

(19)



(11)

**EP 3 825 436 A1**

(12)

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

(43) Date of publication:

**26.05.2021 Bulletin 2021/21**

(21) Application number: **19850397.1**

(22) Date of filing: **05.08.2019**

(51) Int Cl.:

|  |  |
|--|--|
| <b>C22C 38/38</b> <small>(2006.01)</small> | <b>C22C 38/32</b> <small>(2006.01)</small> |
| <b>C22C 38/02</b> <small>(2006.01)</small> | <b>C22C 38/06</b> <small>(2006.01)</small> |
| <b>C22C 38/00</b> <small>(2006.01)</small> | <b>C22C 38/58</b> <small>(2006.01)</small> |
| <b>C22C 38/26</b> <small>(2006.01)</small> | <b>C22C 38/28</b> <small>(2006.01)</small> |
| <b>C22C 38/20</b> <small>(2006.01)</small> | <b>C22C 38/22</b> <small>(2006.01)</small> |
| <b>C22C 38/24</b> <small>(2006.01)</small> | <b>C22C 38/60</b> <small>(2006.01)</small> |
| <b>C22C 38/54</b> <small>(2006.01)</small> | <b>C21D 9/46</b> <small>(2006.01)</small>  |
| <b>C21D 8/02</b> <small>(2006.01)</small>  | <b>C21D 6/00</b> <small>(2006.01)</small>  |

(86) International application number:

**PCT/JP2019/030769**

(87) International publication number:

**WO 2020/036090 (20.02.2020 Gazette 2020/08)**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

**BA ME**

**KH MA MD TN**

(30) Priority: **15.08.2018 PCT/JP2018/030364**

(71) Applicant: **JFE Steel Corporation**  
**Tokyo 100-0011 (JP)**

(72) Inventors:

- **IKEDA Hiroshi**  
**Tokyo 100-0011 (JP)**
- **KITSUYA Shigeki**  
**Tokyo 100-0011 (JP)**
- **UEDA Keiji**  
**Tokyo 100-0011 (JP)**

(74) Representative: **Haseltine Lake Kempner LLP**  
**Bürkleinstrasse 10**  
**80538 München (DE)**

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

(57) Provided is a high-Mn steel having excellent corrosion resistance particularly in salt corrosive environments. A steel plate comprises a chemical composition containing C: 0.20 % or more and 0.70 % or less, Si: 0.05 % or more and 1.00 % or less, Mn: 15.0 % or more and 35.0 % or less, P: 0.030 % or less, S: 0.0200 % or less,

Al: 0.010 % or more and 0.100 % or less, Cr: 0.5 % or more and 8.0 % or less, and N: 0.0010 % or more and 0.0300 % or less, with a balance consisting of Fe and inevitable impurities, wherein 60 % or more of the Cr is solute Cr.

**EP 3 825 436 A1**

**Description**

## TECHNICAL FIELD

5 **[0001]** The present disclosure relates to a steel plate having excellent corrosion resistance particularly in saltwater corrosive environments and suitable for structural steel used in very-low-temperature environments such as liquefied gas storage tanks, and a method of producing the same.

## BACKGROUND

10 **[0002]** Attempts have been made to use hot-rolled steel plates for structures such as liquefied gas storage tanks. Operating environments of such structures reach very low temperatures, and thus hot-rolled steel plates used for such structures are required to have excellent toughness at very low temperatures as well as high strength. For example, a hot-rolled steel plate used for a liquefied natural gas storage needs to have excellent toughness at temperatures lower  
15 than or equal to -164 °C which is the boiling point of liquefied natural gas. If the low-temperature toughness of the steel material is insufficient, the safety of the very-low-temperature storage structure is likely to be undermined. There is thus strong need to improve the low-temperature toughness of the steel material used.

**[0003]** In response to this need, austenitic stainless steel having austenite microstructure which is not embrittled at very low temperatures, 9 % Ni steel, and 5000 series aluminum alloys have been conventionally used. However, due  
20 to high alloy costs or production costs of these metal materials, there has been demand for a steel plate that is inexpensive and has excellent very-low-temperature toughness. In view of this, studies have been conducted to use, as a new steel plate to replace conventional steels for very low temperature use, high-Mn steel containing a large amount of Mn which is a relatively inexpensive austenite-stabilizing element and having austenite microstructure, as a structural steel plate in very-low-temperature environments.

