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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, in particular including one or more of Cu: 0.01 % to 0.5 %, Cr: 0.01 % to 1.0 %, Sb: 0.01 % to 0.50 %, or Sn: 0.01 % to 0.50 %, and the chemical composition satisfies a defined relationship

of the Cu, Cr, Sb, and Sn content. Further, a hardness property at a 1.0 mm depth position from the surface of the steel plate is 300 HV or less, and the metallic structure at a 1/2 thickness position of the steel plate has a volume fraction of bainitic microstructure of 20 % or more and a total volume fraction of ferritic microstructure and bainitic microstructure of 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.

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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 adding elements such as Cu, Cr, Sb, and Sn in defined amounts or

more and controlling hardness at a 1.0 mm depth position from the surface of the steel plate to be 300 HV or less, SCC resistance in liquid ammonia environments can be obtained and costly heat treatment as in conventional technology can be eliminated.

[0012] The present disclosure is based on the above discoveries, that is, 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

and further, at least one selected from the group consisting of

Cu: 0.01 % to 0.50 %,

Cr: 0.01 % to 1.00 %,

Sb: 0.01 % to 0.50 %, and

Sn: 0.01 % to 0.50 %,

with the balance being Fe and inevitable impurity, wherein

a CR value obtained by the following Expression (1) is 0.70 or more,

the steel plate has a hardness property such that, at a 1.0 mm depth position from the surface of the steel plate, hardness is 300 HV or less,

the steel plate has a metallic microstructure where, 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, and

$$CR = 2.3[Cu] + 2.8[Cr] + 7.3[Sb] + 3.6[Sn] \quad \dots \text{Expression (1)}$$

where [X] represents content of element X in the steel, in mass%.

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

Ni: 0.01 % to 2.00 %,

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
and further, at least one selected from the group consisting of

Cu: 0.01 % to 0.50 %,
Cr: 0.01 % to 1.00 %,

Sb: 0.01 % to 0.50 %, and
Sn: 0.01 % to 0.50 %,

with the balance being Fe and inevitable impurity, wherein a CR value obtained by the following Expression (1)

is 0.70 or more, the method comprising:

hot rolling with a rolling finish temperature that is Ar_3 transformation temperature or more; followed by cooling from a cooling start temperature that is the Ar_3 transformation temperature or more to a cooling stop temperature of 600 °C or less, wherein, in the cooling, cooling rate at a 1.0 mm depth position from the steel plate surface is 150 °C/s or less, and cooling rate at a 1/2 thickness position of the steel plate is 10 °C/s or more, and

$$CR = 2.3[Cu] + 2.8[Cr] + 7.3[Sb] + 3.6[Sn] \quad \dots \text{Expression (1)}$$

where [X] represents content of element X in the steel, in mass%.

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

Ni: 0.01 % to 2.00 %,

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.

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

Al: 0.060 % or less

[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 and decreases cleanliness, and may decrease 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 %. 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 %. 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 %. Excessive reduction leads to higher refining costs, and therefore from a cost perspective, the O content is preferably 0.0010 % or more.

[0024] At least one selected from the group consisting of Cu: 0.01 % to 0.50 %, Cr: 0.01 % to 1.00 %, Sb: 0.01 % to 0.50 %, and Sn: 0.01 % to 0.50 %, where a CR value obtained by Expression (1) is 0.70 or more

Cu, Cr, Sb, and Sn are particularly important elements for improving ammonia SCC resistance. Therefore, according to the present disclosure, at least one of these needs to be included in the amounts specified above, and the CR value obtained by the following Expression (1) is required to be 0.70 or more.

$$CR = 2.3[Cu] + 2.8[Cr] + 7.3[Sb] + 3.6[Sn] \quad \dots \text{Expression (1)}$$

[0025] Here, [X] represents content of element X in the steel, in mass%.

[0026] That is, Cu, Cr, Sb, and Sn rapidly form protective corrosion products in a liquid ammonia environment, and suppress stress corrosion cracking. To obtain this effect, when Cu is added, Cu content is required to be 0.01 % or more, when Cr is added, Cr content is required to be 0.01 % or more, when Sb is added, Sb content is required to be 0.01 % or more, and when Sn is added, Sn content is required to be 0.01 % or more.

