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(54) **STEEL PLATE AND METHOD FOR MANUFACTURING SAME**

(57) A high strength steel plate having excellent ammonia SCC resistance and low-temperature toughness for use in storage tanks 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 230HV0.1 or less and hardness variation is 30HV0.1 or less, a maximum value

of hardness in the thickness direction is at a position 1.0 mm or more and 1/4 or less of the thickness of the steel plate from the surface of the steel plate, and hardness variation in the thickness direction is 70HV1 or less. Further, 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.

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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 for low temperature applications 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]** Recently, the use of such liquid ammonia as a hydrogen carrier and liquid ammonia fuel has led to larger tanks for transporting and storing liquefied ammonia.

[0004] 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 **[0005]** 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.

25 **[0006]** Further, liquefied gases such as LPG and liquid ammonia are transported and stored at low temperatures, and therefore steel plates used for storage tanks for such liquefied gases are required to have excellent low-temperature toughness.

[0007] Technologies for meeting the low-temperature toughness and defined 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.

CITATION LIST

35 Patent Literature

[0008]

40 PTL 1: JP H10-140235 A
PTL 2: JP H10-168516 A

SUMMARY

45 (Technical Problem)

[0009] 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.

50 **[0010]** 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.

(Solution to Problem)

55 **[0011]** 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) and an on-line induction heater. As a result, the inventors discovered that the following could effectively obtain SCC resistance in a liquid ammonia environment and eliminate costly multiple heat treatments: causing elements such as C,

Si, Mn, and Al to be included in a steel plate in defined amounts; controlling the metallic microstructure of the steel plate so that a volume fraction of bainitic microstructure at a 0.5 mm position from the surface of the steel plate is 90 % or more; and controlling hardness so that, at a 0.5 mm position from the surface of the steel plate, average hardness is 230HV0.1 or less and hardness variation is 30HV0.1 or less, a maximum value of hardness in the thickness direction is at a position 1.0 mm or more and 1/4 or less of the thickness of the steel plate from the surface of the steel plate, and hardness variation in the thickness direction is 70HV1 or less.

[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: 0.010 % to 0.060 %,
N: 0.0010 % or more and 0.0100 % or less,
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,
at a 0.5 mm depth position from the surface of the steel plate, average hardness is 230HV0.1 or less and hardness variation is 30HV0.1 or less, a maximum value of hardness in the thickness direction is at a position 1.0 mm or more and 1/4 or less of the thickness of the steel plate from the surface of the steel plate, and hardness variation in the thickness direction is 70HV1 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.

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: 0.010 % to 0.060 %,
N: 0.0010 % or more and 0.0100 % or less,

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 accelerated cooling from a cooling start temperature that is the Ar_3 transformation temperature or more; followed by reheating, wherein,
in the accelerated cooling, cooling stop temperature is in a range from 200 °C to 600 °C and cooling rate at a 1/4 plate thickness position is 20 °C/s to 120 °C/s, and
the reheating is performed until end-point temperature at a 0.5 mm depth position from the surface of the steel plate is in a range from 400 °C to 680 °C, with end-point temperature at a 1/4 plate thickness position being 500 °C or less.

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 %, and
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 toughness at low temperatures, 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 %

[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.

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 suppressing a decrease in toughness and weldability, the Mn content is preferably 2.30 % or less.

Al: 0.010 % to 0.060 %

[0019] Al acts as a deoxidizer. To obtain this effect, Al content is specified as 0.010 % 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.

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

[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 %. However, in industrial terms, P is an element that can typically remain in steel, and therefore the lower limit may be greater than 0 %. Further, excessive reduction leads to higher refining costs, and therefore from a cost perspective, the P content is preferably 0.0005 % or more.

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 %. However, in industrial terms, typically, S is an element that may remain in steel, and therefore the lower limit may be greater than 0 %. Further, excessive reduction leads to higher refining costs, and therefore from a cost perspective, the S content is preferably 0.0005 % or more.

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 %. However, in industrial terms, typically, O is an element that may remain in steel, and therefore the

lower limit may be greater than 0 %. Further, 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 %, 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, the 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 %.

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 %.

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 %.