25 **[0004]** There is, however, the following problem: In the case where a steel plate having austenite microstructure is put in a corrosive environment, austenite crystal grain boundaries are eroded through corrosion, and stress corrosion cracking tends to occur when tensile stress is applied. In the production stage of a liquefied gas storage structure or the like, the steel substrate of the steel plate is exposed to the surface in some cases. If the steel material surface comes into contact with water vapor, water, oil, or the like containing a corrosive substance such as salt, the steel material is  
30 corroded. In the corrosion reaction on the steel plate surface, while iron undergoes anodic reaction to form oxides (rust), water undergoes cathodic reaction to form hydrogen. Such hydrogen enters into the steel, causing hydrogen embrittlement. In such a case, if residual stress in bending, welding, or the like during production or load stress in a use environment is applied, there is a possibility that stress corrosion cracking occurs and the structure is fractured. Conventionally studied high-Mn steel may be inferior in corrosion resistance to not only austenitic stainless steel but also 9 % Ni steel and typical  
35 low-alloy steel. In terms of safety, it is important that the steel material used for the structure has excellent corrosion resistance in addition to high strength and very-low-temperature toughness.

**[0005]** For example, JP 2015-508452 A (PTL 1) discloses a steel material that contains Mn: 15 % to 35 %, Cu: 5 % or less, and appropriate amounts of C and Cr to improve the machinability by cutting and the Charpy impact property of a heat-affected zone at -196 °C.

40 **[0006]** JP 2016-84529 A (PTL 2) discloses a high-Mn steel material that contains C: 0.25 % to 0.75 %, Si: 0.05 % to 1.0 %, Mn: more than 20 % and 35 % or less, Ni: 0.1 % or more and less than 7.0 %, and Cr: 0.1 % or more and less than 8.0 % to improve the low-temperature toughness.

**[0007]** JP 2016-196703 A (PTL 3) discloses a high-Mn steel material that contains C: 0.001 % to 0.80 %, Mn: 15 % to 35 %, and elements such as Cr, Ti, Si, Al, Mg, Ca, and REM to improve the very-low-temperature toughness of base  
45 metal and welds.

## CITATION LIST

## Patent Literature

50 **[0008]**

PTL 1: JP 2015-508452 A

PTL 2: JP 2016-84529 A

55 PTL 3: JP 2016-196703 A

## SUMMARY

(Technical Problem)

5 **[0009]** However, the respective steel materials described in PTL 1, PTL 2, and PTL 3 still have room for improvement in the production costs for achieving the strength and the low-temperature toughness, as well as in the corrosion resistance when the foregoing austenite steel material is put in a salt corrosive environment.

10 **[0010]** It could therefore be helpful to provide a high-Mn steel having excellent corrosion resistance particularly in salt corrosive environments. Herein, "having excellent corrosion resistance" means that the fracture stress is 600 MPa or more in the case of immersing a sample in artificial seawater (chloride ion concentration: 18000 ppm) at a temperature of 23 °C and conducting a constant-rate tensile test at a strain rate of  $4 \times 10^{-7}$  inch/s in accordance with the NACE Standard TM0111-2011 Slow Strain Rate Test Method.

(Solution to Problem)

15 **[0011]** We conducted intensive studies on various factors that determine the chemical composition and the production conditions of high-Mn steel, and discovered the following a and b:

20 a. Upon adding Cr to high-Mn steel as a base, appropriate control of the amount of Cr added and of the amount of solute Cr can delay an initial corrosion reaction on the steel plate surface in a saltwater corrosive environment. Thus, the amount of hydrogen entering into the steel can be reduced, and the foregoing stress corrosion cracking of austenite steel can be suppressed.

25 b. An effective way of suppressing fracture from crystal grain boundaries of austenite is to enhance the crystal grain boundary strength. In particular, P is an element that easily segregates together with Mn in a slab solidification process, and decreases the crystal grain boundary strength in the part that intersects with this segregation area. Hence, impurity elements such as P need to be reduced. Meanwhile, B is an element that increases the strength of austenite grain boundaries. By reducing impurity elements such as P and also adding B, grain boundary fracture can be suppressed more effectively.

30 **[0012]** The present disclosure is based on these discoveries and further studies. We thus provide:

35 1. A steel plate comprising: a chemical composition containing (consisting of), in mass%, C: 0.20 % or more and 0.70 % or less, Si: 0.05 % or more and 1.00 % or less, Mn: 15.0 % or more and 35.0 % or less, P: 0.030 % or less, S: 0.0200 % or less, Al: 0.010 % or more and 0.100 % or less, Cr: 0.5 % or more and 8.0 % or less, N: 0.0010 % or more and 0.0300 % or less, and B: 0.0003 % or more and 0.0100 % or less, with a balance consisting of Fe and inevitable impurities, wherein 60 % or more of the Cr is solute Cr.

