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# (54) STEEL SHEET AND PRODUCTION METHOD THEREFOR

(57) A steel plate according to the present disclosure contains, as composition: C: 0.005 mass% or more and 0.07 mass% or less; Si: 0 mass% or more and 0.04 mass% or less; Mn: 1.4 mass% or more and 2.0 mass% or less; P: more than 0 mass% and 0.010 mass% or less; S: more than 0 mass% and 0.007 mass% or less; Al: 0.010 mass% or more and 0.040 mass% or less; Ni: 0.1 mass% or more and 1.50 mass% or less; Cu: 0.1 mass%

or more and 0.8 mass% or less; Nb: 0.004 mass% or more and 0.025 mass% or less; Ti: 0.010 mass% or more and 0.025 mass% or less; N: 0.0040 mass% or more and 0.0080 mass% or less; and Ca: 0.0005 mass% or more and 0.0030 mass% or less, with the balance being Fe and inevitable impurities, a proportion of a content of acid insoluble Ti being 0.80 or less in a content of Ti based on the composition as a whole.

#### Description

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#### **TECHNICAL FIELD**

5 [0001] The present disclosure relates to a steel plate and a production method of the steel plate.

#### **BACKGROUND ART**

[0002] Along with an increase in size of a structure to be welded in a shipbuilding field, gradually enlarging is application of a high-strength steel plate having a plate thickness of 50 mm or more and a yield strength of 490 MPa or more. In such a steel plate that requires increased heat input, a demand for large heat input welding is increasing along with a viewpoint of improving efficiency in welding procedure. In the large heat input welding, a heat affected zone (HAZ) of the steel plate is retained, by heating, at temperature of austenite for a long period to form a coarse austenite structure and then, in a cooling process, generates coarse grain boundary ferrite and coarse grain boundary bainite along a prior austenite grain boundary. This results in acquisition of no stable toughness in the HAZ (hereinafter, also referred to as "HAZ toughness").

[0003] In order to solve such an inconvenience, proposed are methods of improving the HAZ toughness against the large heat input welding by controlling a form of a Ti-containing nitride (see Japanese Unexamined Patent Application Publication Nos. 2010-95781 and 2011-21263). These methods, however, restricts a casting step due to control of the Ti-containing nitride to possibly cause an increase in production costs. In addition, strength of base metal is not considered. [0004] Another proposal is a method of improving the HAZ toughness against the large heat input welding by controlling size of an oxide-based inclusion (see Japanese Unexamined Patent Application Publication No. 2010-222652). This method, however, requires a sophisticated steelmaking process for control of an oxide to possibly cause an increase in production costs. Also in this process, strength of base metal is not considered.

[0005] Another proposal is a method of improving the HAZ toughness by micronizing a structure of the HAZ through control of amounts of, for example, Ca, S, and O and introduction of a nucleus for intragranular transformation (see Japanese Unexamined Patent Application Publication No. 2013-147740). Most of base metal obtained by this method, however, has a yield strength as insufficient as less than 490 MPa, while one having a yield strength of 490 MPa or more is far from having sufficient HAZ toughness.

**[0006]** Another proposal is a method of realizing high strength of base metal and good HAZ toughness by Ti-Ca combined addition and optimization of amounts of CaO and CaS (see Japanese Unexamined Patent Application Publication No. 2002-317243). In this method, however, retention temperature before rolling is as high as 1150 to 1250°C, and this method still has room for improvement on productivity. In addition, characteristics of a thick steel plate having a plate thickness of 50 mm or more are not considered.

[0007] Another proposal is a method of improving the HAZ toughness by controlling a TiN precipitate with 0.1  $\mu$ m or less (see Japanese Unexamined Patent Application Publication No. 2001-98340). The heat input considered, however, is 450 kJ/cm at a maximum, and improvement of the HAZ toughness against the large heat input welding is somewhat less than enough. In addition, strength of base metal is not considered.

#### 40 CITATION LIST

## PATENT LITERATURES

## [8000]

LOOOG

Patent Literature 1: Japanese Unexamined Patent Application Publication No. 2010-95781 Patent Literature 2: Japanese Unexamined Patent Application Publication No. 2011-21263 Patent Literature 3: Japanese Unexamined Patent Application Publication No. 2010-222652 Patent Literature 4: Japanese Unexamined Patent Application Publication No. 2013-147740 Patent Literature 5: Japanese Unexamined Patent Application Publication No. 2002-317243 Patent Literature 6: Japanese Unexamined Patent Application Publication No. 2001-98340

## SUMMARY OF THE INVENTION

## 55 TECHNICAL PROBLEM

**[0009]** The present disclosure has been made in the circumstances described above, and an object is to provide a steel plate excellent in strength of base metal and HAZ toughness, and a production method of the steel plate.

#### SOLUTIONS TO PROBLEM

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**[0010]** As a result of earnest studies, the inventors have found that increasing addition amount of Ti in a steel plate increases fine TiN effective for improving the HAZ toughness, while also increasing coarse TiN with a particle diameter of, for example,  $2.0~\mu m$  or more that decreases the HAZ toughness. Therefore, the inventors have reduced an amount of coarse TiN generated when the addition amount of Ti is increased, to attain the present disclosure capable of improving the HAZ toughness when large heat input welding is performed.

[0011] That is, the invention that has been made to solve the above problem is a steel plate containing, as composition, C: 0.005 mass% or more and 0.07 mass% or less; Si: 0 mass% or more and 0.04 mass% or less; Mn: 1.4 mass% or more and 2.0 mass% or less; P: more than 0 mass% and 0.010 mass% or less; S: more than 0 mass% and 0.007 mass% or less; Al: 0.010 mass% or more and 0.040 mass% or less; Ni: 0.1 mass% or more and 1.50 mass% or less; Cu: 0.1 mass% or more and 0.8 mass% or less; Nb: 0.004 mass% or more and 0.025 mass% or less; Ti: 0.010 mass% or more and 0.025 mass% or less; N: 0.0040 mass% or more and 0.0080 mass% or less; and Ca: 0.0005 mass% or more and 0.0030 mass% or less, with the balance being Fe and inevitable impurities, the steel plate satisfying a following formula (1) when a content [mass%] of acid insoluble Ti is defined as [insol.Ti] and a content [mass%] of Ti based on the composition as a whole is defined as [Ti].

$$[insol.Ti]/[Ti] \le 0.80...(1)$$

**[0012]** In the steel plate, a proportion of the content of acid insoluble Ti, which mainly exists as TiN, in the whole content of Ti is adjusted to a value satisfying the formula (1), so that fine TiN increases relative to coarse TiN to suppress brittle fracture caused by coarse TiN. Thus, the steel plate is excellent in HAZ toughness. The steel plate that has the above composition is also excellent in strength of base metal.

[0013] When a content [mass%] of N is defined as [N], [Ti]/[N] is preferred to be 2.0 or more and 5.0 or less, a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less is preferred to be 2.0  $\times$  10<sup>5</sup> pieces/mm² or more, and a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less in the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less is preferred to be 15% or less. As described above, adjustment is made to provide the above ranges of [Ti]/[N], the sectional density of the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less, and the proportion in number of the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less, thus suppressing Ostwald ripening of TiN when the large heat input welding is performed and suppressing enlargement of diameters of prior austenite grains by TiN that remains unmelted after heat input. This results in suppressing generation of coarse grain boundary ferrite and coarse grain boundary bainite, so that it is possible to promote improvement of the HAZ toughness.

[0014] The steel plate is preferred to satisfy a following formula (2) when contents [mass%] of C, Si, Mn, Cu, Ni, Cr, Mo, V, and B are defined as [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], [V], and [B], respectively.

$$([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times [B]) \times 1.115 \ge 0.72...(2)$$

**[0015]** By satisfying the formula (2), it is possible to further improve the strength of the base metal while maintaining the HAZ toughness.

**[0016]** The steel plate is preferred to satisfy a following formula (3) when the contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

$$110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [V] \le 21.5 \dots (3)$$

**[0017]** By satisfying the formula (3), solidus temperature increases to allow solidification of molten steel to be completed early during casting, so that it is possible to easily achieve reduction of coarse TiN. This results in further improvement

of the HAZ toughness.

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**[0018]** The steel plate is preferred to further contain at least one of Cr: more than 0 mass% and 1.00 mass% or less, Mo: more than 0 mass% and 0.50 mass% or less, V: more than 0 mass% and 0.50 mass% or less, B: more than 0 mass% and 0.0009 mass% or less, a rare-earth metal: more than 0 mass% and 0.0050 mass% or less, and Zr: more than 0 mass% and 0.0050 mass% or less. By further adding such an element, it is possible to further improve the strength of the base metal.

**[0019]** Another invention that has been made to solve the above problem is a production method of a steel plate, the method including a casting step of casting molten steel containing, as composition, C: 0.005 mass% or more and 0.07 mass% or less; Si: 0 mass% or more and 0.04 mass% or less; Mn: 1.4 mass% or more and 2.0 mass% or less; P: more than 0 mass% and 0.010 mass% or less; S: more than 0 mass% and 0.007 mass% or less; Al: 0.010 mass% or more and 0.040 mass% or less; Ni: 0.1 mass% or more and 1.50 mass% or less; Cu: 0.1 mass% or more and 0.8 mass% or less; Nb: 0.004 mass% or more and 0.025 mass% or less; Ti: 0.010 mass% or more and 0.025 mass% or less; N: 0.0040 mass% or more and 0.0080 mass% or less; and Ca: 0.0005 mass% or more and 0.0030 mass% or less, with the balance being Fe and inevitable impurities; a hot rolling step of subjecting an ingot obtained by the casting step to hot rolling at a final rolling temperature of 750°C or higher and 820°C or lower; and a cooling step of cooling a steel material obtained after the hot rolling step at a cooling speed of 5°C/s or more, the casting step including cooling the molten steel from 1,500°C to 1,450°C within less than 300 seconds.

**[0020]** In the production method of a steel plate, the casting step that includes cooling the molten steel having the above composition from 1,500°C to 1,450°C within less than 300 seconds increases fine TiN relative to coarse TiN to suppress brittle fracture caused by coarse TiN, so that it is possible to produce a steel plate excellent in HAZ toughness. Further, in the production method of a steel plate, the hot rolling and the cooling are performed under the above conditions, so that it is possible to obtain a steel plate also excellent in strength of base metal.

**[0021]** The molten steel is preferred to further contain at least one of Cr: more than 0 mass% and 1.00 mass% or less, Mo: more than 0 mass% and 0.50 mass% or less, V: more than 0 mass% and 0.50 mass% or less, B: more than 0 mass% and 0.0050 mass% or less, a rare-earth metal: more than 0 mass% and 0.0050 mass% or less, and Zr: more than 0 mass% and 0.0050 mass% or less. By further adding such an element to the molten steel, it is possible to further improve the strength of the base metal of the steel plate obtained.

[0022] Another invention that has been made to solve the above problem is a steel plate containing, as composition, C: 0.005 mass% or more and 0.07 mass% or less; Si: 0 mass% or more and 0.04 mass% or less; Mn: 1.4 mass% or more and 2.0 mass% or less; P: more than 0 mass% and 0.010 mass% or less; S: more than 0 mass% and 0.007 mass% or less; Al: 0.010 mass% or more and 0.040 mass% or less; Ni: 0.1 mass% or more and 1.50 mass% or less; Cu: 0.1 mass% or more and 0.8 mass% or less; Nb: 0.004 mass% or more and 0.025 mass% or less; Ti: 0.010 mass% or more and 0.025 mass% or less; N: 0.0040 mass% or more and 0.0080 mass% or less; and Ca: 0.0005 mass% or more and 0.0030 mass% or less, with the balance being Fe and inevitable impurities, [Ti]/[N] being 2.0 or more and 5.0 or less when a content [mass%] of N based on the composition as a whole is defined as [N] and a content [mass%] of Ti is defined as [Ti], a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less in the TiN-containing precipitates with a circle equivalent diameter of 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 1  $\mu$ m or less is 0.0400  $\mu$ m or more and 0.0400  $\mu$ 

[0023] In the steel plate, adjustment is made to provide the above ranges of [Ti]/[N], the sectional density of the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less, and the proportion in number of the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less, thus suppressing Ostwald ripening of TiN when the large heat input welding is performed and suppressing enlargement of diameters of prior austenite grains by TiN that remains unmelted after heat input. This results in suppressing coarse grain boundary ferrite and coarse grain boundary bainite generated when welding is performed, so that the steel plate is excellent in HAZ toughness. The steel plate that has the above composition is also excellent in strength of base metal. [0024] The steel plate is preferred to further contain at least one of Cr: more than 0 mass% and 1.00 mass% or less, Mo: more than 0 mass% and 0.50 mass% or less, B: more than 0 mass% and 0.0009 mass% or less, a rare-earth metal: more than 0 mass% and 0.0050 mass% or less, and Zr: more than 0 mass% and 0.0050 mass% or less. By further adding such an element, it is possible to further improve the strength of the base metal.