[0027] Further, the above expression for calculating CR value is an expression designed to estimate ammonia SCC resistance based on the content of each element, and the higher the CR value, the better the ammonia SCC resistance. By setting the CR value to 0.70 or more, stress corrosion cracking in a liquid ammonia environment can be suppressed.

[0028] However, excessive addition of Cu, Cr, Sb, and Sn degrades weldability and toughness, and is also detrimental in view of alloy cost. Accordingly, the Cu content is limited to 0.50 % or less, the Cr content is limited to 1.00 % or less, the Sb content is limited to 0.50 % or less, and the Sn content is limited to 0.50 % or less. The Cu content is preferably 0.40 % or less. The Cr content is preferably 0.80 % or less. The Sb content is preferably 0.40 % or less. The Sn content is preferably 0.40 % or less. Further, an upper limit of the CR value is not particularly limited. The CR value exceeding 7.00 leads to saturation of the effect and excessive addition of the above elements leads to a steep rise in price, and therefore the upper limit of the CR value is preferably about 7.00.

[0029] 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.

[0030] At least one selected from the group consisting of Ni: 0.01 % to 2.00 %, Mo: 0.01 % to 0.50 %, and W: 0.01 % to 1.00 %

[0031] Ni, Mo, and W are elements that further improve ammonia SCC resistance, and one or more of these may be included. To achieve these effects, it is preferable that when Ni is contained, Ni 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 addition of Mo and W degrades weldability and toughness, and is detrimental in view of alloy cost. Accordingly, the Ni content is preferably 2.00 % or less, the Mo content is preferably 0.50 % or less, and the W content is preferably 1.00 % or less. More preferably, the Ni content is 1.50 % 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 %

[0032] 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 %

[0033] 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 %

[0034] 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 %

[0035] 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 0.005 % or more. Further, 0.007 % or more is 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 %

[0036] 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 %

[0037] 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 %

[0038] 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 %

[0039] 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

[0040] In addition to having the chemical composition described above, the steel plate has hardness properties such that, at a 1.0 mm depth position from the surface of the steel plate (hereinafter also referred to as a 1.0 mm position),

hardness is 300 HV or less.

[0041] 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 bainitic microstructure (hereinafter also referred to simply as 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.

[0042] The reasons for limiting the hardness properties and metallic microstructure of the steel plate as described above are explained below.

[Hardness at 1.0 mm position is 300 HV or less]

[0043] The hardness at the 1.0 mm position is 300 HV or less. The presence of a high hardness region in the outermost surface layer of the steel plate, specifically at the 1.0 mm position from the surface of the steel plate, promotes stress corrosion cracking in a liquid ammonia environment. Therefore, in the steel plate of the present disclosure, the hardness at the 1.0 mm position is 300 HV or less in order to secure excellent ammonia SCC resistance. A lower limit of hardness at the 1.0 mm position is not particularly limited. The lower limit of hardness at the 1.0 mm position is preferably about 130 HV.

[0044] Here, the hardness can be calculated by measuring Vickers hardness at multiple locations (for example, 100 points) at the 1.0 mm position.

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

[0045] 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 %.

[0046] 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.

[0047] 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.

[0048] The volume fraction of each microstructure can be measured by a method described in the EXAMPLES section below.

(3) Production conditions

[0049] 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, at least one selected from the group consisting of Cu: 0.01 % to 0.50 %, Cr: 0.01 % to 1.00 %, Sb: 0.01 % to 0.50 %, and Sn: 0.01 % to 0.50 %, where a CR value obtained by Expression (1) is 0.70 or more, and in addition, as required, at least once selected from the group consisting of Ni: 0.01 % to 2.00 %, 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.

[0050] 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.

[0051] 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 A_{r3} transformation point temperature (hereinafter also referred to simply as the A_{r3} transformation temperature) or more. Following the hot rolling, cooling from the cooling

start temperature of the Ar_3 transformation temperature or more to the cooling stop temperature of 600 °C or less is performed under defined conditions.