40 2. The steel plate with excellent corrosion resistance according to 1., wherein the chemical composition further contains, in mass%, one or more selected from Nb: 0.003 % or more and 0.030 % or less, V: 0.01 % or more and 0.10 % or less, and Ti: 0.003 % or more and 0.040 % or less.

45 3. The steel plate according to 1. or 2., wherein the chemical composition further contains, in mass%, one or more selected from Cu: 0.01 % or more and 0.50 % or less, Ni: 0.01 % or more and 0.50 % or less, Sn: 0.01 % or more and 0.30 % or less, Sb: 0.01 % or more and 0.30 % or less, Mo: 0.01 % or more and 2.0 % or less, and W: 0.01 % or more and 2.0 % or less.

50 4. The steel plate according to any one of 1. to 3., wherein the chemical composition further contains, in mass%, one or more selected from Ca: 0.0005 % or more and 0.0050 % or less, Mg: 0.0005 % or more and 0.0100 % or less, and REM: 0.0010 % or more and 0.0200 % or less.

55 5. A method of producing a steel plate, the method comprising: heating a steel raw material having the chemical composition according to any one of 1. to 4. to 1000 °C or more and 1300 °C or less; thereafter subjecting the steel raw material to hot rolling at a rolling finish temperature of 750 °C or more with a residence time of the steel raw material in a temperature range of 950 °C or less and 600 °C or more being 30 min or less, to obtain a hot-rolled steel plate; and thereafter cooling the hot-rolled steel plate at an average cooling rate of 3 °C/s or more in a temperature range of 700 °C or less and 600 °C or more.

(Advantageous Effect)

**[0013]** It is thus possible to provide a steel plate having excellent corrosion resistance particularly in salt corrosive environments. By using the presently disclosed steel plate for a steel structure used in a very-low-temperature environment such as a liquefied gas storage tank, the safety and life of the steel structure are greatly improved. This yields

significantly advantageous effects in industrial terms. Moreover, the presently disclosed steel plate is less expensive than existing materials, and thus has excellent economic advantage.

#### DETAILED DESCRIPTION

**[0014]** A steel plate according to one of the disclosed embodiments will be described in detail below. The present disclosure is not limited to the embodiment described below.

#### [Chemical composition]

**[0015]** First, the chemical composition of the steel plate according to one of the disclosed embodiments and the reasons for limiting the chemical composition will be described below. In the present disclosure, the chemical composition of the steel plate is defined as follows, in order to ensure excellent corrosion resistance. Herein, "%" used with regard to the chemical composition denotes "mass%" unless otherwise specified.

C: 0.20 % or more and 0.70 % or less

**[0016]** C is effective in strengthening, and is an inexpensive austenite-stabilizing element that is important in obtaining austenite. To achieve the effects, the C content needs to be 0.20 % or more. If the C content is more than 0.70 %, excessive precipitation of Cr carbides and Nb-, V-, and Ti-based carbides is facilitated, and these precipitates form a corrosion initiation point. In addition, the low-temperature toughness decreases. The C content is therefore 0.20 % or more and 0.70 % or less. The C content is preferably 0.25 % or more and 0.60 % or less.

Si: 0.05 % or more and 1.00 % or less

**[0017]** Si acts as a deoxidizer, and not only is necessary for steelmaking but also has an effect of strengthening the steel plate through solid solution strengthening by dissolving in the steel. To achieve the effects, the Si content needs to be 0.05 % or more. If the Si content is more than 1.00 %, the weldability and the surface characteristics degrade and the stress corrosion cracking resistance decreases in some cases. The Si content is therefore 0.05 % or more and 1.00 % or less. The Si content is preferably 0.07 % or more and 0.50 % or less.

Mn: 15.0 % or more and 35.0 % or less

**[0018]** Mn is a relatively inexpensive austenite-stabilizing element. In the present disclosure, Mn is an important element for achieving both the strength and the very-low-temperature toughness. To achieve the effects, the Mn content needs to be 15.0 % or more. If the Mn content is more than 35.0 %, the effect of improving the very-low-temperature toughness is saturated, and the alloy costs increase. Moreover, the weldability and the cuttability degrade. Furthermore, segregation of Mn is caused, and stress corrosion cracking is promoted. The Mn content is therefore 15.0 % or more and 35.0 % or less. The Mn content is preferably 18.0 % or more and 28.0 % or less.