[0025] Another invention that has been made to solve the above problem is a production method of a steel plate, the method including a casting step of casting molten steel containing, as composition, C: 0.005 mass% or more and 0.07 mass% or less; Si: 0 mass% or more and 0.04 mass% or less; Mn: 1.4 mass% or more and 2.0 mass% or less; P: more than 0 mass% and 0.010 mass% or less; S: more than 0 mass% and 0.007 mass% or less; Al: 0.010 mass% or more and 0.040 mass% or less; Ni: 0.1 mass% or more and 1.50 mass% or less; Cu: 0.1 mass% or more and 0.8 mass% or less; Nb: 0.004 mass% or more and 0.025 mass% or less; Ti: 0.010 mass% or more and 0.025 mass% or less; N: 0.0040 mass% or more and 0.0080 mass% or less; and Ca: 0.0005 mass% or more and 0.0030 mass% or less, with the balance

being Fe and inevitable impurities; a hot rolling step of subjecting an ingot obtained by the casting step to hot rolling; and a cooling step of cooling a steel material obtained after the hot rolling step at a cooling speed of 5°C/s or more, the casting step including cooling the molten steel from 1,500°C to 1,450°C within less than 300 seconds and from 1,300°C to 1,200°C in 450 seconds or more and 680 seconds or less, and the hot rolling step including retaining the ingot before the rolling at 1,050°C or higher and 1,200°C or lower for 20 minutes or more and 5 hours or less and setting cumulative rolling reduction to 30% or more at 900°C or higher and to 15% or more at 820°C or higher and lower than 900°C.

[0026] The production method of a steel plate increases the number of TiN that remains unmelted after the large heat input welding and that has a certain size, by the casting step that includes cooling the molten steel having the above composition under the above conditions and the hot rolling step that includes retaining temperature of the ingot under the above conditions and then subjecting the ingot to the rolling. This suppresses coarsening of a prior austenite grain boundary, leading to suppressing generation of coarse grain boundary ferrite and coarse grain boundary bainite, so that the production method of a steel plate is capable of producing a steel plate excellent in HAZ toughness. Further, in the production method of a steel plate, the hot rolling and the cooling are performed under the above conditions, so that it is possible to obtain a steel plate also excellent in strength of base metal.

[0027] The molten steel is preferred to further contain at least one of Cr: more than 0 mass% and 1.00 mass% or less, Mo: more than 0 mass% and 0.50 mass% or less, V: more than 0 mass% and 0.50 mass% or less, B: more than 0 mass% and 0.0009 mass% or less, a rare-earth metal: more than 0 mass% and 0.0050 mass% or less, and Zr: more than 0 mass% and 0.0050 mass% or less. By further adding such an element to the molten steel, it is possible to further improve the strength of the base metal of the steel plate obtained.

#### ADVANTAGEOUS EFFECTS OF INVENTION

**[0028]** A steel plate according to the present disclosure that is excellent in strength of base metal and HAZ toughness can be suitably used for a large structure to be welded. A production method of a steel plate according to the present disclosure is capable of giving a steel plate excellent in strength of base metal and HAZ toughness.

## **DESCRIPTION OF EMBODIMENTS**

[0029] Hereinafter, described is embodiments of a steel plate and a production method of the steel plate according to the present disclosure.

# FIRST EMBODIMENT

[0030] First, a first embodiment of the present invention is described.

<Steel plate>

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[0031] A steel plate contains, as composition, C (carbon): 0.005 mass% or more and 0.07 mass% or less; Si (silicon): 0 mass% or more and 0.04 mass% or less; Mn (manganese): 1.4 mass% or more and 2.0 mass% or less; P (phosphorus): more than 0 mass% and 0.010 mass% or less; S (sulfur): more than 0 mass% and 0.007 mass% or less; Al (aluminum): 0.010 mass% or more and 0.040 mass% or less; Ni (nickel): 0.1 mass% or more and 1.50 mass% or less; Cu (copper): 0.1 mass% or more and 0.8 mass% or less; Nb (niobium): 0.004 mass% or more and 0.025 mass% or less; Ti (titanium): 0.010 mass% or more and 0.025 mass% or less; N (nitrogen): 0.0040 mass% or more and 0.0080 mass% or less; and Ca (calcium): 0.0005 mass% or more and 0.0030 mass% or less, with the balance being Fe (iron) and inevitable impurities. [0032] The steel plate is not particularly limited in terms of a lower limit of average thickness, and the lower limit is, for example, 50 mm, more preferably 60 mm. On the other hand, the steel plate is not particularly limited in terms of an upper limit of average thickness, and the upper limit is, for example, 100 mm. The steel plate having an average thickness of less than the lower limit may possibly be unsuitable for application to, for example, ships. In contrast, the steel plate having an average thickness of more than the upper limit may possibly have trouble in, for example, processing.

[C (carbon)]

**[0033]** Hereinafter, the components of the steel plate are described. C is an element necessary for securing strength of the steel plate. The content of C as a lower limit is 0.005 mass%, preferably 0.01 mass%, more preferably 0.02 mass%. On the other hand, the content of C as an upper limit is 0.07 mass%, preferably 0.06 mass%, more preferably 0.05 mass%. With the content of C less than the lower limit, the strength of the steel plate may possibly become insufficient. In contrast, with the content of C more than the upper limit, the steel plate decreases in solidus temperature to accelerate generation of coarse TiN, so that the HAZ toughness may possibly decrease.

[Si (silicon)]

**[0034]** Si is an element useful for deoxidation of the steel plate. The content of Si as a lower limit is 0 mass%. On the other hand, the content of Si as an upper limit is 0.04 mass%, preferably 0.03 mass%, more preferably 0.02 mass%. With the content of Si more than the upper limit, activity of Ti increases to accelerate generation of coarse TiN, so that the HAZ toughness may possibly decrease.

[Mn (manganese)]

[0035] Mn is an element necessary for securing strength of the steel plate. The content of Mn as a lower limit is 1.4 mass%, preferably 1.50 mass%, more preferably 1.60 mass%. On the other hand, the content of Mn as an upper limit is 2.0 mass%, preferably 1.95 mass%, more preferably 1.92 mass%. With the content of Mn less than the lower limit, the strength of the steel plate may possibly become insufficient. In contrast, with the content of Mn more than the upper limit, hardness excessively increases along with generation of an island-shaped martensite in the HAZ by the large heat input welding to possibly decrease the toughness.

[P (phosphorus)]

[0036] P is an element that is inevitably contained in the steel plate and decreases the HAZ toughness. The content of P is more than 0 mass%. The content of P is preferably smaller, but it is industrially difficult to make the content of P 0 mass%. On the other hand, the content of P as an upper limit is 0.010 mass%, preferably 0.009 mass%, more preferably 0.008 mass%. With the content of P more than the upper limit, the HAZ toughness of the steel plate may possibly decrease.

[S (sulfur)]

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**[0037]** S is an element that is inevitably contained in the steel plate and decreases the HAZ toughness. The content of S is more than 0 mass%. The content of S is preferably smaller, but it is industrially difficult to make the content of S 0 mass%. On the other hand, the content of S as an upper limit is 0.007 mass%, preferably 0.005 mass%, more preferably 0.003 mass%. With the content of S more than the upper limit, the HAZ toughness of the steel plate may possibly decrease.

[Al (aluminum)]

**[0038]** Al is an element necessary for deoxidation of the steel plate. The content of Al as a lower limit is 0.010 mass%, preferably 0.015 mass%, more preferably 0.020 mass%. On the other hand, the content of Al as an upper limit is 0.040 mass%, preferably 0.038 mass%, more preferably 0.036 mass%. With the content of Al less than the lower limit, oxygen concentration in the steel plate increases to possibly decrease the HAZ toughness due to an increase of an oxide. In contrast, with the content of Al more than the upper limit, a coarse oxide increases to possibly decrease the HAZ toughness.

40 [Ni (nickel)]

[0039] Ni is an element that contributes to improving strength of the steel plate. The content of Ni as a lower limit is 0.1 mass%, preferably 0.15 mass%, more preferably 0.20 mass%. On the other hand, the content of Ni as an upper limit is 1.50 mass%, preferably 1.00 mass%, more preferably 0.80 mass%. With the content of Ni less than the lower limit, the strength of the steel plate may possibly decrease. In contrast, with the content of Ni more than the upper limit, hardness excessively increases to possibly decrease the toughness.

[Cu (copper)]

[0040] Cu is an element that contributes to improving strength of the steel plate. The content of Cu as a lower limit is 0.1 mass%, preferably 0.12 mass%, more preferably 0.15 mass%. On the other hand, the content of Cu as an upper limit is 0.8 mass%, preferably 0.60 mass%, more preferably 0.50 mass%. With the content of Cu less than the lower limit, the strength of the steel plate may possibly decrease. In contrast, with the content of Cu more than the upper limit, hardness excessively increases to possibly decrease the toughness.

[Nb (niobium)]

[0041] Nb is an element necessary for securing strength of the steel plate. The content of Nb as a lower limit is 0.004

mass%, preferably 0.006 mass%, more preferably 0.007 mass%. On the other hand, the content of Nb as an upper limit is 0.025 mass%, preferably 0.022 mass%, more preferably 0.020 mass%. With the content of Nb less than the lower limit, the strength of the steel plate may possibly become insufficient. In contrast, with the content of Nb more than the upper limit, hardness excessively increases along with generation of an island-shaped martensite in the HAZ by the large heat input welding to possibly decrease the toughness.

[Ti (titanium)]

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**[0042]** Ti is an element that is, together with N, precipitated as TiN and micronize a structure of the HAZ by the large heat input welding to improve the toughness. The content of Ti as a lower limit is 0.010 mass%, preferably 0.012 mass%, more preferably 0.013 mass%. On the other hand, the content of Ti as an upper limit is 0.025 mass%, preferably 0.022 mass%, more preferably 0.020 mass%. With the content of Ti less than the lower limit, an absolute amount of fine TiN is short to possibly give an insufficient effect for improving the HAZ toughness. In contrast, with the content of Ti more than the upper limit, solid solution Ti increases in the HAZ to form a coarse bainite structure, possibly enabling no securement of the HAZ toughness.

[N (nitrogen)]

[0043] N is an element that is, together with Ti, precipitated as TiN and micronize a structure of the HAZ by the large heat input welding to improve the toughness. The content of N as a lower limit is 0.0040 mass%, preferably 0.0045 mass%, more preferably 0.0050 mass%. On the other hand, the content of N as an upper limit is 0.0080 mass%, preferably 0.0075 mass%, more preferably 0.0070 mass%. With the content of N less than the lower limit, an effect of improving the HAZ toughness by fine TiN may possibly become insufficient. In contrast, with the content of N more than the upper limit, solid solution N in the HAZ by the large heat input welding increases to possibly decrease the HAZ toughness.

[Ca (calcium)]

**[0044]** Ca is an element necessary for deoxidation of the steel plate. The content of Ca as a lower limit is 0.0005 mass%, preferably 0.0008 mass%, more preferably 0.0010 mass%. On the other hand, the content of Ca as an upper limit is 0.0030 mass%, preferably 0.0025 mass%, more preferably 0.0022 mass%. With the content of Ca less than the lower limit, generation of coarse TiN is accelerated that originates from oxide particles to possibly decrease the HAZ toughness. In contrast, with the content of Ca more than the upper limit, a coarse oxide increases to possibly decrease the HAZ toughness.

**[0045]** The steel plate is preferred to further contain, in addition to the composition described above, at least one of Cr (chromium): more than 0 mass% and 1.00 mass% or less; Mo (molybdenum): more than 0 mass% and 0.50 mass% or less; V (vanadium): more than 0 mass% and 0.50 mass% or less; B (boron): more than 0 mass% and 0.0009 mass% or less; a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; or Zr (zirconium): more than 0 mass% and 0.0050 mass% or less.