(2) Hardness properties and metallic microstructure

[0035] In addition to having the chemical composition described above, the steel plate according to the present disclosure 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 230HV0.1 or less and hardness variation is 30HV0.1 or less, a maximum value of hardness in the thickness direction is at a position 1.0 mm or more and 1/4 or less of the thickness of the steel plate from the surface of the steel plate, and hardness variation in the thickness direction is 70HV1 or less.

[0036] Further, the steel plate has a metallic microstructure where, at the 0.5 mm position, a volume fraction of bainitic microstructure (hereinafter also referred to simply as bainite) is 90 % or more.

[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 230HV0.1 or less and hardness variation 30HV0.1 or less]

[0038] At the 0.5 mm position, the average hardness is 230HV0.1 or less and the hardness variation is 30HV0.1 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 230HV0.1 or less and the hardness variation is adjusted to 30HV0.1 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 130HV0.1. A lower limit of hardness variation at the 0.5 mm position may be 0HV0.1. Industrially, the lower limit of hardness variation is about 10HV0.1.

[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 hardness variation means the standard deviation of the Vickers hardness measured to obtain the average hardness.

[Maximum hardness value in thickness direction is 1.0 mm or more and 1/4 plate thickness or less from surface of steel plate]

[0040] When the maximum hardness of the steel plate is positioned some distance from the surface, the hardness of only a surface layer can be reduced while maintaining the hardness of the majority of the steel plate. Accordingly, excellent ammonia SCC resistance properties can be secured while maintaining the strength of the steel plate.

[0041] Specifically, when the maximum value is less than 1.0 mm from the surface of the steel plate, hardness at the 0.5 mm position cannot be sufficiently reduced. On the other hand, when the maximum value is more than 1/4 of the plate thickness from the surface of the steel plate, the steel plate cannot be sufficiently strong. Accordingly, the maximum value of hardness (Vickers hardness (HV1)) in the thickness direction of the steel plate is specified to be 1.0 mm or more and 1/4 of plate thickness or less from the surface of the steel plate.

[Hardness variation in thickness direction 70HV1 or less]

[0042] When the hardness variation in the thickness direction is large, not only is uniform elongation of the steel plate reduced, but the residual stress due to internal stress introduced by accelerated cooling is increased, which may degrade ammonia SCC resistance. Accordingly, the hardness variation in the thickness direction is specified as 70HV1 or less.

[0043] The variation is calculated by measuring Vickers hardness (HV1) in the thickness direction at a pitch of 0.5 mm and determining the difference between maximum and minimum values.

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

[0044] 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 hardness variation 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 or ammonia SCC resistance is not obtained.

[0045] Here, bainite includes bainitic ferrite or microstructure referred to as granular ferrite, which transforms during or after accelerated cooling, contributing to transformation strengthening, and tempered microstructure thereof.

[0046] 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.

[0047] The volume fraction of each metallic microstructure can be measured by a method described in the EXAMPLES section below.

(3) Production conditions

[0048] The method of production according to the present disclosure is to heat and hot roll steel material having the same chemical composition as that described above for the steel plate, followed by accelerated cooling, and then reheating. The following explains the reasons for limiting the production conditions of the steel plate.

[0049] 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.

[0050] The steel material thus obtained is either hot rolled directly without cooling or reheated before hot rolling. Hot rolling is performed with the rolling finish temperature at the Ar_3 transformation temperature or more, followed by accelerated cooling from the cooling start temperature at the Ar_3 transformation temperature or more under defined conditions, followed by reheating under defined conditions.

[0051] The heating temperature of the steel material 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: Ar_3 transformation temperature or more]

5 **[0052]** According to the present disclosure, hot rolling is started after heating steel material to the temperature described above, and the hot rolling finishes at the Ar_3 transformation temperature or more.

[0053] When the rolling finish temperature is less than the Ar_3 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.

10 **[0054]** Accordingly, the rolling finish temperature in the hot rolling is the Ar_3 transformation temperature or more. Preferably, the rolling finish temperature is the Ar_3 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.

15 **[0055]** Here, the Ar_3 transformation temperature (°C) is obtainable by the following expression.

$$Ar_3 \text{ (°C)} = 910 - 310 \times C - 80 \times Mn - 20 \times Cu - 15 \times Cr - 55 \times Ni - 80 \times Mo$$

20 **[0056]** Here, each element indicates the content (mass%) of the element in the steel.