P: 0.030 % or less

**[0019]** If the P content is more than 0.030 %, P segregates to grain boundaries and decreases the grain boundary strength, and forms a stress corrosion cracking initiation point. It is therefore desirable to reduce the P content as much as possible, with its upper limit being set to 0.030 %. Since lower P content contributes to improved properties, the P content is preferably 0.024 % or less, and more preferably 0.020 % or less. Reducing the P content to less than 0.001 % requires considerable steelmaking costs and impairs the economic efficiency. Hence, P content of 0.001 % or more is allowable from the viewpoint of economic efficiency.

S: 0.0200 % or less

**[0020]** S decreases the low-temperature toughness and the ductility of the base metal. It is therefore desirable to reduce the S content as much as possible, with its upper limit being set to 0.0200 %. The S content is therefore 0.0200 % or less, and preferably 0.0180 % or less. Reducing the S content to less than 0.0001 % requires considerable steelmaking costs and impairs the economic efficiency. Hence, S content of 0.0001 % or more is allowable from the viewpoint of economic efficiency.

A1: 0.010 % or more and 0.100 % or less

**[0021]** A1 acts as a deoxidizer, and is most generally used in the molten steel deoxidation process. A1 also has an effect of suppressing coarsening of crystal grains by fixing solute N in the steel and forming A1N. A1 further has an effect of suppressing a decrease in toughness due to reduction of solute N. To achieve the effects, the A1 content needs to be 0.01 % or more. If the A1 content is more than 0.100 %, coarse nitrides form and become a corrosion initiation point or a fracture origin to thus cause a decrease in stress corrosion cracking resistance in some cases. Moreover, A1 diffuses into a weld metal portion during welding and decreases the toughness of the weld metal. The A1 content is therefore 0.100 % or less. The A1 content is preferably 0.020 % or more and 0.070 % or less.

Cr: 0.5 % or more and 8.0 % or less, and 60 % or more of Cr: solute Cr

**[0022]** Cr has an effect of delaying initial corrosion reaction on the steel plate surface in a saltwater corrosive environment when added in an appropriate amount. Cr is an important element that, by this effect, decreases the amount of hydrogen that enters into the steel plate and improves the stress corrosion cracking resistance. To achieve the effects, the Cr content needs to be 0.5 % or more. If the Cr content is more than 8.0 %, the effects are saturated, and the economic efficiency is impaired. The Cr content is therefore 0.5 % or more and 8.0 % or less. The Cr content is preferably 1.0 % or more.

**[0023]** The solute content in the added Cr contributes to improved stress corrosion cracking resistance, but the precipitate content in the added Cr has a possibility of hindering improvement in stress corrosion cracking resistance. Accordingly, it is important that at least 60 % of Cr is solute Cr. In other words, if solute Cr is 60 % or more of the Cr content, the foregoing effects can be achieved, and improvement in stress corrosion cracking resistance by addition of Cr can be achieved. Solute Cr is preferably 70 % or more of the Cr content, and more preferably 100 % of the Cr content.

**[0024]** Herein, "solute Cr" denotes a state in which solute atoms exist in an atom state without forming a precipitate or the like. Specifically, the amount of solute Cr can be calculated as follows: A test piece for electrolytic extraction is collected from the steel plate, and a precipitate is extracted by electrolytic extraction using a 10 % AA (10 % acetylacetone-1 % tetramethylammonium chloride-methanol) solution. The Cr content in the precipitate is measured by ICP optical emission spectrometry, and the measured Cr content is subtracted from all Cr in the test piece to yield the amount of solute Cr.

N: 0.0010 % or more and 0.0300 % or less

**[0025]** N is an austenite-stabilizing element, and is effective in improving the very-low-temperature toughness. N also has an effect of combining with Nb, V, and Ti to form nitrides or carbonitrides which finely precipitate and suppress stress corrosion cracking as a diffusible hydrogen trapping site. To achieve the effects, the N content needs to be 0.0010 % or more. If the N content is more than 0.0300 %, excessive formation of nitrides or carbonitrides is facilitated, as a result of which not only the amount of solute element decreases and the corrosion resistance decreases but also the toughness decreases. The N content is therefore 0.0010 % or more and 0.0300 % or less. The N content is preferably 0.0020 % or more and 0.0150 % or less.

B: 0.0003 % or more and 0.0100 % or less

**[0026]** B is an element that strengthens the austenite grain boundaries, and is effective in improving the stress corrosion cracking resistance by suppressing cracking in the grain boundaries. To achieve the effects, the B content needs to be 0.0003 % or more. The B content is preferably 0.0005 % or more, further preferably more than 0.0007 %, and particularly preferably more than 0.0010 %. If the B content is more than 0.0100 %, the effects are saturated. The B content is therefore 0.0100 % or less. The B content is preferably 0.0070 % or less.