[Cr (chromium)]

**[0046]** Cr is an element that contributes to improving strength of the steel plate. In order to improve the strength, Cr is contained in an amount of preferably 0.01 mass% or more, more preferably 0.05 mass% or more. On the other hand, addition of Cr probably excessively increases hardness of the HAZ by the large heat input welding to decrease the toughness. Therefore, the content of Cr as an upper limit is preferably 1.00 mass%, more preferably 0.50 mass%, further preferably 0.10 mass%.

[Mo (molybdenum)]

**[0047]** Mo is an element that contributes to improving strength of the steel plate. In order to improve the strength, Mo is contained in an amount of preferably 0.01 mass% or more, more preferably 0.03 mass% or more, further preferably 0.05 mass% or more. On the other hand, addition of Mo probably excessively increases hardness of the HAZ by the large heat input welding to decrease the toughness. Therefore, the content of Mo as an upper limit is preferably 0.50 mass%, more preferably 0.30 mass%, further preferably 0.20 mass%.

[V (vanadium)]

[0048] V is an element that contributes to improving strength of the steel plate. In order to improve the strength, V is contained in an amount of preferably 0.003 mass% or more, more preferably 0.02 mass% or more, further preferably 0.05 mass% or more. On the other hand, the content of V as an upper limit is preferably 0.50 mass%, more preferably 0.35 mass%, further preferably 0.15 mass%. With the content of V more than the upper limit, hardness of the HAZ by the large heat input welding may possibly excessively increase to decrease the toughness.

[B (boron)]

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**[0049]** B is an element that contributes to improving strength and the HAZ toughness of the steel plate. In order to improve the strength, B is contained in an amount of preferably 0.0002 mass% or more, more preferably 0.0004 mass% or more, further preferably 0.0005 mass% or more. On the other hand, the content of B as an upper limit is preferably 0.0009 mass%, more preferably 0.0008 mass%, further preferably 0.0007 mass%. With the content of B more than the upper limit, the toughness of the steel plate may possibly become unstable.

[Rare-earth metal]

[0050] The rare-earth metal is an element that contributes to deoxidation of the steel plate, and is contained in an amount of preferably 0.0003 mass% or more, more preferably 0.0010 mass% or more, further preferably 0.0015 mass% or more. On the other hand, the content of the rare-earth metal as an upper limit is preferably 0.0050 mass%, more preferably 0.0040 mass%, further preferably 0.0030 mass%. With the content of the rare-earth metal more than the upper limit, a coarse oxide increases to possibly decrease the HAZ toughness. Here, the "rare-earth metal" means 15 lanthanoid elements from La (lanthanum) with atomic number 57 to Lu (lutetium) with atomic number 71, Sc (scandium), and Y (yttrium).

[Zr (zirconium)]

**[0051]** Zr is an element that contributes to deoxidation of the steel plate, and is contained in an amount of preferably 0.0003 mass% or more, more preferably 0.0008 mass% or more, further preferably 0.0010 mass% or more. On the other hand, the content of Zr as an upper limit is preferably 0.0050 mass%, more preferably 0.0040 mass%, further preferably 0.0030 mass%. With the content of Zr more than the upper limit, a coarse oxide increases to possibly decrease the HAZ toughness.

35 [Balance]

**[0052]** The steel plate contains, as the balance, Fe (iron) and inevitable impurities, in addition to the elements described above. Examples of the inevitable impurities include Sn (tin), As (arsenic), and Pb (lead).

[0053] The steel plate satisfies a following formula (1) when the content [mass%] of acid insoluble Ti is defined as [insol.Ti] and the content [mass%] of Ti based on the composition as a whole is defined as [Ti].

# $[insol.Ti]/[Ti] \le 0.80...(1)$

[0054] Acid insoluble Ti is Ti in an acid insoluble Ti compound (e.g., TiN and a Ti oxide) and a concept that includes Ti in a so-called precipitate and a so-called crystallized product. In the present embodiment, acid insoluble Ti is defined as Ti in a precipitate and a crystallized product that are insoluble in an electrolytic solution by an electroextraction method described later.

[0055] A right-hand value of the formula (1) is preferably 0.77, more preferably 0.75. When [insol.Ti]/[Ti] is larger than these values, the HAZ toughness easily decreases due to coarse TiN. When steel materials are compared that are equal in [insol.Ti]/[Ti] but different in addition amount of Ti, one that is larger in addition amount of Ti is also larger in generation amount of coarse TiN. One that is large in addition amount of Ti, however, also simultaneously increases fine TiN that contributes to micronizing a structure of the HAZ, so that steel materials that are equal in [insol.Ti.]/[Ti] give almost equal HAZ toughness.

[0056] Here, the content of acid insoluble Ti is obtained by performing, with use of an electrolytic solution, an electroextraction method on a test piece taken at a position of 1/4 the plate thickness along the thickness of the steel plate, extracting a compound by filtrating a resultant residue, and measuring the content of Ti in this compound through, for example, ICP emission spectrometric analysis.

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**[0057]** Acid insoluble Ti in the embodiments of the present invention mainly exists as TiN but also includes Ti that exists as another compound such as a Ti oxide. In addition, acid insoluble Ti is mostly a crystallized product generated in molten steel in a casting step described later but partially includes a precipitate generated in solid iron.

**[0058]** When the content [mass%] of N is defined as [N], [Ti]/[N] as a lower limit is preferably 2.0, more preferably 2.5. On the other hand, [Ti]/[N] as an upper limit is preferably 5.0, more preferably 4.5. With [Ti]/[N] less than the lower limit, TiN increases in number but decreases in size to possibly make short the sectional density of later-described TiN-containing precipitates with a circle equivalent diameter in a certain range. In contrast, with [Ti]/[N] more than the upper limit, Ti diffusion-controlled growth is promoted to enlarge size of TiN, possibly increasing coarse TiN.

[0059] In the steel plate, a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less is preferred to be 2.0  $\times$  10<sup>5</sup> pieces/mm<sup>2</sup> or more, and a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu m$  or more and 1  $\mu m$  or less in the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less is preferred to be 15% or less.

[0060] A sectional density of the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less is, as a lower limit, more preferably  $2.5 \times 10^5$  pieces/mm², further preferably  $3.0 \times 10^5$  pieces/mm². When the sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less is less than the lower limit, fine TiN is reduced that contributes to suppressing enlargement of diameters of prior austenite grains, to possibly make it easy to decrease the HAZ toughness. On the other hand, the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less are not particularly limited in terms of an upper limit of the sectional density, and the upper limit is, for example,  $1.0 \times 10^6$  pieces/mm².

[0061] A proportion in number of the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less is, as an upper limit, more preferably 10%, further preferably 6%. When the proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less is more than the upper limit, Ostwald ripening is promoted that occurs when high temperature is retained during welding, to eliminate TiN and thus enlarge diameters of prior austenite grains, possibly making it easy to decrease the HAZ toughness. On the other hand, the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less are not particularly limited in terms of a lower limit of the proportion in number, and the lower limit is substantially 0%.

[0062] Here, values measured according to a following method represent the sectional density of the TiN-containing precipitates with a circle equivalent diameter of  $0.040~\mu m$  or more and  $1~\mu m$  or less and the proportion in number of the TiN-containing precipitates with a circle equivalent diameter of  $0.1~\mu m$  or more and  $1~\mu m$  or less. First, any site of the steel plate is cut and a resultant cut surface is observed with an electron microscope such as a transmission electron microscope (TEM). In the observation, precipitates containing Ti are discerned with, for example, an energy dispersive X-ray spectrometry (EDX) apparatus, and the precipitates are defined as TiN-containing precipitates. Next, areas of the TiN-containing precipitates in the observation visual field are measured by image analysis and converted into circle equivalent diameters, measurement is performed to obtain the number of TiN-containing precipitates with a circle equivalent diameter of  $0.040~\mu m$  or more and  $1~\mu m$  or less and the number of TiN-containing precipitates with a circle equivalent diameter of  $0.1~\mu m$  or more and  $1~\mu m$  or less, and calculation is performed to obtain the numbers of the precipitates per  $1~mm^2$  to derive the sectional density and the proportion in number from a ratio between the numbers.

[0063] The steel plate preferably satisfies a following formula (2) when the contents [mass%] of C, Si, Mn, Cu, Ni, Cr, Mo, V, and B are defined as [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], [V], and [B], respectively.

$$Di = ([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times [B]) \times 1.115 \ge 0.72 \dots (2)$$

**[0064]** A right-hand value of the formula (2) is more preferably 0.75, further preferably 0.77. With Di smaller than these values, strength of base metal may possibly become in sufficient.

[0065] The steel plate preferably satisfies a following formula (3) when the contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

$$A = 110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [V] \le 21.5 \dots (3)$$

**[0066]** A right-hand value of the formula (3) is more preferably 21.2, further preferably 21.0. With A larger than these values, coarse TiN is easily generated due to a decrease of solidus temperature to possibly make the HAZ toughness insufficient.

<sup>5</sup> [Application]

**[0067]** The steel plate is excellent in strength and HAZ toughness when large heat input welding is performed, so that it is possible to suitably use the steel plate for a large structure to be welded, such as ships.

10 <Production method of steel plate>

**[0068]** As a production method of the steel plate according to the first embodiment, there is exemplified a method including a casting step of casting molten steel, a hot rolling step of subjecting a resultant ingot to hot rolling, and a cooling step of cooling a steel material obtained after the hot rolling. Hereinafter, the steps are described.

[Casting step]

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**[0069]** In the present step, molten steel having the above composition is cast into, for example, a slab shape to give an ingot. The molten steel having the above composition can be obtained by appropriate combination of conventionally known methods such as a desulfurization treatment, a deoxidation treatment, and addition of the elements.

[0070] In the casting step, a cooling treatment in a temperature range from 1,500°C to 1,450°C is performed in a cooling period of less than 300 seconds. Coarse TiN is generated in a temperature range (solid-liquid coexisting temperature range), where steel is partially solidified, in a casting process. That is, in a process where liquid phase iron is solidified into a solid, Ti is discharged from solid iron to liquid phase iron to increase concentration of Ti in the liquid phase iron. In the liquid phase iron having a higher concentration of Ti, TiN is easily generated, and TiN generated in the liquid phase is easily coarsened. Therefore, in order to reduce coarse TiN, it is important to promptly make it through the solid-liquid coexisting temperature range and thus suppress generation and coarsening of TiN. Accordingly, with the cooling period for a temperature decrease from 1,500°C to 1,450°C being 300 seconds or more, coarse TiN is generated during casting not to allow [insol.Ti]/[Ti] to satisfy the formula (1), leading to a decrease of the HAZ toughness. The cooling period for a temperature decrease from 1,500°C to 1,450°C is more preferably less than 285 seconds. When the ingot has a tabular shape with a thickness t [mm], the cooling temperature is temperature measured at a position of t/4 from a surface of the ingot along the thickness.

[Hot rolling step]

**[0071]** In the present step, the ingot obtained by the casting step is subjected to hot rolling to give a steel plate. Final rolling temperature for the ingot during the hot rolling is 750°C or higher and 820°C or lower. With the final rolling temperature lower than the lower limit, austenite grains are micronized to accelerate precipitation of ferrite in the following cooling step, possibly making it difficult to give predetermined strength. In contrast, with the final rolling temperature higher than the upper limit, the toughness of the steel material may possibly decrease.

[Cooling step]

**[0072]** After the hot rolling, the steel material is cooled. The cooling speed is 5°C/s or more. With the cooling speed less than the lower limit, ferrite is precipitated to possibly make it difficult to give predetermined strength.

SECOND EMBODIMENT

[0073] Next, a second embodiment of the present invention is described.

<Steel plate>

[0074] A steel plate contains, as composition, C (carbon): 0.005 mass% or more and 0.07 mass% or less; Si (silicon): 0 mass% or more and 0.04 mass% or less; Mn (manganese): 1.4 mass% or more and 2.0 mass% or less; P (phosphorus): more than 0 mass% and 0.010 mass% or less; S (sulfur): more than 0 mass% and 0.007 mass% or less; Al (aluminum): 0.010 mass% or more and 0.040 mass% or less; Ni (nickel): 0.1 mass% or more and 1.50 mass% or less; Cu (copper): 0.1 mass% or more and 0.8 mass% or less; Nb (niobium): 0.004 mass% or more and 0.025 mass% or less; Ti (titanium): 0.010 mass% or more and 0.025 mass% or less; N (nitrogen): 0.0040 mass% or more and 0.0080 mass% or less; and

Ca (calcium): 0.0005 mass% or more and 0.0030 mass% or less, with the balance being Fe (iron) and inevitable impurities. **[0075]** The average thickness of the steel plate can be made the same as the average thickness of the steel plate according to the first embodiment. Preferable contents of C, Si, Mn, P, S, Al, Ni, Cu, Nb, Ti, N, and Ca, and the balance in the steel plate can also be made the same as in the steel plate according to the first embodiment.