(Accelerated cooling)

[Cooling start temperature: Ar_3 transformation temperature or more]

25 **[0057]** Next, accelerated cooling is performed on the steel plate after the hot rolling to cool from the cooling start temperature that is the Ar_3 transformation temperature or more. When the cooling start temperature is less than the Ar_3 transformation temperature, excessive ferrite forms. The cooling rate being large results in coexistence of ferrite with martensitic microstructure or bainite that have large strength differences from ferrite, resulting in insufficient strength and toughness deterioration, as well as deterioration of ammonia SCC resistance. The cooling start temperature is therefore the Ar_3 transformation temperature or more.

[Cooling rate at 1/4 plate thickness position: 20 °C/s to 120 °C/s]

35 **[0058]** Accelerated cooling at a cooling rate of 20 °C/s or more at the 1/4 plate thickness position is an essential process for obtaining a high-strength and high-toughness steel plate, and cooling at a high cooling rate provides a strength increasing effect by transformation strengthening. Accordingly, to obtain the effect, the cooling rate at the 1/4 plate thickness position during the accelerated cooling according to the present disclosure is specified as 20 °C/s or more. However, the cooling rate exceeding 120 °C/s causes the volume fraction of martensite to become too large and toughness to decrease. Accordingly, the cooling rate at the 1/4 plate thickness position of the steel plate is specified as 120 °C/s or less.

40 **[0059]** The cooling rate can be increased by active cooling operations such as water cooling and the like, and can be controlled by performing the cooling operations intermittently (by setting a period of time when the cooling operations are stopped), as appropriate. The temperature at the 1/4 plate thickness position is difficult to physically measure directly. However, the temperature distribution in a thickness cross-section, in particular at the 1/4 plate thickness 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.

50 [Cooling stop temperature: 200 °C to 600 °C]

[0060] According to the present disclosure, after the hot rolling finishes, the defined accelerated cooling is performed to a cooling stop temperature set anywhere in the range from 200 °C to 600 °C. This allows ferrite and bainite to be brought to defined volume fractions at the mid-thickness part, thereby improving strength and toughness.

55 **[0061]** Here, when the cooling stop temperature is less than 200 °C, a volume fraction of martensite austenite constituent microstructure becomes too large, resulting in a decrease in toughness. On the other hand, when the cooling stop temperature exceeds 600 °C, excessive ferrite and pearlite microstructures are formed, resulting in insufficient strength and leading to toughness deterioration. Accordingly, the cooling stop temperature is specified to be in the range from

200 °C to 600 °C. Further, the cooling stop temperature according to the present disclosure is the temperature at the 1/4 plate thickness position of the steel plate.

(Reheating)

[End-point temperature at 0.5 mm position from surface: 400 °C to 680 °C]

[0062] According to the present disclosure, reheating after the accelerated cooling is required. Accelerated cooling of a thick steel plate results in a faster cooling rate in the surface layer of the steel plate and lower temperatures in the surface layer of the steel plate compared to the interior of the steel plate. Therefore, the surface layer of the steel plate is prone to the formation of hard microstructure such as martensite, which may degrade ammonia SCC resistance. Therefore, according to the present disclosure, in order to reduce the hardness of the surface layer, the surface layer of the steel plate is reheated after the accelerated cooling. Preferably, reheating is performed immediately after the accelerated cooling.

[0063] When the reheating temperature at the 0.5 mm position from the surface is less than 400 °C, the reduction in hardness is not sufficient, while when the temperature exceeds 680 °C, the overall strength of the steel plate is reduced, making obtaining the defined strength difficult.

[0064] Accordingly, when reheating after the accelerated cooling, the end-point temperature at the 0.5 mm position from the surface is specified to be in the range from 400 °C to 680 °C.

[End-point temperature at 1/4 plate thickness position: 500 °C or less]

[0065] When the end-point temperature at the 1/4 plate thickness position exceeds 500 °C during reheating, a decrease in strength and deterioration of toughness occurs. Accordingly, the end-point temperature at the 1/4 plate thickness position at the time of the reheating is specified to be 500 °C or less.