**[0027]** The chemical composition of the steel plate according to one of the disclosed embodiments may optionally contain, in addition to the above-described essential elements, Nb: 0.003 % or more and 0.030 % or less, V: 0.01 % or more and 0.10 % or less, and Ti: 0.003 % or more and 0.040 % or less, for the purpose of further improving the corrosion resistance.

Nb: 0.003 % or more and 0.030 % or less

**[0028]** Nb is an element that has an effect of suppressing stress corrosion cracking by forming carbonitrides that precipitate and function as a diffusible hydrogen trapping site. To achieve the effect, the Nb content is preferably 0.003 % or more. If the Nb content is more than 0.030 %, coarse carbonitrides may precipitate and form a fracture origin. In addition, precipitates may coarsen and cause a decrease in base metal toughness. Accordingly, in the case of containing

Nb, the Nb content is preferably 0.003 % or more and 0.030 % or less. The Nb content is more preferably 0.005 % or more and 0.025 % or less, and further preferably 0.007 % or more and 0.022 % or less.

V: 0.01 % or more and 0.10 % or less

**[0029]** V is an element that has an effect of suppressing stress corrosion cracking by forming carbonitrides that precipitate and function as a diffusible hydrogen trapping site. To achieve the effect, the V content is preferably 0.01 % or more. If the V content is more than 0.10 %, coarse carbonitrides may precipitate and form a fracture origin. In addition, precipitates may coarsen and cause a decrease in base metal toughness. Accordingly, in the case of containing V, the V content is preferably 0.01 % or more and 0.10 % or less. The V content is more preferably 0.02 % or more and 0.09 % or less, and further preferably 0.03 % or more and 0.08 % or less.

Ti: 0.003 % or more and 0.040 % or less

**[0030]** Ti is an element that has an effect of suppressing stress corrosion cracking by forming nitrides or carbonitrides that precipitate and function as a diffusible hydrogen trapping site. To achieve the effect, the Ti content is preferably 0.003 % or more. If the Ti content is more than 0.040 %, precipitates may coarsen and cause a decrease in base metal toughness. In addition, coarse carbonitrides may precipitate and form a fracture origin. Accordingly, in the case of containing Ti, the Ti content is preferably 0.003 % or more and 0.040 % or less. The Ti content is more preferably 0.005 % or more and 0.035 % or less, and further preferably 0.007 % or more and 0.032 % or less.

**[0031]** The chemical composition of the steel plate according to one of the disclosed embodiments may optionally further contain one or more selected from Cu: 0.01 % or more and 0.50 % or less, Ni: 0.01 % or more and 0.50 % or less, Sn: 0.01 % or more and 0.30 % or less, Sb: 0.01 % or more and 0.30 % or less, Mo: 0.01 % or more and 2.0 % or less, and W: 0.01 % or more and 2.0 % or less, for the purpose of further improving the corrosion resistance.

**[0032]** Cu, Ni, Sn, Sb, Mo, and W are each an element that, when added in combination with Cr, improves the corrosion resistance of the high-Mn steel in saltwater corrosive environments. Cu, Sn, and Sb each have an effect of suppressing hydrogen evolution reaction which is cathode reaction by increasing the hydrogen overvoltage of the steel material. Ni forms a precipitation coating on the steel material surface, and physically suppresses the permeation of corrosive anions such as Cl<sup>-</sup> into the steel substrate. Moreover, Cu, Ni, Sn, Sb, Mo, and W each separate from the steel material surface as metal ions upon corrosion, and refine the corrosion product to thus suppress the permeation of corrosive anions through the steel interface (the interface between the rust layer and the steel substrate). Mo and W separate respectively as Mo<sub>4</sub><sup>2-</sup> and WO<sub>4</sub><sup>2-</sup> and are adsorbed in the corrosion product or on the steel plate surface, thereby imparting cation selective permeability and electrically suppressing the permeation of corrosive anions into the steel substrate.

**[0033]** The effects of each of these elements are realized in the case where the element is present together with Cr in the high-Mn steel, and are exhibited when the content of the element is 0.01 % or more. Meanwhile, high contents of these elements cause decreases in weldability and toughness, and are also disadvantageous in terms of cost.

**[0034]** Hence, preferably the Cu content is 0.01 % or more and 0.50 % or less, the Ni content is 0.01 % or more and 0.50 % or less, the Sn content is 0.01 % or more and 0.30 % or less, the Sb content is 0.01 % or more and 0.30 % or less, the Mo content is 0.01 % or more and 2.0 % or less, and the W content is 0.01 % or more and 2.0 % or less.