**[0076]** The steel plate is preferred to further contain, in addition to the composition described above, at least one of Cr (chromium): more than 0 mass% and 1.00 mass% or less; Mo (molybdenum): more than 0 mass% and 0.50 mass% or less; V (vanadium): more than 0 mass% and 0.50 mass% or less; B (boron): more than 0 mass% and 0.0009 mass% or less; a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; or Zr (zirconium): more than 0 mass% and 0.0050 mass% or less. Preferable contents of the components in this composition can also be made the same as in the steel plate according to the first embodiment.

[0077] The steel plate has, as a lower limit, a [Ti]/[N] of 2.0, preferably 2.5. On the other hand, the steel plate has, as an upper limit, a [Ti]/[N] of 5.0, preferably 4.5. With [Ti]/[N] less than the lower limit, TiN increases in number but decreases in size to easily make short the sectional density of later-described TiN-containing precipitates with a circle equivalent diameter in a certain range. In contrast, with [Ti]/[N] more than the upper limit, Ti diffusion-controlled growth is promoted to enlarge size of TiN, easily increasing coarse TiN.

[0078] In the steel plate, a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less is  $2.0 \times 10^5$  pieces/mm² or more, and a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less in the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less is 15% or less.

[0079] A sectional density of the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less is, as a lower limit, preferably  $2.5 \times 10^5$  pieces/mm<sup>2</sup>, more preferably  $3.0 \times 10^5$  pieces/mm<sup>2</sup>. When the sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less is less than the lower limit, fine TiN is reduced that contributes to suppressing enlargement of diameters of prior austenite grains, to make it easy to decrease the HAZ toughness. On the other hand, the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less are not particularly limited in terms of an upper limit of the sectional density, and the upper limit is, for example,  $5.0 \times 10^5$  pieces/mm<sup>2</sup>.

[0080] A proportion in number of the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu m$  or more and 1  $\mu m$  or less is, as an upper limit, preferably 10%, more preferably 6%. When the proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu m$  or more and 1  $\mu m$  or less is more than the upper limit, Ostwald ripening is promoted that occurs when high temperature is retained during welding, to decrease the number of TiN that contributes to suppressing enlargement of diameters of prior austenite grains, making it easy to decrease the HAZ toughness. On the other hand, the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu m$  or more and 1  $\mu m$  or less are not particularly limited in terms of a lower limit of the proportion in number, and the lower limit is substantially 0%.

[Application]

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**[0081]** The steel plate is excellent in strength and HAZ toughness when large heat input welding is performed, so that it is possible to suitably use the steel plate for a large structure to be welded, such as ships.

<Production method of steel plate>

**[0082]** As a production method of the steel plate according to the second embodiment, there is exemplified a method including a casting step of casting molten steel, a hot rolling step of subjecting a resultant ingot to hot rolling, and a cooling step of cooling a steel material obtained after the hot rolling. Hereinafter, the steps are described.

[Casting step]

**[0083]** In the present step, molten steel having the above composition is cast into, for example, a slab shape to give an ingot. The molten steel having the above composition can be obtained by appropriate combination of conventionally known methods such as a desulfurization treatment, a deoxidation treatment, and addition of the elements.

[0084] In the casting step, a cooling treatment in a temperature range from 1,500°C to 1,450°C is performed in a cooling period of less than 300 seconds. Coarse TiN is generated in a temperature range (solid-liquid coexisting temperature range), where steel is partially solidified, in a casting process. That is, in a process where liquid phase iron is solidified into a solid, Ti is discharged from solid iron to liquid phase iron to increase concentration of Ti in the liquid phase iron. In the liquid phase iron having a higher concentration of Ti, TiN is easily generated, and TiN generated in the liquid phase is easily coarsened. Therefore, in order to reduce coarse TiN, it is important to promptly make it through the solid-liquid coexisting temperature range and thus suppress generation and coarsening of TiN. Accordingly, with the

cooling period for a temperature decrease from 1,500°C to 1,450°C being 300 seconds or more, coarse TiN is generated during casting to decrease the sectional density of the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less, leading to a decrease of the HAZ toughness. The cooling period for a temperature decrease from 1,500°C to 1,450°C is more preferably less than 285 seconds. When the ingot has a tabular shape with a thickness t [mm], the cooling temperature is temperature measured at a position of t/4 from a surface of the ingot along the thickness.

[0085] In the casting step, a cooling treatment in a temperature range from 1,300°C to 1,200°C is performed in a cooling treatment period of 450 seconds or more and 680 seconds or less. The cooling treatment period for the temperature range is preferably 500 seconds as a lower limit and 600 seconds as an upper limit. With the cooling treatment period less than the lower limit, the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less are reduced to decrease the HAZ toughness. On the other hand, with the cooling treatment period more than the upper limit, TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more increase to increase the proportion in number of the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less and thus decrease the HAZ toughness.

[Hot rolling step]

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[0086] In the present step, the ingot obtained by the casting step is subjected to hot rolling to give a steel plate. In the present step, the ingot before the hot rolling is retained, before subjected to the rolling, at a retention temperature of 1,050°C or higher and 1,200°C or lower in a retention period of 20 minutes or more and 5 hours or less. The retention period is preferably 2 hours as a lower limit. With the retention temperature or the retention period less than the lower limit, fine TiN with less than 0.040  $\mu m$  does not grow to reduce the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less and thus decrease the HAZ toughness. On the other hand, with the retention temperature or the retention period more than the upper limit, Ostwald ripening excessively proceeds to reduce the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less and thus decrease the HAZ toughness.

[0087] In the hot rolling step, the rolling is performed so as to give a cumulative rolling reduction of 30% or more at 900°C or higher and a cumulative rolling reduction of 15% or more at 820°C or higher and lower than 900°C. This grows fine TiN due to diffusion of Ti induced from strain, to increase the number of the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less and thus be capable of improving the HAZ toughness. On the other hand, with the rolling performed beyond the ranges, the number of the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less is reduced to decrease the HAZ toughness. The cumulative rolling reduction is not particularly limited in terms of an upper limit for each of the temperature ranges, and the upper limit is, for example, 50%. The "cumulative rolling reduction" is a sum of rolling reduction per pass and the "rolling reduction" is a value calculated by a following formula (4).

# Rolling reduction = $(t0 - t1)/t0 \times 100 \dots (4)$

[0088] In the formula (4), t0 represents rolling start thickness [mm] of a steel piece having a surface temperature in the rolling temperature ranges, and t1 represents rolling completion thickness [mm] of the steel piece having a surface temperature in the rolling temperature ranges.

[Cooling step]

**[0089]** After the hot rolling, the steel material is cooled. The cooling speed is 5°C/s or more, more preferably 6°C/s or more. With the cooling speed less than the lower limit, ferrite is precipitated to possibly make it difficult to give predetermined strength.

## 50 OTHER EMBODIMENTS

**[0090]** The steel plate and the production method of the steel plate according to the present disclosure are not to be limited to the foregoing embodiments.

## 55 EXAMPLES

[0091] Hereinafter, the present disclosure is described in further detail by way of examples. The present disclosure,

however, is not to be limited to these examples.

<Pre><Preparation of steel plate (1)>

[0092] With use of a 150 kg vacuum induction furnace, molten steel having composition indicated in Table 1 was prepared by melting, and the molten steel was casted to prepare a slab. Here, a cooling period for a temperature decrease from 1,500°C to 1,450°C was set to a period indicated in Table 2. This slab was retained at 1,100°C for 3 hours, subjected to hot rolling at a final finishing temperature of 780°C, and water-cooled at a cooling speed of 7.5°C/s to give a steel plate having an average thickness of 65 mm in each of Examples 1 to 10 and Comparative Examples 1 to 6.

<Measurement of [insol.Ti]>

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[0093] Measurement of [insol.Ti] was performed by taking a test piece at a position of 1/4 the plate thickness along the thickness of the resultant steel plate and measuring concentration of acid insoluble Ti extracted from the test piece according to an electroextraction method with use of an electrolytic solution. As the electrolytic solution, used was a solution containing 2 cc of triethanolamine and 1 g of tetramethylammonium chloride in 100 cc of methanol. The measurement was performed by filtrating, with a filter having a pore diameter of 2.0  $\mu$ m, a solution obtained by electroextraction with the electrolytic solution to give a residue and then analyzing this residue for its chemical components by ICP emission spectrometric analysis to derive [insol.Ti]. Insoluble Ti in the electroextraction with the electrolytic solution can be determined to be acid insoluble Ti defined in the present disclosure. Table 2 shows this measurement result.

<Evaluation of steel plate (1)>

[0094] Each of the steel plate was evaluated for yield strength and HAZ toughness according to following methods. Table 2 shows the evaluation results. In Table 2, "Di" represents a left-hand value in the formula (2) and "A" represents a left-hand value in the formula (3).

[Yield strength]

[0095] A no. 4 bar-shaped test piece specified in JIS-Z2241: 2011 was cut out from each of the steel plates. The test piece was cut out with an axis line of the test piece along width of the steel plate and with a distance from a central axis of the test piece to one surface of the steel plate set to 1/4 the plate thickness of the steel plate. Next, a tensile test was performed according to a method described in JIS-Z2241: 2011 to measure yield strength YS [MPa]. A value of the yield strength that is larger indicates more excellent strength, and a yield strength of 490 MPa or more can be determined as "good" and a yield strength of less than 490 MPa as "poor."

[HAZ toughness]

[0096] A test piece having a size of 12.5 mm (thickness direction) × 32 mm (C-direction) × 55 mm (rolling L-direction) was cut out from a position of 1/4 the plate thickness along the thickness of each of the steel plates, retained at 1400°C for 60 seconds, and then cooled while the cooling speed was controlled so as to give a cooling period of 400 seconds for a temperature decrease from 800°C to 500°C. This is a heat cycle simulating large heat input welding at a heat input of 55 kJ/mm. Next, in accordance with JIS-Z2242: 2005, three test pieces specified for a Charpy impact test were taken and subjected to the Charpy impact test at -20°C to measure absorption energy vE [J]. As the HAZ toughness, a vE of more than 100 J can be determined as "good" and a vE of 100 J or less as "poor."