[0052] 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: Ar_3 transformation temperature or more]

[0053] According to the present disclosure, hot rolling is started after heating to the temperature described above, and the hot rolling finishes at the Ar_3 transformation temperature or more.

[0054] When the rolling finish temperature is less than the Ar_3 transformation temperature, ferrite forms and toughness will deteriorate because the formed ferrite is affected by processing. Further, the load on the hot rolling mill increases. Accordingly, the rolling finish temperature in the hot rolling is the Ar_3 transformation temperature or more. Preferably, the rolling finish temperature in the hot rolling 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.

[0055] Here, the Ar_3 transformation temperature is obtainable by the following expression.

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

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

(Cooling)

[Cooling start temperature: Ar_3 transformation temperature or more]

[0057] Next, 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. The cooling start temperature being less than the Ar_3 transformation temperature leads to excessive ferrite formation and insufficient strength. The cooling start temperature is therefore the Ar_3 transformation temperature or more.

[Cooling stop temperature: 600 °C or less]

[0058] According to the present disclosure, after the hot rolling finishes, cooling is performed under defined conditions to any cooling stop temperature of 600 °C or less to bring ferrite and bainite to a defined volume fraction at the mid-thickness part. Here, when the cooling stop temperature exceeds 600 °C, excessive ferritic 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 microstructure becomes too high and toughness is reduced. The cooling stop temperature is therefore preferably 200 °C or more.

[0059] The cooling stop temperature is the temperature at the 1/2 position of the steel plate.

[Cooling rate at 1.0 mm position: 150 °C/s or less]

[0060] In the cooling, the cooling rate at the 1.0 mm position exceeding 150 °C/s causes the hardness at the 1.0 mm position to exceed 300 HV and the ammonia SCC resistance to deteriorate. Accordingly, the cooling rate at the 1.0 mm position is specified as 150 °C/s or less.

[0061] A lower limit of the cooling rate is not particularly limited. When the cooling rate is excessively small, excessive ferritic microstructure or pearlitic microstructure may form, leading to insufficient strength and deterioration of toughness. Therefore, from the viewpoint of more reliable prevention of such outcomes, the cooling rate is preferably 50 °C/s or more.

[0062] The cooling rate can be controlled by controlled cooling by intermittent cooling including cooling stop periods. The temperature at the 1.0 mm position is difficult to physically measure directly. However, the temperature distribution in a thickness cross-section, in particular at the 1.0 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.

[Cooling rate at 1/2 position: 10 °C/s or more]

[0063] Cooling at a cooling rate of 10 °C/s or more at the 1/2 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. To obtain the effect, the cooling rate at the 1/2 position during cooling according to the present disclosure is specified as 10 °C/s or more. When the cooling rate is less than 10 °C/s, excessive ferrite and pearlite are formed and sufficient strength is unobtainable. Accordingly, the cooling rate at the 1/2 thickness position is specified to be 10 °C/s or more.

[0064] An upper limit of the cooling rate is not particularly limited. The cooling rate being excessively large, may lead to the volume fraction of martensite austenite constituent becoming too large, and deterioration of toughness. Accordingly, the cooling rate at the 1/2 position is preferably 80 °C/s or less.

[0065] The cooling rate can be controlled by controlled cooling by intermittent cooling including cooling stop 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.

[0066] The cooling rate at the 1.0 mm position and the cooling rate at the 1/2 position can be varied, for example, by adjusting the cooling start temperature, water volume, and the like.

[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 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.

[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 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 44) each having a thickness of 30 mm. Then, the hot rolling and the 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 microstructure at the 1/2 thickness position, measurement of hardness at the 1.0 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 1/2 position]

[0070] Samples were taken from each steel plate so that 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 (microstructure 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.

[0071] 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 at 1.0 mm position]

[0072] For a cross-section perpendicular to the rolling direction of each steel plate, Vickers hardness (HV10) was measured at 100 points at the 1.0 mm position in accordance with JIS Z 2244, and the maximum value thereof was obtained.

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[Strength properties]

[0073] 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]

[0074] 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 Charpy impact tests were conducted according to JIS Z 2242 to measure vTrs (fracture appearance transition temperature). Steel plates having a vTrs of -30 °C or less were evaluated as having excellent toughness.