**[0035]** More preferably, the Cu content is 0.02 % or more and 0.40 % or less, the Ni content is 0.02 % or more and 0.40 % or less, the Sn content is 0.02 % or more and 0.25 % or less, the Sb content is 0.02 % or more and 0.25 % or less, the Mo content is 0.02 % or more and 0.40 % or less, and the W content is 0.02 % or more and 0.40 % or less.

**[0036]** Likewise, the chemical composition of the steel plate according to one of the disclosed embodiments may optionally further contain one or more selected from Ca: 0.0005 % or more and 0.0050 % or less, Mg: 0.0005 % or more and 0.0100 % or less, and REM: 0.0010 % or more and 0.0200 % or less, for the purpose of further improving the corrosion resistance.

**[0037]** Ca, Mg, and REM are each an element useful for morphological control of inclusions, and may be optionally contained. Morphological control of inclusions means turning elongated sulfide-based inclusions into granular inclusions. Through such morphological control of inclusions, the ductility, the toughness, and the sulfide stress corrosion cracking resistance can be improved. To achieve the effects, the Ca content and the Mg content are each preferably 0.0005 % or more, and the REM content is preferably 0.0010 % or more. If the Ca content, the Mg content, and the REM content are each high, the amount of nonmetallic inclusions increases, which may decrease the ductility, the toughness, and the sulfide stress corrosion cracking resistance. Moreover, high contents of these elements are likely to be economically disadvantageous.

**[0038]** Accordingly, in the case of containing Ca, the Ca content is preferably 0.0005 % or more and 0.0050 % or less. In the case of containing Mg, the Mg content is preferably 0.0005 % or more and 0.0100 % or less. In the case of containing REM, the REM content is preferably 0.0010 % or more and 0.0200 % or less. More preferably, the Ca content is 0.0010 % or more and 0.0040 % or less, the Mg content is 0.0010 % or more and 0.0040 % or less, and the REM

content is 0.0020 % or more and 0.0150 % or less.

**[0039]** The production conditions according to one of the disclosed embodiments will be described below. The temperature of the material to be rolled in hot rolling and the cooling rate in subsequent cooling are the temperature and the cooling rate measured on the surface of the material to be rolled. In detail, the steel plate is produced by: heating a steel raw material having the foregoing chemical composition to 1000 °C or more and 1300 °C or less; thereafter subjecting the steel raw material to hot rolling at a rolling reduction ratio of 3 or more and 30 or less and a rolling finish temperature of 750 °C or more, with the residence time during which the material to be rolled is in a temperature range of 950 °C or less and 600 °C or more being 30 min or less; and thereafter cooling the material at an average cooling rate of 3 °C/s or more in a temperature range of 700 °C or less and 600 °C or more.

[Heating temperature of steel raw material: 1000 °C or more and 1300 °C or less]

**[0040]** The steel raw material is heated to 1000 °C or more in order to dissolve carbonitrides in the microstructure and homogenize the crystal grain size and the like. If the heating temperature is less than 1000 °C, carbonitrides do not dissolve sufficiently, making it impossible to obtain desired properties. If the heating temperature is more than 1300 °C, the material properties degrade due to coarsening of crystal grains. Moreover, excessive energy is required, and the productivity decreases. The upper limit of the heating temperature is therefore 1300 °C. The heating temperature is preferably 1050 °C or more and 1250 °C or less, and more preferably 1070 °C or more and 1250 °C or less. The steel raw material is preferably a continuously-cast slab, or a slab, a billet, or the like produced by a well-known method such as ingot casting. The molten steel may be additionally subjected to treatments such as ladle refining and vacuum degassing.

[Hot-rolling finish temperature: 750 °C or more]

**[0041]** If the rolling finish temperature of the hot rolling is less than 750 °C, the amount of carbides precipitated during the rolling increases significantly, and the amount of solute Cr may be unable to be ensured even in the case where the residence time in a temperature range of 600 °C or more and 900 °C or less is less than 30 min as described later. This causes a decrease in corrosion resistance. If the rolling finish temperature of the hot rolling is less than 750 °C, the deformation resistance increases, and an excessive load is put on the production line. The rolling finish temperature is therefore 750 °C or more.

[Average cooling rate in temperature range of 700 °C or less and 600 °C or more: 3 °C/s or more]

**[0042]** In the cooling after the hot rolling, if the average cooling rate in a temperature range of 700 °C or less and 600 °C or more is less than 3 °C/s, precipitates such as Cr carbides form in large amounts. The average cooling rate is therefore limited to 3 °C/s or more. The average cooling rate is preferably 10 °C/s or more and 150 °C/s or less.