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|    |           | В  | mass% | ı         | 0.0008    | ı         | 0.0005    | 0.0003    | ı         | 0.0009    | ı         | ı         | 0.0004     | ı                        | ı                        | ı                        | ı                        | ı                        | ı                        |
|----|-----------|----|-------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 5  |           | >  | mass% | -         | 1         | ı         | 1         | 0.053     | 1         | 1         | ı         | 1         | 0.181      | ı                        | 1                        | 0.110                    | 1                        |                          | 1                        |
| 10 |           | Мо | wass% | -         | -         | ı         | 0.15      | -         | -         | -         | -         | 0.42      | 0.05       | -                        | -                        | -                        | -                        | -                        | 0.41                     |
|    |           | Cr | mass% | -         | -         | -         | -         | -         | 0.15      | 0.65      | 0.91      | -         | -          | -                        | -                        | -                        | -                        | 0.55                     | -                        |
| 15 |           | Са | mass% | 0.0010    | 0.0013    | 0.0013    | 0.0020    | 0.0011    | 0.0018    | 0.0012    | 0.0013    | 0.0009    | 0.0007     | 0.0017                   | 0.0013                   | 0.0010                   | 0.0004                   | 0.0013                   | 0.0015                   |
| 20 |           | z  | mass% | 0.0052    | 0.0073    | 0.0045    | 0.0071    | 0900'0    | 0900'0    | 0900'0    | 0.0077    | 0.0056    | 0.0049     | 0.0062                   | 0.0082                   | 0.0066                   | 0.0061                   | 0.0059                   | 0.0038                   |
|    |           | Ti | mass% | 0.015     | 0.020     | 0.017     | 0.019     | 0.015     | 0.018     | 0.018     | 0.018     | 0.024     | 0.014      | 0.015                    | 0.014                    | 0.015                    | 0.014                    | 0.027                    | 0.009                    |
| 25 |           | Nb | mass% | 0.015     | 0.008     | 0.008     | 0.022     | 0.005     | 0.010     | 600.0     | 600.0     | 0.023     | 0.008      | 0.017                    | 0.010                    | 0.008                    | 600.0                    | 0.003                    | 0.008                    |
| 30 | [Table 1] | Cu | mass% | 0.21      | 0.45      | 0.39      | 0.50      | 0.34      | 0.21      | 0.20      | 0.12      | 0.14      | 0.20       | 0.44                     | 0.12                     | 0.35                     | 0.08                     | 0.31                     | 0.32                     |
|    | Π         | Ni | mass% | 0.71      | 0.85      | 0.50      | 0.95      | 0.52      | 0.30      | 0.51      | 0.13      | 0.22      | 1.21       | 0.82                     | 0.11                     | 0.55                     | 0.08                     | 0.41                     | 0.54                     |
| 35 |           | A  | mass% | 0.032     | 0.038     | 0.024     | 0.030     | 0.011     | 0.022     | 0.030     | 0.030     | 0.019     | 0.020      | 0.029                    | 0:030                    | 0.031                    | 0.035                    | 0.031                    | 0.030                    |
| 40 |           | S  | mass% | 0.002     | 0.002     | 0.002     | 0.001     | 0.002     | 0.001     | 0.005     | 0.002     | 0.002     | 0.002      | 0.002                    | 0.002                    | 0.002                    | 0.002                    | 0.002                    | 0.002                    |
|    |           | Р  | mass% | 0.007     | 0.007     | 0.007     | 0.006     | 0.007     | 0.008     | 900'0     | 0.007     | 900.0     | 0.007      | 0.007                    | 0.007                    | 0.007                    | 0.007                    | 0.007                    | 0.007                    |
| 45 |           | Mn | mass% | 1.52      | 1.66      | 1.88      | 1.81      | 1.84      | 1.52      | 1.96      | 1.60      | 1.72      | 1.50       | 1.88                     | 1.44                     | 1.38                     | 1.80                     | 1.62                     | 1.55                     |
| 50 |           | Si | mass% | 0.00      | 0.01      | 0.01      | 0.00      | 0.00      | 0.00      | 0.00      | 0.04      | 0.01      | 0.00       | 0.00                     | 0.00                     | 0.05                     | 0.00                     | 0.00                     | 0.00                     |
|    |           | С  | mass% | 90.0      | 0.04      | 0.03      | 0.01      | 0.02      | 0.07      | 0.02      | 0.02      | 0.02      | 0.02       | 0.004                    | 0.08                     | 0.03                     | 0.02                     | 0.02                     | 0.02                     |
| 55 |           |    |       | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 | Example 7 | Example 8 | Example 9 | Example 10 | Comparative<br>Example 1 | Comparative<br>Example 2 | Comparative<br>Example 3 | Comparative<br>Example 4 | Comparative<br>Example 5 | Comparative<br>Example 6 |

[Table 2]

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|                       | [insol.Ti]/ [Ti] | Di   | Α    | Cooling period | YS  | νE  |
|-----------------------|------------------|------|------|----------------|-----|-----|
|                       | -                | -    | -    | second         | MPa | J   |
| Example 1             | 0.80             | 0.71 | 21.6 | 276            | 507 | 139 |
| Example 2             | 0.80             | 0.81 | 22.1 | 278            | 556 | 144 |
| Example 3             | 0.76             | 0.60 | 20.5 | 280            | 503 | 211 |
| Example 4             | 0.79             | 0.62 | 21.3 | 272            | 492 | 186 |
| Example 5             | 0.73             | 0.55 | 19.4 | 262            | 502 | 193 |
| Example 6             | 0.78             | 0.89 | 21.1 | 259            | 542 | 140 |
| Example 7             | 0.78             | 1.35 | 21.1 | 282            | 561 | 135 |
| Example 8             | 0.78             | 1.05 | 17.1 | 255            | 535 | 128 |
| Example 9             | 0.67             | 0.86 | 18.0 | 271            | 531 | 149 |
| Example 10            | 0.71             | 0.75 | 21.1 | 265            | 522 | 168 |
| Comparative Example 1 | 0.87             | 0.24 | 19.5 | 305            | 446 | 88  |
| Comparative Example 2 | 0.93             | 0.63 | 19.9 | 271            | 517 | 45  |
| Comparative Example 3 | 0.87             | 0.57 | 17.9 | 264            | 476 | 88  |
| Comparative Example 4 | 0.86             | 0.37 | 15.5 | 277            | 421 | 86  |
| Comparative Example 5 | 0.78             | 0.89 | 18.4 | 270            | 470 | 81  |
| Comparative Example 6 | 0.67             | 0.91 | 19.1 | 269            | 539 | 78  |

**[0097]** As is clear from Tables 1 and 2, the steel plates of Examples 1 to 10 were good in both yield strength and HAZ toughness.

**[0098]** Further, in Examples 2 and 6 to 10 where Di was 0.72 or more, the yield strength was as high a value as 515 MPa or more, and the steel plates of Examples 2 and 6 to 10 were more excellent in yield strength than the steel plates of Examples 1 and 3 to 5. This demonstrates that it is possible to improve strength of base metal while retaining the HAZ toughness by setting the value of Di to 0.72 or more.

**[0099]** Further, in Examples 3 to 5, 9, and 10 where A was 21.5 or less, the HAZ toughness was as good as 146 J or more, and the steel plates of Examples 3 to 5, 9, and 10 were more excellent in HAZ toughness than the steel plates of Examples 1 and 2. This demonstrates that it is possible to more improve the HAZ toughness by setting the value of A to 21.5 or less.

**[0100]** In Examples 6 to 8, the value of A was 21.5 or less but Cr was contained in an amount of more than 0.10 mass%, so that the steel plates were, due to an influence of Cr, inferior in HAZ toughness to the steel plates of Examples 3 to 5, 9, and 10.

**[0101]** Further, in Examples 3 to 5 and 10 where the content of Cr was 0.10 mass% or less and the content of Mo was 0.20 mass% or less, the HAZ toughness was as good as 160 J or more, and the steel plates of Examples 3 to 5 and 10 were more excellent in HAZ toughness than the steel plates of Examples 6 to 9. This demonstrates that it is possible to more improve the HAZ toughness by setting the content of Cr to 0.10 mass% or less and the content of Mo to 0.20 mass% or less.

**[0102]** In Examples 1 and 2, the steel plates contained neither Cr nor Mo but the value of A was more than 21.5, so that the steel plates were, due to an influence of A, inferior in HAZ toughness to the steel plates of Examples 3 to 5 and 10.

**[0103]** On the other hand, in Examples 6 to 9 where the content of Cr was more than 0.10 mass% or the content of Mo was more than 0.20 mass%, the yield strength was as high a value as 527 MPa or more, and the steel plates of Examples 6 to 9 were more excellent in yield strength than the steel plates of Examples 1, 3 to 5, and 10. This demonstrates that it is possible to more improve the yield strength by setting the content of Cr to more than 0.10 mass% or the content of Mo to more than 0.20 mass%.

**[0104]** In Example 2, the steel plate contained neither Cr nor Mo but Di was as high as 0.81, so that the steel plate was, due to an influence of Di, higher in yield strength than the steel plates of Examples 1, 3 to 5, and 10.

[0105] On the other hand, in Comparative Examples 1 to 4, [insol.Ti]/[Ti] was more than 0.8, so that coarse TiN

increased to make the HAZ toughness poor. In Comparative Example 5, [insol.Ti]/[Ti] was 0.8 or less but the content of Ti was excessive, so that solid solution Ti increased to make the HAZ toughness poor. In Comparative Example 6, [insol.Ti]/[Ti] was also 0.8 or less but the contents of Ti and N were small, so that the absolute amount of fine TiN was short to make the HAZ toughness poor.

<Pre><Pre>reparation of steel plate (2)>

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**[0106]** Next, with use of a 150 kg vacuum induction furnace, molten steel having composition indicated in Table 3 was prepared by melting, and the molten steel was casted to prepare a slab. Here, the cooling periods for a temperature decrease from 1,500°C to 1,450°C and a temperature decrease from 1,300°C to 1,200°C were set to periods indicated in Table 4. This slab was retained at a temperature and in a period that are indicated in Table 4, then subjected to hot rolling at 900°C or higher and at 820°C or higher and lower than 900°C so as to give a cumulative rolling reduction indicated in Table 4 for each of the temperature ranges, and further water-cooled at a cooling speed indicated in Table 4 to give a steel plate having an average thickness of 65 mm in each of Examples 11 to 20 and Comparative Examples 7 to 15. "REM" in Table 3 represents a rare-earth metal.

<Measurement of TiN-containing precipitate>

[0107] A test piece was taken at a position of 1/4 the plate thickness along the thickness of the resultant steel plate and a cylindrical test piece was cut out from each of the steel plates. In this cutting-out method, an axis line of the test piece was made along the rolling direction of the steel plate. A distance from a central axis of the test piece to one surface of the steel plate was set to 1/4 the average thickness of the steel plate. Further, one bottom surface of the test piece was made to be a vertical section of the steel plate. Next, a test piece for replica TEM was made from the bottom surface of this test piece that corresponds to the vertical section of the steel plate, and the test piece for replica TEM was observed with a transmission electron microscope (TEM). Observation conditions were an observation magnification of 15,000 times and an observation visual field of 52.7 μm<sup>2</sup>, and two visual fields were observed. In the observation, precipitates containing Ti were discerned by an energy dispersive X-ray (EDX) fluorescence analyzer, and the precipitates were defined as TiN-containing precipitates. Next, areas of the TiN-containing precipitates in the observation visual fields were measured by image analysis and converted into circle equivalent diameters, measurement was performed to obtain the number of TiN-containing precipitates with a circle equivalent diameter of 0.040 µm or more and 1 µm or less and the number of TiN-containing precipitates with a circle equivalent diameter of 0.1 µm or more and 1 µm or less, and calculation was performed to obtain the numbers of the precipitates per 1 mm<sup>2</sup> to derive the sectional density and the proportion in number of the TiN-containing precipitates with a circle equivalent diameter of 0.1 µm or more and 1  $\mu m$  or less. Table 4 shows the measurement results.

<Evaluation of steel plate (2)>

**[0108]** Each of the steel plates was evaluated for yield strength and HAZ toughness according to the methods described above. Table 4 shows the evaluation results.