[Ammonia SCC resistance]

[0075] 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.

[0076] 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 °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%)																							CR	Ar ₃ (°C)	Remarks
C	Si	Mn	Al	N	P	S	O	Cu	Cr	Sb	Sn	Ni	Mo	W	V	Ti	Co	Nb	B	Ca	Mg	REM					
A	0.049	0.26	1.51	0.001	0.0021	0.014	0.0081	0.0000	0.26	-	0.04	-	-	-	-	-	-	-	-	-	-	-	-	0.74	769		
B	0.089	0.23	0.77	0.019	0.0075	0.005	0.0062	0.0050	-	0.15	0.05	-	-	-	-	-	-	-	-	-	-	-	-	0.79	819		
C	0.106	0.32	1.73	0.017	0.0039	0.020	0.0100	0.0000	-	-	0.13	-	-	-	-	-	-	-	-	-	-	-	-	0.95	739		
D	0.093	0.28	1.10	0.009	0.0063	0.019	0.0042	0.0040	0.16	0.50	-	-	-	-	-	-	-	-	-	-	-	-	-	1.77	782		
E	0.024	0.29	0.80	0.012	0.0045	0.019	0.0026	0.0010	0.16	-	0.26	-	-	-	-	-	-	-	-	-	-	-	-	2.27	835		
F	0.100	0.33	2.30	0.014	0.0057	0.014	0.0011	0.0000	-	0.16	0.30	-	-	-	-	-	-	-	-	-	-	-	-	2.64	693		
G	0.049	0.27	1.86	0.047	0.0047	0.007	0.0045	0.0030	0.08	0.55	0.18	-	-	-	-	-	-	-	-	-	-	-	-	3.04	736		
H	0.121	0.17	2.13	0.041	0.0021	0.003	0.0051	0.0030	0.32	0.40	0.39	-	1.40	-	-	-	-	-	-	-	-	-	-	4.70	613		
I	0.070	0.05	1.60	0.039	0.0037	0.020	0.0019	0.0040	0.15	0.65	0.20	-	-	0.39	-	-	-	-	-	-	-	-	-	3.63	716		
J	0.124	0.37	2.25	0.046	0.0038	0.012	0.0071	0.0030	0.36	0.50	0.12	0.15	-	-	-	-	-	-	-	-	-	-	-	3.64	677		
K	0.027	0.08	1.40	0.003	0.0060	0.008	0.0016	0.0030	0.21	0.60	0.24	-	-	0.12	-	-	-	-	-	-	-	-	-	3.92	776		
L	0.166	0.22	1.25	0.045	0.0038	0.014	0.0007	0.0010	0.11	0.15	0.30	0.27	1.43	0.06	0.63	-	-	-	-	-	-	-	-	3.84	671		
M	0.095	0.27	1.51	0.013	0.0044	0.007	0.0096	0.0020	0.10	0.35	0.09	0.36	0.32	0.10	0.08	0.22	-	-	-	-	-	-	-	3.16	727		
N	0.050	0.07	0.77	0.014	0.0021	0.015	0.0010	0.0010	0.28	0.19	0.32	0.06	0.36	0.07	0.26	-	0.089	-	-	-	-	-	-	3.73	799		
O	0.145	0.33	1.08	0.007	0.0074	0.013	0.0032	0.0000	0.38	0.28	0.21	0.13	0.55	0.21	0.14	-	0.47	-	-	-	-	-	-	3.66	720		
P	0.112	0.11	1.12	0.045	0.0032	0.014	0.0049	0.0050	0.17	0.15	0.33	0.13	0.30	0.11	0.37	-	-	0.018	-	-	-	-	-	3.69	755		
Q	0.074	0.35	1.62	0.030	0.0029	0.017	0.0055	0.0040	0.20	0.10	0.10	0.04	0.21	0.05	0.05	-	-	-	0.001	-	-	-	-	1.61	736		
R	0.157	0.06	2.11	0.041	0.0074	0.002	0.0090	0.0010	0.11	0.77	0.32	0.20	0.28	0.24	0.70	-	-	-	-	-	0.0057	-	-	5.47	644		