[Residence time in temperature range of 950 °C or less and 600 °C or more: 30 min or less]

**[0043]** In the hot rolling, if the residence time during which the raw material to be rolled is in a temperature range of 950 °C or less and 600 °C or more is more than 30 min, carbonitrides and carbides precipitate in large amounts during the rolling, and the amount of solute Cr decreases to less than the necessary amount, which causes a decrease in corrosion resistance and a decrease in very-low-temperature toughness. Accordingly, the residence time in a temperature range of 950 °C or less and 600 °C or more is limited to 30 min or less. The residence time is preferably 5 min or more and 25 min or less.

**[0044]** To limit the residence time in a temperature range of 950 °C or less and 600 °C or more to 30 min or less, it is preferable to set the length of the material to be rolled to 5000 mm or less and set the rolling reduction ratio in the hot rolling from the material to be rolled to 30 or less. That is, as a result of setting the length of the material to be rolled to 5000 mm or less and setting the rolling reduction ratio to 30 or less, the rolling time can be shortened, and consequently the residence time in a range of 950 °C or less and 600 °C or more can be limited to 30 min or less.

**[0045]** Thus, the rolling reduction ratio in the hot rolling is preferably 30 or less. If the rolling reduction ratio in the hot rolling is less than 3, there is a possibility that, as a result of lessening of the effect of facilitating recrystallization to achieve homogenization, coarse austenite grains remain and this part oxidizes preferentially, and consequently the corrosion resistance decreases. Accordingly, the rolling reduction ratio in the hot rolling is preferably 3 or more.

**[0046]** Herein, the rolling reduction ratio is defined as "(the thickness of the raw material to be rolled in hot rolling)/(the thickness of the steel plate after the hot rolling)".

# EXAMPLES

**[0047]** Steels No. 1 to No. 57 in Table 1 prepared by steelmaking were melted to form slabs, and then steel plates of samples No. 1 to No. 65 with a thickness of 6 mm or more and 50 mm or less were produced under the production conditions indicated in Table 2. The obtained steel plates were then subjected to the following corrosion resistance test. In addition, the result of measuring the amount of solute Cr in each sample by the foregoing electrolytic extraction is also indicated in Table 2.

**[0048]** The corrosion resistance test was conducted in accordance with the NACE Standard TM0111-2011 Slow Strain Rate Test Method (hereafter "SSRT test"). In detail, using a type A notched round bar test piece as the test piece shape, the test piece was immersed in artificial seawater (chloride ion concentration: 18000 ppm) at a temperature of 23 °C, and a constant-rate tensile test was conducted at a strain rate of  $4 \times 10^{-7}$  inch/s. In the case where the fracture stress was 600 MPa or more, the stress corrosion cracking resistance was evaluated as excellent.

**[0049]** The results are indicated in Table 2.



[Table 1]