[0066] Induction heating is the preferred means of the reheating after the accelerated cooling. In particular, high-frequency induction heating is preferably used so that heating is concentrated on the surface layer of the steel plate. After the reheating, cooling may be performed as appropriate. Although cooling after the reheating is not particularly limited, there may be concerns about toughness degradation due to coagulated and coarsened carbide in a steel plate exceeding 40 mm in thickness due to slow cooling rates. In such a case, cooling by water cooling or mist may be performed after the reheating treatment.

[0067] By producing the steel material having the chemical composition described above and according to the production conditions described above, the steel plate having the chemical composition, hardness properties, and metallic microstructure according to the present invention is obtainable. The steel plate obtained has excellent strength properties and toughness, and has excellent ammonia SCC resistance. Here, excellent strength properties are defined as yield stress YS (yield point YP when present, otherwise 0.2 % proof stress $\sigma_{0.2}$): 450 MPa or more, tensile strength (TS): 570 MPa or more, and uniform elongation (uEl): 10 % or more. Further, excellent toughness is defined as $vTrs$ of -30 °C or less in accordance with Japanese Industrial Standard JIS Z 2241. A steel plate having these properties is the steel plate having excellent ammonia SCC resistance according to the present disclosure.

[0068] In the method of production according to the present disclosure, anything not described herein may be a conventional method.

EXAMPLES

[0069] Steels having the chemical compositions listed in Table 1 (steel sample IDs A to AI, the balance of each being Fe and inevitable impurity) were made into slabs by a continuous casting method, and hot rolling, accelerated cooling, and reheating were performed in this order under the conditions listed in Table 2 to obtain steel plates (No. 1 to No. 50) each having a thickness of 30 mm. The obtained steel plates were each subjected to measurement of the microstructure proportion of the metallic microstructure at the 0.5 mm position from the surface of the steel plate, evaluation of hardness properties, 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 microstructure at 0.5 mm position from surface of steel plate]

[0070] Samples were taken from each steel plate so that the 0.5 mm position 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 (microstructure proportion of the metallic micro-

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.

[0071] For the present Examples, when calculating fractions of the metallic microstructure of the samples, the microstructures were distinguished as follows.

[0072] In the images captured, polygonal ferrite was distinguished as ferrite, 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]

[0073] 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 hardness variation 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.

[0074] Further, Vickers hardness (HV1) was measured in the thickness direction, and the position of the maximum value in the thickness direction (distance from the surface) was measured. Further, the difference between the maximum value and minimum value of Vickers hardness (HV1) in such measurements was calculated and used as the hardness variation in the thickness direction.

[Strength properties]

[0075] From the full thickness of each steel plate, a 1B test piece according to JIS Z 2201 was taken so the direction perpendicular to the rolling direction was the longitudinal direction of the test piece, 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 $\sigma_{0.2}$), tensile strength (TS), and uniform elongation (uEl). Steel plates having a yield stress of 450 MPa or more, tensile strength of 570 MPa or more, and uniform elongation of 10 % or more were evaluated as having excellent strength properties.

[Toughness]

[0076] 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 so the rolling direction was the longitudinal direction of the test pieces, and 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 °C or less was evaluated as having excellent toughness.

[Ammonia SCC resistance]

[0077] 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.

[0078] 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 equivalent to the 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, which was filled with a solution of 12.5 g ammonium carbamate mixed with 1 L liquid ammonia, and then a potentiostat was used to apply a voltage of +2.0 V vs Pt to the test piece immersed at room temperature (25 °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]