S	0.050	0.24	0.91	0.043	0.0053	0.018	0.0006	0.0010	0.39	0.28	0.23	0.31	1.09	0.08	0.44	-	-	-	-	-	-	-	-	4.48	743		
T	0.070	0.37	1.57	0.006	0.0033	0.005	0.0092	0.0020	0.18	0.28	0.30	0.35	0.93	0.07	0.30	-	-	-	-	-	-	-	0.0079	4.65	698		
U	0.021	0.15	1.86	0.001	0.0027	0.009	0.0044	0.0020	0.10	0.39	0.33	0.05	0.92	0.14	0.27	0.23	0.063	0.23	0.032	0.001	0.0099	0.0037	0.0086	3.91	685		
V	0.008	0.19	1.69	0.035	0.0041	0.004	0.0099	0.0030	0.38	0.33	0.32	-	-	-	-	-	-	-	-	-	-	-	-	4.13	760		
W	<u>0.215</u>	0.27	1.90	0.002	0.0048	0.009	0.0018	0.0000	0.07	0.43	0.07	-	-	-	-	-	-	-	-	-	-	-	-	1.88	684		
X	0.104	0.52	1.97	0.010	0.0053	0.009	0.0071	0.0010	0.14	0.55	0.06	-	-	-	-	-	-	-	-	-	-	-	-	2.30	709		
Y	0.079	0.24	<u>0.48</u>	0.035	0.0039	0.004	0.0042	0.0040	0.22	0.27	0.22	-	-	-	-	-	-	-	-	-	-	-	-	2.87	839		
Z	0.029	0.19	<u>2.55</u>	0.011	0.0042	0.009	0.0066	0.0010	0.25	0.75	0.26	-	-	-	-	-	-	-	-	-	-	-	-	4.57	681		
AA	0.078	0.12	1.24	<u>0.064</u>	0.0076	0.015	0.0008	0.0000	0.14	0.17	0.26	-	-	-	-	-	-	-	-	-	-	-	-	2.70	781		
AB	0.023	0.26	1.81	0.006	0.0007	0.009	0.0042	0.0040	0.10	0.72	0.21	-	-	-	-	-	-	-	-	-	-	-	-	3.78	745		
AC	0.131	0.06	2.18	0.016	<u>0.0108</u>	0.014	0.0036	0.0020	0.33	0.55	0.29	-	-	-	-	-	-	-	-	-	-	-	-	4.42	680		
AD	0.057	0.35	1.07	0.036	0.0023	0.022	0.0082	0.0020	0.10	0.20	0.40	-	-	-	-	-	-	-	-	-	-	-	-	3.71	802		
AE	0.079	0.30	0.71	0.041	0.0072	0.007	<u>0.0132</u>	0.0030	0.13	0.22	0.04	-	-	-	-	-	-	-	-	-	-	-	-	1.21	823		
AF	0.155	0.12	1.36	0.012	0.0027	0.020	0.0035	<u>0.0120</u>	0.26	0.25	0.37	-	-	-	-	-	-	-	-	-	-	-	-	4.00	744		
AG	0.134	0.11	2.20	0.019	0.0064	0.006	0.0063	<u>0.0040</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.00	692		
AH	0.080	0.13	1.67	0.020	0.0051	0.000	0.0003	0.0010	0.05	0.03	0.02	0.02	-	-	-	-	-	-	-	-	-	-	-	0.42	750		
* Underlining indicates value outside scope of present disclosure.																											
* CR = 2.3Cu + 2.8Cr + 7.3Sb + 3.6Sn (element symbol indicates content (mass%) of each element)																											
* Ar ₃ = 910 – 310C – 80Mn – 20Cu – 15Cr – 55Ni – 80Mo (element symbol indicates content (mass%) of each element)																											