|    |          | Zr     | mass% |            | ,          | ,          | ı          | ı          | ,          |            | •          | 0.001      |            | 1                            | 1                            | 1                            |                               | 1                             | 1                             |
|----|----------|--------|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------------------------|------------------------------|------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 5  |          | REM    | mass% | -          |            |            | 1          | ı          | -          | -          | -          | 0.0005     |            | 1                            | 1                            | 1                            |                               | 1                             | 1                             |
|    |          | В      | mass% | -          |            | 0.0008     | 0.0006     | ı          | -          | -          | 0.0006     | 0.0004     | 0.0008     | 1                            | 1                            | 1                            | 0.0008                        | 0.0005                        | 0.0004                        |
| 10 |          | >      | mass% |            |            |            |            | -          |            | 0.153      | -          |            |            | 1                            | 1                            | 1                            | 1                             | 1                             | 1                             |
| 15 |          | Mo     | mass% | -          | -          | -          | -          | -          | 0.10       | -          | -          | -          | -          | -                            | -                            | -                            | -                             | -                             | 1                             |
|    |          | ပ်     | mass% | -          | 0.42       | -          | ı          | 0.20       | -          | -          | 0.15       | -          | -          | -                            | -                            | -                            | -                             | -                             | ı                             |
| 20 |          | Ca     | mass% | 0.0013     | 0.0015     | 0.0012     | 0.0015     | 0.0014     | 0.0013     | 0.0012     | 0.0012     | 0.0011     | 0.0012     | 0.0015                       | 0.0012                       | 0.0013                       | 0.0017                        | 0.0012                        | 0.0011                        |
|    |          | z      | mass% | 8900'0     | 0.0051     | 0.0044     | 0.0051     | 0.0062     | 0.0050     | 0.0047     | 0.0050     | 0.0046     | 0.0044     | 0.0060                       | 0.0050                       | 0.0048                       | 0.0044                        | 0.0057                        | 0.0050                        |
| 25 |          | ï      | mass% | 0.017      | 0.016      | 0.018      | 0.020      | 0.016      | 0.018      | 0.018      | 0.017      | 0.017      | 0.018      | 0.029                        | 0.015                        | 0.018                        | 0.015                         | 0.016                         | 0.017                         |
| 30 | Table 3] | q<br>N | mass% | 0.008      | 0.012      | 0.008      | 0.008      | 0.008      | 0.007      | 0.008      | 0.008      | 0.012      | 0.008      | 0.015                        | 0.005                        | 0.007                        | 0.018                         | 0.008                         | 0.008                         |
|    | Ë        | J.     | mass% | 0.31       | 0.41       | 0.37       | 0.35       | 0.28       | 0.35       | 0.36       | 0.35       | 0.55       | 0.37       | 0.41                         | 0.15                         | 0.42                         | 90.0                          | 0.36                          | 0.35                          |
| 35 |          | Ż      | mass% | 0.84       | 1.02       | 0.50       | 0.61       | 0.36       | 0.65       | 0.47       | 0.55       | 0.92       | 0.50       | 0.62                         | 0.50                         | 0.60                         | 0.08                          | 0.51                          | 0.50                          |
|    |          | ¥      | mass% | 0.032      | 0.026      | 0.034      | 0.036      | 0.031      | 0.032      | 0.032      | 0.032      | 0.021      | 0.034      | 0.032                        | 0.032                        | 0.025                        | 0.032                         | 0.035                         | 0.028                         |
| 40 |          | တ      | wass% | 0.002      | 0.002      | 0.001      | 0.002      | 0.002      | 0.002      | 0.003      | 0.003      | 0.002      | 0.001      | 0.003                        | 0.003                        | 0.002                        | 0.002                         | 0.002                         | 0.002                         |
| 45 |          | Д      | mass% | 900'0      | 900'0      | 200'0      | 0.007      | 0.006      | 900'0      | 800'0      | 200'0      | 0.005      | 200'0      | 0.006                        | 0.005                        | 0.005                        | 0.007                         | 0.008                         | 0.007                         |
|    |          | Mn     | mass% | 1.61       | 1.90       | 1.92       | 1.76       | 1.85       | 1.80       | 1.65       | 1.90       | 1.62       | 1.92       | 1.90                         | 1.75                         | 1.72                         | 1.90                          | 1.84                          | 1.75                          |
| 50 |          | S      | mass% | 00'0       | 0.01       | 00.00      | 00.00      | 0.03       | 00'0       | 00.00      | 0.00       | 00'0       | 00.00      | 0.00                         | 0.00                         | 0.15                         | 0.00                          | 0.00                          | 0.00                          |
|    |          | ပ      | mass% | 0.05       | 0.01       | 0.02       | 0.02       | 0.05       | 0.02       | 0.03       | 0.02       | 0.04       | 0.02       | 0.05                         | 0.09                         | 0.03                         | 0.04                          | 0.04                          | 0.05                          |
| 55 |          |        |       | Example 11 | Example 12 | Example 13 | Example 14 | Example 15 | Example 16 | Example 17 | Example 18 | Example 19 | Example 20 | Compara-<br>tiveExample<br>7 | Compara-<br>tiveExample<br>8 | Compara-<br>tiveExample<br>9 | Compara-<br>tiveExample<br>10 | Compara-<br>tiveExample<br>11 | Compara-<br>tiveExample<br>12 |

|    |             | Zr  | %ss   | ,                              |  |
|----|-------------|-----|---|--------------------------------|--|
|    |             |     | % mas   |                                |  |
| 5  |             | REM | mass <sup>9</sup>   | ı                              | 1  |
|    |             | В   | mass%   | ı                              | 1  |
| 10 |             | >   | mass%   | 1                              | -  |
| 15 |             | Mo  | mass%   | ı                              | ı  |
|    |             | ပ်  | mass%   | 1                              | -  |
| 20 |             | Ca  | mass%   | 0.0015                         | 0.0014                                   |
|    |             | z   | mass%   | 0.35 0.008 0.015 0.0050 0.0015 | 0.0045                                   |
| 25 |             | iΞ  | mass%   | 0.015                          | 0.014                                    |
| 30 | (continued) | qN  | mass%   | 0.008                          | 0.008                                    |
|    | (cor        | Cu  | mass%   | 0.35                           | 0.36                                     |
| 35 |             | Z   | mass%   | 0.50                           | .035 0.72 0.36 0.008 0.014 0.0045 0.0014 |
|    |             | A   | mass%   | 0.032                          | 0  |
| 40 |             | S   | mass%   | 0.005                          | 0.002                                    |
| 45 |             | ۵   | mass%   | 1.75 0.006 0.002               | 0.007                                    |
|    |             | Mn  | mass%   | 1.75                           | 1.68                                     |
| 50 |             | Si  | mass% | 00.00                          | 00.00                                    |
|    |             | ပ   | mass%   | 0.03                           | 0.04                                     |
| 55 |             |     |   | Comparative Example 0.03       | Example 14 0.04 0.00 1.68 0.007 0.002    |

|                        |           | ∃^  | ſ                     | 144        | 133        | 161        | 176        | 128        | 107        | 137        | 180        | 149        | 126        | 21                       | 45                       | 23                       | 112                       | 31                        | 82                        | 83                        |
|------------------------|-----------|---|-----------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|--------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 5                      |           | ΥS  | МРа                   | 527        | 514        | 498        | 495        | 517        | 521        | 493        | 497        | 516        | 503        | 530                      | 562                      | 501                      | 467                       | 521                       | 202                       | 501                       |
| 10                     |           | Cooling<br>speed after<br>rolling   | s/J。                  | 7.9        | 5.7        | 9.7        | 6.7        | 0.7        | 8.9        | 6.4        | 7.4        | 7.2        | 8.1        | 8.9                      | 0.7                      | 9:9                      | 7.3                       | 0.7                       | 7.2                       | 7.1                       |
| 15                     |           | Cumulative<br>rolling<br>reduction at<br>900 to 820°C   | %                     | 23         | 23         | 23         | 23         | 23         | 23         | 23         | 23         | 23         | 23         | 23                       | 23                       | 23                       | 23                        | 23                        | 23                        | 36                        |
| 20                     |           | Cumulative rolling reduction at 900°C or higher   | %                     | 35         | 35         | 35         | 35         | 35         | 35         | 35         | 35         | 35         | 35         | 35                       | 35                       | 35                       | 35                        | 35                        | 35                        | 25                        |
| 20                     |           | Retention<br>period before<br>rolling   | hour                  | 3.0        | 3.0        | 3.0        | 3.0        | 3.0        | 4.0        | 3.0        | 3.0        | 3.0        | 0.33       | 2.5                      | 3.0                      | 3.0                      | 3.0                       | 3.0                       | 3.0                       | 3.0                       |
| 25                     | le 4]     | Retention<br>temperature<br>before rolling  | ၁့                    | 1100       | 1200       | 1100       | 1100       | 1100       | 1100       | 1100       | 1100       | 1100       | 1200       | 1100                     | 1100                     | 1100                     | 1100                      | 1100                      | 1100                      | 1100                      |
| <i>30</i><br><i>35</i> | [Table 4] |   | puoses                | 504        | 524        | 524        | 536        | 522        | 502        | 202        | 501        | 909        | 524        | 488                      | 504                      | 481                      | 501                       | 481                       | 762                       | 482                       |
| 40                     |           | Cooling period Cooling period for temperature decrease from decrease from 1500 to 1450°C 1300 to 1200°C | second                | 280        | 264        | 263        | 243        | 272        | 263        | 260        | 253        | 252        | 263        | 265                      | 262                      | 264                      | 256                       | 364                       | 247                       | 272                       |
| 45                     |           | Proportion of<br>TiN with 0.1 to<br>1 µ.m   | %                     | 4          | 2          | 4          | 3          | 2          | 14         | 10         | 4          | 8          | 3          | 10                       | 3                        | 7                        | 0                         | 14                        | 19                        | 0                         |
| 50                     |           | Density in<br>number of TiN<br>with 0.040 to 1<br>µm  | piece/mm <sup>2</sup> | 436433     | 284630     | 246679     | 528772     | 388994     | 341556     | 294118     | 227704     | 246679     | 275142     | 673624                   | 370019                   | 256167                   | 284630                    | 132827                    | 256167                    | 142315                    |
|                        |           | [N]   | ı                     | 2.5        | 3.1        | 4.1        | 3.9        | 2.6        | 3.6        | 3.6        | 3.4        | 3.7        | 4.1        | 4.8                      | 3.0                      | 3.8                      | 3.4                       | 2.8                       | 3.4                       | 3.0                       |
| 55                     |           |   |                       | Examole 11 | Example 12 | Example 13 | Example 14 | Example 15 | Example 16 | Example 17 | Example 18 | Example 19 | Example 20 | Comparative<br>Example 7 | Comparative<br>Example 8 | Comparative<br>Example 9 | Comparative<br>Example 10 | Comparative<br>Example 11 | Comparative<br>Example 12 | Comparative<br>Example 13 |

|                | ٧Ē   | ſ                     | 69                        |
|----------------|--|-----------------------|---------------------------|
| 5              | ΥS   | МРа                   | 513                       |
| 10             | Cooling<br>speed after<br>rolling  | s/J。                  | 9.7                       |
| 15             | Cumulative<br>rolling<br>reduction at<br>900 to 820°C  | %                     | 12                        |
| 20             | Cumulative rolling reduction at 900°C or higher  | %                     | 35                        |
|                | Retention Retention rolling temperature period before rolling rolling 900°C or higher  | hour                  | 3.0                       |
| 25 (continued) | Retention<br>temperature<br>before rolling   | J.                    | 1100                      |
| 30 ijuoo)      | Cooling period or temperature decrease from 300 to 1200°C  | second                | 529                       |
| 40             | Density in Proportion of [Ti]/ number of TiN TiN with 0.1 to decrease from decrease from thm 0.040 to 1 mm 1500 to 1450°C 1300 to 1200°C | second                | 273                       |
| 45             | Proportion of FIN with 0.1 to  | %                     | 9                         |
| 50             | Density in<br>number of TiN<br>with 0.040 to 1<br>µm   | piece/mm <sup>2</sup> | 161290                    |
|                | )[E]   | 1                     | 3.3                       |
| 55             |  |                       | Comparative<br>Example 14 |

**[0109]** As is clear from Tables 3 and 4, the steel plates of Examples 11 to 20 were good in both yield strength and HAZ toughness.

**[0110]** In comparison among the examples, the HAZ toughness tends to be more excellent according as the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less have a smaller proportion in number. Particularly, in Examples 11, 13, 14, and 18 where the proportion in number is 6% or less, the steel plates have better HAZ toughness than the steel plates of the other examples.

[0111] On the other hand, in Comparative Examples 7 to 10, the composition does not satisfy the ranges of the present invention, so that either the yield strength or the HAZ toughness is poor. In Comparative Examples 11, 13, and 14, an sectional density of the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less is insufficient, so that the HAZ toughness is poor. The insufficient sectional density is considered to have been brought about by an excessively long cooling period for a temperature decrease from 1,500°C to 1,450°C in Comparative Example 11, by an excessively small cumulative rolling reduction at 900°C or higher in Comparative Example 13, and by an excessively small cumulative rolling reduction at 820°C or higher and lower than 900°C in Comparative Example 14. In Comparative Examples 12, a proportion in number of the TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less is excessively large, so that the HAZ toughness is poor. In Comparative Example 12, the proportion in number is considered to have increased by an excessively long cooling period for a temperature decrease from 1,300°C to 1,200°C.

[0112] The contents disclosed in the present specification include following aspects.

20 (Aspect 1)

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[0113] A steel plate containing, as composition:

C: 0.005 mass% or more and 0.07 mass% or less;

Si: 0 mass% or more and 0.04 mass% or less;

Mn: 1.4 mass% or more and 2.0 mass% or less;

P: more than 0 mass% and 0.010 mass% or less;

S: more than 0 mass% and 0.007 mass% or less;

Al: 0.010 mass% or more and 0.040 mass% or less;

Ni: 0.1 mass% or more and 1.50 mass% or less;

Cu: 0.1 mass% or more and 0.8 mass% or less;

Nb: 0.004 mass% or more and 0.025 mass% or less;

Ti: 0.010 mass% or more and 0.025 mass% or less;

N: 0.0040 mass% or more and 0.0080 mass% or less; and

Ca: 0.0005 mass% or more and 0.0030 mass% or less,

with the balance being Fe and inevitable impurities,

the steel plate satisfying a following formula (1) when a content [mass%] of acid insoluble Ti is defined as [insol.Ti] and a content [mass%] of Ti based on the composition as a whole is defined as [Ti].

 $[insol.Ti]/[Ti] \le 0.80...(1)$ 

(Aspect 2)

[0114] The steel plate according to aspect 1, wherein

when a content [mass%] of N is defined as [N], [Ti]/[N] is 2.0 or more and 5.0 or less,

a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less being  $2.0 \times 10^5$  pieces/mm<sup>2</sup> or more, and

a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less in the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less being 15% or less.