Table 1		Chemical composition (mass%)																							Ar ₃ (°C)	Remarks
Steel sample ID		C	Si	Mn	Al	N	P	S	O	Cu	Ni	Cr	Mo	Sn	Sb	W	V	Ti	Co	Nb	B	Ca	Mg	REM		
A		0.075	0.39	1.77	0.028	0.0061	0.006	0.0079	0.0024	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	745	Examples
B		0.063	0.27	2.28	0.023	0.0040	0.020	0.0035	0.0029	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	708	
C		0.107	0.19	1.71	0.043	0.0057	0.019	0.0035	0.0014	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	738	
D		0.037	0.30	1.65	0.046	0.0026	0.008	0.0090	0.0038	-	1.02	-	-	-	-	-	-	-	-	-	-	-	-	-	710	
E		0.075	0.15	1.82	0.044	0.0039	0.006	0.0006	0.0008	-	-	0.04	-	-	-	-	-	-	-	-	-	-	-	-	741	
F		0.070	0.16	1.86	0.015	0.0054	0.006	0.0059	0.0019	-	-	-	0.22	-	-	-	-	-	-	-	-	-	-	-	722	
G		0.068	0.17	1.92	0.046	0.0068	0.003	0.0062	0.0028	-	-	-	-	0.23	-	-	-	-	-	-	-	-	-	-	735	
H		0.081	0.27	1.77	0.014	0.0026	0.001	0.0066	0.0025	-	-	-	-	-	0.39	-	-	-	-	-	-	-	-	-	743	
I		0.029	0.24	1.56	0.036	0.0061	0.010	0.0098	0.0027	0.35	-	0.65	-	-	-	-	-	-	-	-	-	-	-	-	759	
J		0.125	0.21	1.31	0.020	0.0044	0.007	0.0055	0.0041	-	0.62	-	0.18	-	-	-	-	-	-	-	-	-	-	-	718	
K		0.131	0.25	1.22	0.048	0.0070	0.015	0.0071	0.0023	-	-	0.26	-	0.30	-	-	-	-	-	-	-	-	-	-	768	
L		0.110	0.28	1.66	0.032	0.0027	0.005	0.0006	0.0015	-	-	-	0.11	-	0.36	-	-	-	-	-	-	-	-	-	734	
M		0.160	0.37	1.30	0.019	0.0049	0.006	0.0087	0.0021	-	-	-	-	0.25	-	0.07	-	-	-	-	-	-	-	-	756	
N		0.118	0.33	1.71	0.017	0.0024	0.010	0.0062	0.0020	0.08	-	0.07	-	-	0.13	-	-	-	-	-	-	-	-	-	734	
O		0.063	0.32	1.04	0.041	0.0045	0.014	0.0058	0.0049	0.10	0.08	0.44	0.28	0.06	0.16	0.60	-	-	-	-	-	-	-	-	772	
P		0.076	0.28	1.59	0.044	0.0023	0.013	0.0039	0.0037	0.35	0.28	-	-	-	-	-	0.46	-	-	-	-	-	-	-	737	
Q		0.162	0.10	1.68	0.018	0.0056	0.015	0.0028	0.0035	0.36	-	0.66	-	-	-	-	-	0.048	-	-	-	-	-	-	708	
R		0.017	0.05	1.51	0.026	0.0023	0.002	0.0058	0.0038	0.40	-	-	0.27	-	-	-	-	-	0.07	-	-	-	-	-	754	
S		0.113	0.30	1.16	0.042	0.0071	0.018	0.0025	0.0022	0.05	-	-	-	0.24	-	-	-	-	-	0.016	-	-	-	-	781	
T		0.067	0.07	1.71	0.011	0.0031	0.001	0.0085	0.0046	0.33	-	-	-	-	0.09	-	-	-	-	-	0.0019	-	-	-	746	
U		0.069	0.30	1.81	0.010	0.0046	0.003	0.0019	0.0015	0.34	-	-	-	-	-	0.75	-	-	-	-	-	0.0073	-	-	737	
V		0.085	0.38	1.63	0.030	0.0059	0.008	0.0013	0.0028	0.37	-	-	-	0.10	-	-	-	-	-	-	-	-	0.0034	-	746	
W		0.146	0.10	1.67	0.034	0.0055	0.017	0.0046	0.0016	0.38	-	0.58	-	-	-	-	-	-	-	-	-	-	-	0.0028	715	
X		0.081	0.30	0.72	0.042	0.0030	0.018	0.0018	0.0046	0.07	0.81	0.54	0.10	0.29	0.18	0.56	0.15	0.037	0.06	0.044	0.0020	0.0073	0.0077	0.0082	765	
Y		0.008	0.10	1.65	0.017	0.0051	0.019	0.0058	0.0037	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	776	
Z		0.217	0.15	1.36	0.026	0.0070	0.018	0.0025	0.0042	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	734	
AA		0.071	0.54	1.80	0.045	0.0037	0.005	0.0086	0.0023	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	744	
AB		0.151	0.15	0.33	0.042	0.0023	0.018	0.0100	0.0028	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	837	
AC		0.164	0.05	2.61	0.013	0.0049	0.005	0.0079	0.0010	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	650	
AD		0.082	0.10	1.87	0.063	0.0047	0.017	0.0047	0.0050	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	735	
AE		0.101	0.18	1.68	0.017	0.0007	0.008	0.0066	0.0044	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	744	
AF		0.082	0.32	2.10	0.012	0.0116	0.005	0.0087	0.0018	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	717	
AG		0.145	0.04	1.55	0.023	0.0076	0.022	0.0078	0.0035	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	741	
AH		0.085	0.13	1.74	0.040	0.0044	0.019	0.0116	0.0021	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	744	
AI		0.107	0.35	1.63	0.013	0.0062	0.014	0.0082	0.0152	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	746	