[Table 2]

Table 2

No.	Steel material		Steel plate Thickness (mm)	Hot rolling Finish temp. (°C)	Cooling			Metallic structure		Hardness		Strength properties		Toughness vTrs (°C)	Ammonia SCC resistance	Remarks
	Steel sample ID	Ar ₃ (°C)			Start temp. (°C)	Cooling Rate (°C/s)		1/2 position		1.0 mm position	HV10	YS (MPa)	TS (MPa)			
						1.0 mm position	1/2 position	B fraction (%)	F+B fraction (%)							
1	A	769	30	840	830	61	12	400	52	97	192	424	497	-103	Good	Examples
2	B	819	30	870	850	111	38	270	59	92	226	414	537	-86	Good	
3	C	739	30	770	750	96	27	480	34	82	205	433	516	-78	Good	
4	D	782	30	820	810	103	37	480	30	86	224	425	602	-77	Good	
5	E	835	30	870	860	74	23	550	39	89	151	388	502	-92	Good	
6	F	693	30	760	740	123	43	360	77	99	267	483	638	-76	Good	
7	G	736	30	780	760	91	31	380	48	82	246	464	640	-73	Good	
8	G	736	30	750	740	122	28	240	32	89	274	456	629	-78	Good	
9	G	736	30	790	770	55	12	460	59	88	210	423	498	-81	Good	
10	G	736	30	770	750	146	50	370	61	68	271	493	702	-63	Good	
11	G	736	30	810	790	122	36	210	71	87	292	478	648	-67	Good	
12	G	736	30	800	790	121	37	590	31	81	252	472	645	-72	Good	
13	H	613	30	670	660	128	34	500	55	88	290	487	653	-76	Good	
14	I	716	30	810	790	107	33	540	46	93	247	470	644	-88	Good	
15	J	677	30	710	690	98	26	530	32	96	268	475	621	-78	Good	
16	K	776	30	820	800	87	34	490	37	85	214	435	584	-87	Good	
17	L	671	30	700	680	83	33	430	28	86	218	440	574	-82	Good	
18	M	727	30	770	750	97	33	240	36	81	251	462	655	-67	Good	
19	N	799	30	880	870	122	32	420	82	93	222	421	524	-84	Good	
20	O	720	30	790	780	106	25	210	74	92	253	471	624	-39	Good	
21	P	755	30	840	830	130	41	440	53	86	240	434	603	-75	Good	
22	Q	736	30	780	760	91	24	480	43	82	276	493	711	-80	Good	

Table 2 (cont'd)

No.	Steel material		Steel plate	Hot rolling	Cooling				Metallic structure		Hardness	Strength properties		Toughness	Ammonia SCC resistance	Remarks
	Steel sample ID	Ar ₃ (°C)			Thickness (mm)	Finish temp. (°C)	Start temp. (°C)	Cooling Rate (°C/s)		1/2 position						
								1.0 mm position	1/2 position	B fraction (%)		F+B fraction (%)	YS (MPa)			
23	R	644	30	710	690	86	29	72	92	268	506	721	-66	Good	Examples	
24	S	743	30	820	800	113	27	68	83	245	418	555	-72	Good		
25	T	698	30	780	760	62	13	31	75	210	420	597	-70	Good		
26	U	685	30	730	720	121	39	30	93	266	457	641	-67	Good		
27	G	736	30	690	680	136	42	15	90	267	460	560	-28	Good	Comparative Examples	
28	G	736	30	790	700	123	27	16	77	260	350	470	-57	Good		
29	G	736	30	770	760	160	50	22	79	312	442	620	-89	Poor		
30	G	736	30	780	760	85	6	11	57	219	342	476	-82	Good		
31	G	736	30	810	800	107	33	12	58	241	355	468	-55	Good		
32	V	760	30	820	800	120	33	50	78	260	418	476	-70	Good		
33	W	684	30	780	770	135	33	77	95	264	511	710	-26	Good		
34	X	709	30	770	750	113	29	38	73	271	487	668	-28	Good		
35	Y	839	30	860	850	137	33	80	89	279	355	462	-85	Good		
36	Z	681	30	730	710	107	37	61	98	246	457	618	-27	Good		
37	AA	781	30	820	800	136	46	31	93	228	416	554	-28	Good		
38	AB	745	30	800	780	76	25	61	90	236	455	644	-28	Good		
39	AC	680	30	740	730	120	25	79	90	290	482	710	-26	Good		
40	AD	802	30	860	850	77	16	85	98	196	414	495	-17	Good		
41	AE	823	30	870	860	128	31	43	90	237	423	509	-5	Good		
42	AF	744	30	790	770	63	18	61	82	215	446	604	-26	Good		
43	AG	692	30	730	720	77	31	74	99	250	433	607	-72	Poor		
44	AH	750	30	830	820	110	38	55	88	248	492	602	-70	Poor		

[0077] As can be seen in Tables 1 and 2, for the Examples (No. 1 to No. 26) 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.