(Aspect 3)

**[0115]** The steel plate according to aspect 1 or 2, satisfying a following formula (2) when contents [mass%] of C, Si, Mn, Cu, Ni, Cr, Mo, V, and B are defined as [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], [V], and [B], respectively.

$$([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times [B]) \times 1.115 \ge 0.72 \dots (2)$$

(Aspect 4)

[0116] The steel plate according to aspect 1, 2 or 3, satisfying a following formula (3) when the contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

$$110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [V] \le 21.5 \dots (3)$$

(Aspect 5)

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20 [0117] The steel plate according to any one of aspects 1 to 4, further containing at least one of:

Cr: more than 0 mass% and 1.00 mass% or less;

Mo: more than 0 mass% and 0.50 mass% or less;

V: more than 0 mass% and 0.50 mass% or less;

B: more than 0 mass% and 0.0009 mass% or less;

a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and

Zr: more than 0 mass% and 0.0050 mass% or less.

(Aspect 6)

[0118] A production method of a steel plate, the method including:

a casting step of casting molten steel containing, as composition,

C: 0.005 mass% or more and 0.07 mass% or less;

Si: 0 mass% or more and 0.04 mass% or less;

Mn: 1.4 mass% or more and 2.0 mass% or less;

P: more than 0 mass% and 0.010 mass% or less;

S: more than 0 mass% and 0.007 mass% or less:

Al: 0.010 mass% or more and 0.040 mass% or less;

Ni: 0.1 mass% or more and 1.50 mass% or less;

Cu: 0.1 mass% or more and 0.8 mass% or less;

Nb: 0.004 mass% or more and 0.025 mass% or less;

Ti: 0.010 mass% or more and 0.025 mass% or less;

N: 0.0040 mass% or more and 0.0080 mass% or less; and Ca: 0.0005 mass% or more and 0.0030 mass% or less,

with the balance being Fe and inevitable impurities;

a hot rolling step of subjecting an ingot obtained by the casting step to hot rolling at a final rolling temperature of 750°C or higher and 820°C or lower; and

a cooling step of cooling a steel material obtained after the hot rolling step at a cooling speed of 5°C/s or more, the casting step including cooling the molten steel from 1,500°C to 1,450°C within less than 300 seconds.

(Aspect 7)

55 **[0119]** The production method of a steel plate according to aspect 6, wherein the molten steel further contains at least one of:

Cr: more than 0 mass% and 1.00 mass% or less;

Mo: more than 0 mass% and 0.50 mass% or less:

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V: more than 0 mass% and 0.50 mass% or less;
          B: more than 0 mass% and 0.0009 mass% or less;
          a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and
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          Zr: more than 0 mass% and 0.0050 mass% or less.
     (Aspect 8)
     [0120] A steel plate containing, as composition:
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          C: 0.005 mass% or more and 0.07 mass% or less;
          Si: 0 mass% or more and 0.04 mass% or less;
          Mn: 1.4 mass% or more and 2.0 mass% or less;
          P: more than 0 mass% and 0.010 mass% or less;
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          S: more than 0 mass% and 0.007 mass% or less:
          Al: 0.010 mass% or more and 0.040 mass% or less:
          Ni: 0.1 mass% or more and 1.50 mass% or less;
          Cu: 0.1 mass% or more and 0.8 mass% or less;
          Nb: 0.004 mass% or more and 0.025 mass% or less;
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          Ti: 0.010 mass% or more and 0.025 mass% or less;
          N: 0.0040 mass% or more and 0.0080 mass% or less; and
          Ca: 0.0005 mass% or more and 0.0030 mass% or less,
     with the balance being Fe and inevitable impurities,
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     [Ti]/[N] being 2.0 or more and 5.0 or less when a content [mass%] of N based on the composition as a whole is defined
     as [N] and a content [mass%] of Ti is defined as [Ti],
     a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040 \mu m or more and 1 \mu m or
     less being 2.0 \times 10^5 pieces/mm<sup>2</sup> or more, and
     a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1 μm or more and 1 μm or
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     less in the TiN-containing precipitates with a circle equivalent diameter of 0.040 \mu m or more and 1 \mu m or less being
      15% or less.
     (Aspect 9)
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     [0121] The steel plate according to aspect 8, further containing at least one of:
          Cr: more than 0 mass% and 1.00 mass% or less;
          Mo: more than 0 mass% and 0.50 mass% or less;
          V: more than 0 mass% and 0.50 mass% or less:
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          B: more than 0 mass% and 0.0009 mass% or less;
          a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and
          Zr: more than 0 mass% and 0.0050 mass% or less.
     (Aspect 10)
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     [0122] A production method of a steel plate, the method including:
          a casting step of casting molten steel containing, as composition,
          C: 0.005 mass% or more and 0.07 mass% or less;
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          Si: 0 mass% or more and 0.04 mass% or less;
          Mn: 1.4 mass% or more and 2.0 mass% or less;
          P: more than 0 mass% and 0.010 mass% or less;
          S: more than 0 mass% and 0.007 mass% or less;
          Al: 0.010 mass% or more and 0.040 mass% or less:
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          Ni: 0.1 mass% or more and 1.50 mass% or less:
          Cu: 0.1 mass% or more and 0.8 mass% or less;
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Nb: 0.004 mass% or more and 0.025 mass% or less; Ti: 0.010 mass% or more and 0.025 mass% or less;

N: 0.0040 mass% or more and 0.0080 mass% or less; and Ca: 0.0005 mass% or more and 0.0030 mass% or less,

with the balance being Fe and inevitable impurities;

- a hot rolling step of subjecting an ingot obtained by the casting step to hot rolling; and a cooling step of cooling a steel material obtained after the hot rolling step at a cooling speed of 5°C/s or more, the casting step including cooling the molten steel from 1,500°C to 1,450°C within less than 300 seconds and from 1,300°C to 1,200°C in 450 seconds or more and 680 seconds or less, and
- the hot rolling step including retaining the ingot before the rolling at 1,050°C or higher and 1,200°C or lower for 20 minutes or more and 5 hours or less and setting cumulative rolling reduction to 30% or more at 900°C or higher and to 15% or more at 820°C or higher and lower than 900°C.

(Aspect 11)

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15 **[0123]** The production method of a steel plate according to aspect 10, wherein the molten steel further contains at least one of:

Cr: more than 0 mass% and 1.00 mass% or less;

Mo: more than 0 mass% and 0.50 mass% or less;

V: more than 0 mass% and 0.50 mass% or less;

B: more than 0 mass% and 0.0009 mass% or less;

a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and

Zr: more than 0 mass% and 0.0050 mass% or less.

- [0124] The present application claims priority based on Japanese Patent Application No. 2016-026380 filed on February 15, 2016, Japanese Patent Application No. 2016-132915 filed on July 4, 2016, and Japanese Patent Application No. 2016-213579 filed on October 31, 2016. Japanese Patent Application Nos. 2016-026380, 2016-132915, and 2016-213579 are incorporated herein by reference.
- 30 INDUSTRIAL APPLICABILITY

**[0125]** A steel plate according to the present disclosure is excellent in strength of base metal and HAZ toughness. A production method of a steel plate according to the present disclosure is capable of giving a steel plate excellent in strength of base metal and HAZ toughness.

Claims

1. A steel plate comprising, as composition:

C: 0.005 mass% or more and 0.07 mass% or less;

Si: 0 mass% or more and 0.04 mass% or less;

Mn: 1.4 mass% or more and 2.0 mass% or less;

P: more than 0 mass% and 0.010 mass% or less;

S: more than 0 mass% and 0.007 mass% or less;

Al: 0.010 mass% or more and 0.040 mass% or less;

Ni: 0.1 mass% or more and 1.50 mass% or less;

Cu: 0.1 mass% or more and 0.8 mass% or less;

Nb: 0.004 mass% or more and 0.025 mass% or less;

Ti: 0.010 mass% or more and 0.025 mass% or less; N: 0.0040 mass% or more and 0.0080 mass% or less; and

Ca: 0.0005 mass% or more and 0.0030 mass% or less,

with the balance being Fe and inevitable impurities,

the steel plate satisfying a following formula (1) when a content [mass%] of acid insoluble Ti is defined as [insol.Ti] and a content [mass%] of Ti based on the composition as a whole is defined as [Ti].

$$[insol.Ti]/[Ti] \le 0.80...(1)$$

- 2. The steel plate according to claim 1, wherein when a content [mass%] of N is defined as [N], [Ti]/[N] is 2.0 or more and 5.0 or less, a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040 μm or more and 1 μm or less being 2.0 × 10<sup>5</sup> pieces/mm² or more, and a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1 μm or more and 1 μm or less in the TiN-containing precipitates with a circle equivalent diameter of 0.040 μm or more and 1 μm or less
  - 3. The steel plate according to claim 1, satisfying a following formula (2) when contents [mass%] of C, Si, Mn, Cu, Ni, Cr, Mo, V, and B are defined as [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], [V], and [B], respectively.

$$([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times 1.115 \times 1$$

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being 15% or less.

**4.** The steel plate according to claim 2, satisfying a following formula (2) when contents [mass%] of C, Si, Mn, Cu, Ni, Cr, Mo, V, and B are defined as [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], [V], and [B], respectively.

$$([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times 1.115 \times 1$$

5. The steel plate according to claim 1, satisfying a following formula (3) when contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

$$110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [V] \le 21.5 \dots (3)$$

**6.** The steel plate according to claim 2, satisfying a following formula (3) when contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

$$110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [V] \le 21.5 \dots (3)$$

7. The steel plate according to claim 3, satisfying a following formula (3) when the contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

$$110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [V] \le 21.5 \dots (3)$$

**8.** The steel plate according to claim 4, satisfying a following formula (3) when the contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

# $110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [$

 $[V] \le 21.5 \dots (3)$ 

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- 9. The steel plate according to any one of claims 1 to 8, further comprising at least one of:
  - Cr: more than 0 mass% and 1.00 mass% or less;
  - Mo: more than 0 mass% and 0.50 mass% or less;
  - V: more than 0 mass% and 0.50 mass% or less;
  - B: more than 0 mass% and 0.0009 mass% or less;
  - a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and
  - Zr: more than 0 mass% and 0.0050 mass% or less.
- 15 **10.** A production method of a steel plate, the method comprising:
  - a casting step of casting molten steel containing, as composition,
  - C: 0.005 mass% or more and 0.07 mass% or less;
  - Si: 0 mass% or more and 0.04 mass% or less;
  - Mn: 1.4 mass% or more and 2.0 mass% or less;
  - P: more than 0 mass% and 0.010 mass% or less;
  - S: more than 0 mass% and 0.007 mass% or less;
  - Al: 0.010 mass% or more and 0.040 mass% or less;
  - Ni: 0.1 mass% or more and 1.50 mass% or less;
  - Cu: 0.1 mass% or more and 0.8 mass% or less;
  - Nb: 0.004 mass% or more and 0.025 mass% or less;
  - Ti: 0.010 mass% or more and 0.025 mass% or less;
  - N: 0.0040 mass% or more and 0.0080 mass% or less; and
  - Ca: 0.0005 mass% or more and 0.0030 mass% or less,

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- with the balance being Fe and inevitable impurities;
- a hot rolling step of subjecting an ingot obtained by the casting step to hot rolling at a final rolling temperature of 750°C or higher and 820°C or lower; and
- a cooling step of cooling a steel material obtained after the hot rolling step at a cooling speed of  $5^{\circ}$ C/s or more, the casting step including cooling the molten steel from 1,500°C to 1,450°C within less than 300 seconds.
- 11. The production method of a steel plate according to claim 10, wherein the molten steel further contains at least one of
  - Cr: more than 0 mass% and 1.00 mass% or less;
  - Mo: more than 0 mass% and 0.50 mass% or less:
  - V: more than 0 mass% and 0.50 mass% or less;
  - B: more than 0 mass% and 0.0009 mass% or less;
  - a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and
  - Zr: more than 0 mass% and 0.0050 mass% or less.