* Underlining indicates value outside scope of present disclosure.

* Ar₃ = 910 – 310C – 80Mn – 20Cu – 15Cr – 55Ni – 80Mo (element symbol indicates content (mass%) of each element)

* Underlining indicates value outside scope of present disclosure.

* Ar₃ = 910 – 310C – 80Mn – 80Mo (element symbol indicates content (mass%) of each element)

[Table 2]

Steel material		Steel plate	Hot rolling	Accelerated cooling			Reheating		Metallic microstructure	Hardness properties				Strength properties			Toughness	Remarks		
No.	Steel sample ID	Ar ₃ (°C)	Thickness (mm)	Finish temp. (°C)	Cooling rate (°C/s)		Means	End-point temp. (°C)		(*1) Position	(*1) Position		YS (MPa)	TS (MPa)	uEl (%)	vTrs (°C)				
					Start temp. (°C)	Stop temp. (°C)		(*1) Position	(*2) Position		Average hardness HV0.1	Maximum position (mm)					Thickness direction, HV1		Variation ΔHV1	
1	A	745	30	830	810	53	375	Induction heating	603	433	92	155	22	3	22	503	625	15	-103	Good
2	B	708	30	740	720	45	337	Induction heating	610	450	94	189	10	3	40	491	596	15	-79	Good
3	B	708	30	740	720	54	340	Induction heating	603	452	92	202	18	4	28	505	652	14	-65	Good
4	B	708	30	760	740	26	285	Induction heating	621	455	92	168	21	1	24	470	575	15	-64	Good
5	B	708	30	760	750	50	210	Induction heating	610	430	94	193	22	3	32	493	665	13	-42	Good
6	B	708	30	780	760	47	327	Induction heating	601	444	99	177	19	2	21	502	629	16	-73	Good
7	B	708	30	780	760	48	330	Induction heating	433	342	92	206	19	4	35	456	578	16	-69	Good
8	B	708	30	730	710	48	365	Induction heating	536	374	98	162	23	2	38	478	580	15	-80	Good
9	C	738	30	800	790	45	358	Induction heating	586	424	95	193	14	3	35	480	608	17	-81	Good
10	D	710	30	820	800	50	340	Induction heating	626	464	97	160	22	3	35	505	616	15	-81	Good
11	E	741	30	910	890	52	299	Induction heating	618	461	95	163	15	3	46	575	712	19	-96	Good
12	F	722	30	750	730	48	360	Induction heating	602	435	96	175	15	3	47	465	594	15	-89	Good
13	G	735	30	830	810	45	344	Induction heating	600	455	97	201	19	3	61	518	619	16	-71	Good
14	H	743	30	870	860	51	287	Induction heating	594	425	94	168	21	3	32	506	690	16	-83	Good
15	I	759	30	780	770	49	296	Induction heating	626	478	95	200	13	3	34	530	644	15	-68	Good
16	J	718	30	740	720	45	330	Induction heating	626	464	95	208	13	2	62	506	588	14	-75	Good
17	K	768	30	830	820	49	362	Induction heating	628	471	96	179	24	2	46	551	647	17	-93	Good
18	L	734	30	850	830	54	370	Induction heating	598	431	98	165	18	1	27	503	699	18	-77	Good
19	M	756	30	830	820	47	332	Induction heating	577	420	98	181	18	2	60	501	633	17	-81	Good
20	N	734	30	750	740	48	333	Induction heating	594	444	98	199	24	2	52	503	587	13	-68	Good
21	O	772	30	840	820	51	350	Induction heating	612	456	97	209	13	2	32	516	663	11	-72	Good
22	P	737	30	770	760	53	285	Induction heating	628	468	96	184	22	1	49	545	693	16	-67	Good
23	Q	708	30	750	730	48	529	Induction heating	640	488	95	218	20	3	59	586	736	14	-39	Good
24	R	754	30	820	800	52	288	Induction heating	592	365	98	191	19	2	54	505	611	15	-75	Good
25	S	781	30	840	830	53	343	Induction heating	571	404	94	188	21	3	34	491	581	17	-72	Good

* Underlining indicates value outside scope of present disclosure.

