ca: 0.0005 % to 0.0200 %,
Mg: 0.0005 % to 0.0200 %, and
REM: 0.0005 % to 0.0200 %.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/001392

A. CLASSIFICATION OF SUBJECT MATTER

C21D 8/02(2006.01)i; *C22C 38/00*(2006.01)i; *C22C 38/06*(2006.01)i; *C22C 38/60*(2006.01)i
FI: C22C38/00 301A; C21D8/02 B; C22C38/00 301F; C22C38/06; C22C38/60

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)

C21D8/02; C22C38/00; C22C38/06; C22C38/60

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 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2021-088753 A (NIPPON STEEL CORP) 10 June 2021 (2021-06-10)	1-6
A	WO 2021/106368 A1 (JFE STEEL CORPORATION) 03 June 2021 (2021-06-03)	1-6
A	JP 2011-208222 A (SUMITOMO METAL IND LTD) 20 October 2011 (2011-10-20)	1-6
A	JP 2011-105963 A (NIPPON STEEL CORP) 02 June 2011 (2011-06-02)	1-6

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

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Name and mailing address of the ISA/JP

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/001392

Patent document cited in search report			Publication date (day/month/year)		Patent family member(s)		Publication date (day/month/year)	
JP	2021-088753	A	10 June 2021		(Family: none)			
WO	2021/106368	A1	03 June 2021		KR	10-2022-0030288	A	
					CN	114761595	A	
JP	2011-208222	A	20 October 2011		(Family: none)			
JP	2011-105963	A	02 June 2011		(Family: none)			

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP H10140235 A [0007]
- JP H10168516 A [0007]