[0078] In contrast, although the chemical compositions of No. 27 to No. 31 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 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.

[0079] Further, the chemical compositions of No. 32 to No. 44 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

and further, at least one selected from the group consisting of

Cu: 0.01 % to 0.50 %,

Cr: 0.01 % to 1.00 %,

Sb: 0.01 % to 0.50 %, and

Sn: 0.01 % to 0.50 %,

with the balance being Fe and inevitable impurity, wherein

a CR value obtained by the following Expression (1) is 0.70 or more,

the steel plate has a hardness property such that, at a 1.0 mm depth position from the surface of the steel plate, hardness is 300 HV or less,

the steel plate has a metallic microstructure where, 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, and

$$CR = 2.3[Cu] + 2.8[Cr] + 7.3[Sb] + 3.6[Sn] \quad \dots \text{Expression (1)}$$

where [X] represents content of element X in the steel, in mass%.

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

Ni: 0.01 % to 2.00 %,

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

and further, at least one selected from the group consisting of

Cu: 0.01 % to 0.50 %,

Cr: 0.01 % to 1.00 %,

Sb: 0.01 % to 0.50 %, and

Sn: 0.01 % to 0.50 %,

with the balance being Fe and inevitable impurity, wherein a CR value obtained by the following Expression (1) is 0.70 or more, the method comprising:

hot rolling with a rolling finish temperature that is Ar_3 transformation temperature or more; followed by cooling from a cooling start temperature that is the Ar_3 transformation temperature or more to a cooling stop temperature of 600 °C or less, wherein, in the cooling, cooling rate at a 1.0 mm depth position from the steel plate surface is 150 °C/s or less, and cooling rate at a 1/2 thickness position of the steel plate is 10 °C/s or more, and

$$CR = 2.3[Cu] + 2.8[Cr] + 7.3[Sb] + 3.6[Sn] \quad \dots \text{Expression (1)}$$

where [X] represents content of element X in the steel, in mass%.

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

Ni: 0.01 % to 2.00 %,

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/JP2023/001049

A. CLASSIFICATION OF SUBJECT MATTER

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

C22C38/00-38/60; C21D8/02

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 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	WO 2021/106368 A1 (JFE STEEL CORP.) 03 June 2021 (2021-06-03) claims, paragraph [0040], tables 1, 2	3, 6
A		1-2, 4-5
A	JP 55-30062 B2 (NIPPON STEEL CORP.) 08 August 1980 (1980-08-08) claims, p. 1, column 2, lines 20-32, fig. 1	1-6
A	JP 2019-214751 A (NIPPON STEEL CORP.) 19 December 2019 (2019-12-19) claims, paragraphs [0001], [0002], [0011], [0012], [0052], [0053]	1-6
A	JP 2011-105963 A (NIPPON STEEL CORP.) 02 June 2011 (2011-06-02) claims, paragraphs [0001]-[0004], [0011], [0040], [0041]	1-6
A	JP 2020-12168 A (NIPPON STEEL CORP.) 23 January 2020 (2020-01-23) claims, paragraphs [0058]-[0063]	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

24 March 2023

Date of mailing of the international search report

04 April 2023

Name and mailing address of the ISA/IP

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/001049

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO	2021/106368	A1	03 June 2021	CN 114761595 A	
JP	55-30062	B2	08 August 1980	(Family: none)	
JP	2019-214751	A	19 December 2019	(Family: none)	
JP	2011-105963	A	02 June 2011	(Family: none)	
JP	2020-12168	A	23 January 2020	(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]