*1: 0.5 mm depth position from surface of steel sheet

*2: 1/4 sheet thickness position

* Underlining indicates value outside scope of present disclosure.

*1: 0.5 mm depth position from surface of steel sheet

*2: 1/4 sheet thickness position

No.	Steel material		Steel plate thickness (mm)	Hot rolling Finish temp. (°C)	Accelerated cooling			Reheating		Metallic microstructure (*1) Position	Hardness properties				Strength properties			Toughness	Remarks	
	Steel sample ID	Ar ₃ (°C)			Start temp. (°C)	Cooling rate (*2) (°C/s)	Stop temp. (°C)	Means	End-point temp. (°C)		Average hardness HV0.1	(*1) Position	Thickness direction, HV1	YS (MPa)	TS (MPa)	uEl (%)	vTrs (°C)			
											B fraction (%)		Maximum position (mm)	Variation ΔHV1						
26	T	746	30	830	820	46	355	Induction heating	594	438	95	3	59	521	621	15	-73	Good		
27	U	737	30	770	750	53	343	Induction heating	590	433	94	3	37	475	580	13	-81	Good		
28	V	746	30	800	790	53	275	Induction heating	604	451	94	4	54	503	628	13	-77	Good		
29	W	715	30	750	740	48	320	Induction heating	597	445	94	3	41	544	730	13	-80	Good		
30	X	765	30	790	780	54	294	Induction heating	577	410	98	4	27	483	583	12	-62	Good		
31	B	708	30	700	685	50	301	Induction heating	571	410	80	3	59	433	522	13	-27	Poor		
32	B	708	30	750	730	5	328	Induction heating	602	405	92	2	46	392	475	12	-47	Good		
33	B	708	30	770	760	125	250	Induction heating	631	475	91	3	66	521	735	12	-23	Good		
34	B	708	30	780	770	46	190	Induction heating	583	426	93	2	44	521	735	16	-28	Good		
35	B	708	30	760	740	51	620	Induction heating	650	494	92	4	53	418	489	14	-48	Good		
36	B	708	30	740	720	46	290	Induction heating	350	205	95	3	64	521	654	15	-78	Poor		
37	B	708	30	740	720	52	340	Gas-fired furnace	700	495	94	4	62	396	498	15	-41	Good		
38	B	708	30	750	730	48	303	None	=	=	93	1	96	511	621	8	-70	Poor		
39	B	708	30	730	720	55	322	Induction heating	625	610	98	2	12	423	526	19	-25	Good		
40	Y	776	30	820	800	54	320	Induction heating	625	479	91	4	59	411	498	16	-88	Good		
41	Z	734	30	780	760	52	357	Induction heating	597	430	92	3	32	494	630	13	-21	Good		
42	AA	744	30	770	750	47	365	Induction heating	621	472	95	2	32	509	598	15	-27	Good		
43	AB	837	30	880	870	52	304	Induction heating	581	419	93	2	38	434	521	15	-86	Good		
44	AC	650	30	680	670	55	321	Induction heating	621	468	97	4	47	527	645	17	-24	Good		
45	AD	735	30	880	860	53	311	Induction heating	627	465	98	2	63	544	706	17	-27	Good		
46	AE	744	30	850	830	50	314	Induction heating	614	450	93	2	31	525	662	15	-21	Good		
47	AF	717	30	760	750	54	363	Induction heating	602	440	94	4	32	491	615	12	-26	Good		
48	AG	741	30	840	820	50	362	Induction heating	623	453	96	4	65	541	656	18	-15	Good		
49	AH	744	30	870	860	48	306	Induction heating	588	426	98	3	36	501	685	15	-9	Good		
50	AI	746	30	820	800	45	340	Induction heating	621	487	98	3	29	553	598	15	-21	Good		

* Underlining indicates value outside scope of present disclosure.
*1: 0.5 mm depth position from surface of steel sheet
*2: 1/4 sheet thickness position

*2: 1/4 sheet thickness position

[0079] As can be seen in Table 1 and Table 2, for the Examples, all obtained steel plates had a yield stress YS of 450 MPa or more, a tensile strength TS of 570 MPa or more, uniform elongation of 10 % or more, vTrs of -30 °C or less, excellent toughness at low temperature, and excellent ammonia SCC resistance.