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- **12.** A steel plate comprising, as composition:
  - C: 0.005 mass% or more and 0.07 mass% or less;
  - Si: 0 mass% or more and 0.04 mass% or less;
  - Mn: 1.4 mass% or more and 2.0 mass% or less;
  - P: more than 0 mass% and 0.010 mass% or less;
  - S: more than 0 mass% and 0.007 mass% or less;
  - Al: 0.010 mass% or more and 0.040 mass% or less;
  - Ni: 0.1 mass% or more and 1.50 mass% or less; Cu: 0.1 mass% or more and 0.8 mass% or less;
    - Nb: 0.004 mass% or more and 0.025 mass% or less;
  - Ti: 0.010 mass% or more and 0.025 mass% or less;
  - N: 0.0040 mass% or more and 0.0080 mass% or less; and

Ca: 0.0005 mass% or more and 0.0030 mass% or less.

with the balance being Fe and inevitable impurities,

[Ti]/[N] being 2.0 or more and 5.0 or less when a content [mass%] of N based on the composition as a whole is defined as [N] and a content [mass%] of Ti is defined as [Ti],

a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less being 2.0  $\times$  10<sup>5</sup> pieces/mm² or more, and

a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less in the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less being 15% or less.

- 13. The steel plate according to claim 12, further comprising at least one of:
  - Cr: more than 0 mass% and 1.00 mass% or less;
  - Mo: more than 0 mass% and 0.50 mass% or less:
  - V: more than 0 mass% and 0.50 mass% or less;
  - B: more than 0 mass% and 0.0009 mass% or less;
  - a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and
  - Zr: more than 0 mass% and 0.0050 mass% or less.

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- 14. A production method of a steel plate, the method comprising:
  - a casting step of casting molten steel containing, as composition,
  - C: 0.005 mass% or more and 0.07 mass% or less;
  - Si: 0 mass% or more and 0.04 mass% or less;
  - Mn: 1.4 mass% or more and 2.0 mass% or less;
  - P: more than 0 mass% and 0.010 mass% or less;
  - S: more than 0 mass% and 0.007 mass% or less;
  - Al: 0.010 mass% or more and 0.040 mass% or less;
  - Ni: 0.1 mass% or more and 1.50 mass% or less;
  - Cu: 0.1 mass% or more and 0.8 mass% or less;
  - Nb: 0.004 mass% or more and 0.025 mass% or less;
  - Ti: 0.010 mass% or more and 0.025 mass% or less;
  - N: 0.0040 mass% or more and 0.0080 mass% or less; and
  - Ca:  $0.0005\ mass\%$  or more and  $0.0030\ mass\%$  or less,

with the balance being Fe and inevitable impurities;

- a hot rolling step of subjecting an ingot obtained by the casting step to hot rolling; and
- a cooling step of cooling a steel material obtained after the hot rolling step at a cooling speed of 5°C/s or more, the casting step including cooling the molten steel from 1,500°C to 1,450°C within less than 300 seconds and from 1,300°C to 1,200°C in 450 seconds or more and 680 seconds or less, and

the hot rolling step including retaining the ingot before the rolling at 1,050°C or higher and 1,200°C or lower for 20 minutes or more and 5 hours or less and setting cumulative rolling reduction to 30% or more at 900°C or higher and to 15% or more at 820°C or higher and lower than 900°C.

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- 15. The production method of a steel plate according to claim 14, wherein the molten steel further contains at least one of:
  - Cr: more than 0 mass% and 1.00 mass% or less;
  - Mo: more than 0 mass% and 0.50 mass% or less;
  - V: more than 0 mass% and 0.50 mass% or less;
  - B: more than 0 mass% and 0.0009 mass% or less;
  - a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and
  - Zr: more than 0 mass% and 0.0050 mass% or less.
  - [May 31, 2017 (31.05.2017) International Bureau Acceptance]

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#### Amended claims under Art. 19.1 PCT

- 1. (Amended) A steel plate comprising, as composition:
  - C: 0.005 mass% or more and 0.07 mass% or less;

Si: 0 mass% or more and 0.04 mass% or less;

Mn: 1.4 mass% or more and 2.0 mass% or less;

P: more than 0 mass% and 0.010 mass% or less;

S: more than 0 mass% and 0.007 mass% or less;

Al: 0.010 mass% or more and 0.040 mass% or less;

Ni: 0.1 mass% or more and 1.50 mass% or less;

Cu: 0.1 mass% or more and 0.8 mass% or less;

Nb: 0.004 mass% or more and 0.025 mass% or less;

Ti: 0.010 mass% or more and 0.025 mass% or less;

N: 0.0040 mass% or more and 0.0080 mass% or less; and

Ca: 0.0005 mass% or more and 0.0030 mass% or less,

with the balance being Fe and inevitable impurities,

the steel plate satisfying a following formula (1) when a content [mass%] of acid insoluble Ti is defined as [insol.Ti] and a content [mass%] of Ti based on the composition as a whole is defined as [Ti], wherein

when a content [mass%] of N is defined as [N], [Ti]/[N] is 2.0 or more and 5.0 or less,

a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less being 2.0  $\times$  10<sup>5</sup> pieces/mm² or more, and

a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less in the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less being 15% or less.

$$[insol.Ti]/[Ti] \le 0.80...(1)$$

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- 2. (Canceled)
- 3. The steel plate according to claim 1, satisfying a following formula (2) when contents [mass%] of C, Si, Mn, Cu, Ni, Cr, Mo, V, and B are defined as [C], [Si], [Mn], [Cu], [Ni], [Cr], [Mo], [V], and [B], respectively.

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$$([C]/10)^{0.5} \times (1 + 0.7 \times [Si]) \times (1 + 3.33 \times [Mn]) \times (1 + 0.35 \times [Cu]) \times (1 + 0.36 \times [Ni]) \times (1 + 2.16 \times [Cr]) \times (1 + 3 \times [Mo]) \times (1 + 1.75 \times [V]) \times (1 + 200 \times [B]) \times 1.115 \ge 0.72 \dots (2)$$

- 4. (Canceled)
- **5.** The steel plate according to claim 1, satisfying a following formula (3) when contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

$$110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [V] < 21.5 ... (3)$$

- 6. (Canceled)
- 7. The steel plate according to claim 3, satisfying a following formula (3) when the contents [mass%] of C, Mn, Cu, Ni, Cr, Mo, and V are defined as [C], [Mn], [Cu], [Ni], [Cr], [Mo], and [V], respectively.

 $110 \times [C] + 7 \times [Mn] + 4 \times [Cu] + 5 \times [Ni] + 2.8 \times [Cr] + 5 \times [Mo] + 7.2 \times [Mo]$ 

 $[V] \le 21.5 \dots (3)$ 

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- 8. (Canceled)
- 9. (Amended) The steel plate according to any one of claims 1, 3, 5 and 7 further comprising at least one of:

Cr: more than 0 mass% and 1.00 mass% or less;

Mo: more than 0 mass% and 0.50 mass% or less;

V: more than 0 mass% and 0.50 mass% or less;

B: more than 0 mass% and 0.0009 mass% or less;

a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and

Zr: more than 0 mass% and 0.0050 mass% or less.

- 10. (Canceled)
- 11. (Canceled)

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12. A steel plate comprising, as composition:

C: 0.005 mass% or more and 0.07 mass% or less;

Si: 0 mass% or more and 0.04 mass% or less;

Mn: 1.4 mass% or more and 2.0 mass% or less;

P: more than 0 mass% and 0.010 mass% or less:

S: more than 0 mass% and 0.007 mass% or less;

Al: 0.010 mass% or more and 0.040 mass% or less:

74. 0.0 TO THOSE WITH 0.0 TO THOSE WITH 0.0 TO THOSE 70 OF THE

Ni: 0.1 mass% or more and 1.50 mass% or less;

Cu: 0.1 mass% or more and 0.8 mass% or less;

Nb: 0.004 mass% or more and 0.025 mass% or less;

Ti: 0.010 mass% or more and 0.025 mass% or less;

N: 0.0040 mass% or more and 0.0080 mass% or less; and

Ca: 0.0005 mass% or more and 0.0030 mass% or less,

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with the balance being Fe and inevitable impurities,

[Ti]/[N] being 2.0 or more and 5.0 or less when a content [mass%] of N based on the composition as a whole is defined as [N] and a content [mass%] of Ti is defined as [Ti],

a sectional density of TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu m$  or more and 1  $\mu m$  or less being 2.0  $\times$  10  $^5$  pieces/mm² or more, and

a proportion in number of TiN-containing precipitates with a circle equivalent diameter of 0.1  $\mu$ m or more and 1  $\mu$ m or less in the TiN-containing precipitates with a circle equivalent diameter of 0.040  $\mu$ m or more and 1  $\mu$ m or less being 15% or less.

13. The steel plate according to claim 12, further comprising at least one of:

Cr: more than 0 mass% and 1.00 mass% or less;

Mo: more than 0 mass% and 0.50 mass% or less;

V: more than 0 mass% and 0.50 mass% or less;

B: more than 0 mass% and 0.0009 mass% or less;

a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and

Zr: more than 0 mass% and 0.0050 mass% or less.

**14.** A production method of a steel plate, the method comprising:

- a casting step of casting molten steel containing, as composition,
- C: 0.005 mass% or more and 0.07 mass% or less;
- Si: 0 mass% or more and 0.04 mass% or less;

| 5  | Mn: 1.4 mass% or more and 2.0 mass% or less; P: more than 0 mass% and 0.010 mass% or less; S: more than 0 mass% and 0.007 mass% or less; Al: 0.010 mass% or more and 0.040 mass% or less; Ni: 0.1 mass% or more and 1.50 mass% or less; Cu: 0.1 mass% or more and 0.8 mass% or less; Nb: 0.004 mass% or more and 0.025 mass% or less; Ti: 0.010 mass% or more and 0.025 mass% or less; N: 0.0040 mass% or more and 0.0080 mass% or less; and   |
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| 10 | Ca: 0.0005 mass% or more and 0.0030 mass% or less,   |
| 15 | with the balance being Fe and inevitable impurities; a hot rolling step of subjecting an ingot obtained by the casting step to hot rolling; and a cooling step of cooling a steel material obtained after the hot rolling step at a cooling speed of 5°C/s or more, the casting step including cooling the molten steel from 1,500°C to 1,450°C within less than 300 seconds and from 1,300°C to 1,200°C in 450 seconds or more and 680 seconds or less, and the hot rolling step including retaining the ingot before the rolling at 1,050°C or higher and 1,200°C or lower for 20 minutes or more and 5 hours or less and setting cumulative rolling reduction to 30% or more at 900°C or higher and to 15% or more at 820°C or higher and lower than 900°C. |
| 20 | 15. The production method of a steel plate according to claim 14, wherein the moltan steel further contains at least   |
|    | <b>15.</b> The production method of a steel plate according to claim 14, wherein the molten steel further contains at least one of:  |
| 25 | Cr: more than 0 mass% and 1.00 mass% or less; Mo: more than 0 mass% and 0.50 mass% or less; V: more than 0 mass% and 0.50 mass% or less; B: more than 0 mass% and 0.0009 mass% or less; a rare-earth metal: more than 0 mass% and 0.0050 mass% or less; and  |
| 30 | Zr: more than 0 mass% and 0.0050 mass% or less.  |
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#### INTERNATIONAL SEARCH REPORT International application No. PCT/JP2017/003701 A. CLASSIFICATION OF SUBJECT MATTER C22C38/00(2006.01)i, C21D8/02(2006.01)i, C22C38/16(2006.01)i, C22C38/58 5 (2006.01)iAccording to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) 10 C22C38/00-38/60, C21D8/02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2017 15 Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. (Kobe Steel, Ltd.), 2004-250757 A 1,5,9 Y 09 September 2004 (09.09.2004), 3,7 Α claims; paragraph [0008] 2,4,6,8, 25 (Family: none) 12-15 Υ WO 2015/087940 A1 (Kobe Steel, Ltd.), 3,7 18 June 2015 (18.06.2015), paragraph [0049] & US 2016/0244865 A1 30 paragraphs [0109] to [0110] & EP 3081663 A1 & CN 105765098 A & KR 10-2016-0083936 A 35 $\times$ Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: later document published after the international filing date or priority date and not in conflict with the application but cited to understand "A" document defining the general state of the art which is not considered to the principle or theory underlying the invention "E" earlier application or patent but published on or after the international filing document of particular relevance; the claimed invention cannot be "X" considered novel or cannot be considered to involve an inventive step when the document is taken alone document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 45 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 "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 document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 50 21 March 2017 (21.03.17) 18 April 2017 (18.04.17) Name and mailing address of the ISA/ Authorized officer Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, <u>Tokyo 100-8915, Japan</u> Telephone No. 55 Form PCT/ISA/210 (second sheet) (January 2015)

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## REFERENCES CITED IN THE DESCRIPTION

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