[0080] In contrast, although the chemical compositions of No. 31 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 microstructure 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.

[0081] 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: 0.010 % to 0.060 %,

N: 0.0010 % or more and 0.0100 % or less,

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,

at a 0.5 mm depth position from the surface of the steel plate, average hardness is 230HV0.1 or less and

hardness variation is 30HV0.1 or less, a maximum value of hardness in the thickness direction is at a position

1.0 mm or more and 1/4 or less of the thickness of the steel plate from the surface of the steel plate, and

hardness variation in the thickness direction is 70HV1 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.

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: 0.010 % to 0.060 %,

N: 0.0010 % or more and 0.0100 % or less,

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 accelerated cooling from a cooling start temperature that is the Ar_3 transformation temperature or more; followed by reheating, wherein,

in the accelerated cooling, cooling stop temperature is in a range from 200 °C to 600 °C and cooling rate at a 1/4 plate thickness position is 20 °C/s to 120 °C/s, and

the reheating is performed until end-point temperature at a 0.5 mm depth position from the surface of the steel plate is in a range from 400 °C to 680 °C, with end-point temperature at a 1/4 plate thickness position being 500 °C or less.

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/JP2023/002491

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 301F; C22C38/60; C21D8/02 B; C22C38/00 301A; C22C38/06

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; C22C38/00-38/60

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.
X	JP 2020-193374 A (JFE STEEL CORP) 03 December 2020 (2020-12-03) claims, tables 1-2	3, 6
A		1-2, 4-5
A	WO 2020/067210 A1 (JFE STEEL CORP) 02 April 2020 (2020-04-02) claims, paragraphs [0004], [0046], tables 1-2	1-6
A	WO 2020/067209 A1 (JFE STEEL CORP) 02 April 2020 (2020-04-02) claims, paragraphs [0004], [0046], tables 1-2	1-6
A	WO 2018/181564 A1 (JFE STEEL CORP) 04 October 2018 (2018-10-04) claims, all tables	1-6
A	WO 2018/179512 A1 (JFE STEEL CORP) 04 October 2018 (2018-10-04) claims, all tables	1-6
A	JP 2020-193375 A (JFE STEEL CORP) 03 December 2020 (2020-12-03) examples	1-6

☒ 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

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“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

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Date of mailing of the international search report

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Name and mailing address of the ISA/JP

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/002491

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C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2013-139630 A (JFE STEEL CORP) 18 July 2013 (2013-07-18) entire text	1-6
A	JP 2008-25014 A (SUMITOMO METAL IND LTD) 07 February 2008 (2008-02-07) entire text	1-6

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/002491

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP	2020-193374	A	03 December 2020	(Family: none)	
WO	2020/067210	A1	02 April 2020	EP 3859026 A1 claims, paragraphs [0004], [0040], tables 1-2	
				CN 112752858 A	
				KR 10-2021-0064296 A	
WO	2020/067209	A1	02 April 2020	EP 3859027 A1 claims, paragraphs [0004], [0041], tables 1-2	
				CN 112752857 A	
				KR 10-2021-0050548 A	
WO	2018/181564	A1	04 October 2018	EP 3604592 A1 claims, all tables	
				CN 110475894 A	
				KR 10-2019-0129097 A	
WO	2018/179512	A1	04 October 2018	EP 3604584 A1 claims, all tables	
				CN 110462080 A	
				KR 10-2019-0129957 A	
JP	2020-193375	A	03 December 2020	(Family: none)	
JP	2013-139630	A	18 July 2013	(Family: none)	
JP	2008-25014	A	07 February 2008	(Family: none)	

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP H10140235 A [0008]
- JP H10168516 A [0008]