| Steel No. | Chemical composition (mass%) |      |      |       |        |       |     |        |        |       |      |       |      |      |      |      |      |      |        |        |        | REMs |
|-----------|------------------------------|------|------|-------|--------|-------|-----|--------|--------|-------|------|-------|------|------|------|------|------|------|--------|--------|--------|------|
|           | C                            | Si   | Mn   | P     | S      | Al    | Cr  | N      | B      | Nb    | V    | Ti    | Cu   | Ni   | Mo   | W    | Sn   | Sb   | Mg     | Ca     | REM    |      |
| 1         | 0.48                         | 0.39 | 27.4 | 0.015 | 0.0035 | 0.034 | 3.3 | 0.0026 | 0.0010 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 2         | 0.45                         | 0.34 | 26.5 | 0.009 | 0.0020 | 0.035 | 7.1 | 0.0027 | 0.0026 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 3         | 0.42                         | 0.31 | 24.4 | 0.008 | 0.0026 | 0.035 | 0.5 | 0.0330 | 0.0068 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 4         | 0.54                         | 0.50 | 22.8 | 0.007 | 0.0012 | 0.028 | 5.3 | 0.0031 | 0.0037 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 5         | 0.48                         | 0.45 | 25.4 | 0.011 | 0.0020 | 0.036 | 5.1 | 0.0125 | 0.0007 | -     | -    | 0.008 | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 6         | 0.37                         | 0.39 | 21.1 | 0.015 | 0.0036 | 0.031 | 7.6 | 0.0026 | 0.0050 | 0.013 | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 7         | 0.48                         | 0.52 | 24.3 | 0.012 | 0.0040 | 0.037 | 4.7 | 0.0090 | 0.0020 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 8         | 0.47                         | 0.47 | 24.8 | 0.012 | 0.0031 | 0.036 | 4.9 | 0.0105 | 0.0095 | -     | 0.04 | 0.008 | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 9         | 0.37                         | 0.39 | 33.0 | 0.014 | 0.0004 | 0.036 | 4.5 | 0.0031 | 0.0037 | -     | -    | -     | 0.22 | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 10        | 0.64                         | 0.28 | 26.0 | 0.015 | 0.0036 | 0.033 | 5.0 | 0.0026 | 0.0037 | -     | -    | -     | -    | 0.22 | -    | -    | -    | -    | -      | -      | -      |      |
| 11        | 0.46                         | 0.38 | 26.5 | 0.013 | 0.0015 | 0.028 | 2.7 | 0.0022 | 0.0067 | -     | -    | -     | -    | -    | -    | -    | 0.06 | -    | -      | -      | -      |      |
| 12        | 0.43                         | 0.85 | 21.2 | 0.010 | 0.0014 | 0.031 | 4.0 | 0.0026 | 0.0075 | -     | -    | -     | -    | -    | -    | -    | -    | 0.12 | -      | -      | -      |      |
| 13        | 0.47                         | 0.38 | 24.5 | 0.015 | 0.0018 | 0.032 | 4.7 | 0.0029 | 0.0061 | -     | -    | -     | -    | -    | 0.02 | -    | -    | -    | -      | -      | -      |      |
| 14        | 0.55                         | 0.08 | 26.0 | 0.009 | 0.0023 | 0.033 | 5.5 | 0.0026 | 0.0031 | -     | -    | -     | -    | -    | -    | 0.06 | -    | -    | -      | -      | -      |      |
| 15        | 0.54                         | 0.15 | 18.2 | 0.011 | 0.0020 | 0.018 | 5.2 | 0.0118 | 0.0029 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | 0.0021 | -      |      |
| 16        | 0.48                         | 0.45 | 24.4 | 0.008 | 0.0012 | 0.035 | 4.7 | 0.0048 | 0.0045 | -     | -    | -     | -    | -    | -    | -    | -    | -    | 0.0020 | -      | -      |      |
| 17        | 0.26                         | 0.55 | 26.1 | 0.022 | 0.0019 | 0.031 | 1.9 | 0.0031 | 0.0055 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | 0.0015 |      |
| 18        | 0.46                         | 0.37 | 26.9 | 0.013 | 0.0028 | 0.034 | 5.1 | 0.0027 | 0.0003 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 19        | 0.70                         | 0.39 | 33.0 | 0.010 | 0.0014 | 0.021 | 4.5 | 0.0033 | 0.0003 | -     | -    | -     | 0.01 | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 20        | 0.20                         | 0.39 | 26.5 | 0.015 | 0.0018 | 0.038 | 4.9 | 0.0035 | 0.0003 | -     | -    | -     | 0.50 | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 21        | 0.48                         | 1.00 | 21.2 | 0.009 | 0.0023 | 0.030 | 4.5 | 0.0028 | 0.0050 | -     | -    | -     | -    | 0.01 | -    | -    | -    | -    | -      | -      | -      |      |
| 22        | 0.37                         | 0.05 | 33.0 | 0.014 | 0.0020 | 0.019 | 5.0 | 0.0029 | 0.0020 | -     | -    | -     | -    | 0.50 | -    | -    | -    | -    | -      | -      | -      |      |
| 23        | 0.48                         | 0.39 | 35.0 | 0.014 | 0.0012 | 0.033 | 2.7 | 0.0026 | 0.0095 | -     | -    | -     | -    | -    | -    | -    | 0.01 | -    | -      | -      | -      |      |
| 24        | 0.47                         | 0.52 | 15.0 | 0.014 | 0.0019 | 0.028 | 4.0 | 0.0023 | 0.0037 | -     | -    | -     | -    | -    | -    | -    | 0.30 | -    | -      | -      | -      |      |
| 25        | 0.35                         | 0.47 | 26.0 | 0.030 | 0.0004 | 0.031 | 4.7 | 0.0020 | 0.0037 | -     | -    | -     | -    | -    | -    | -    | -    | 0.01 | -      | -      | -      |      |
| 26        | 0.64                         | 0.39 | 26.5 | 0.020 | 0.0200 | 0.031 | 4.5 | 0.0017 | 0.0020 | -     | -    | -     | -    | -    | -    | -    | -    | 0.30 | -      | -      | -      |      |
| 27        | 0.46                         | 0.28 | 21.2 | 0.009 | 0.0014 | 0.100 | 3.4 | 0.0027 | 0.0029 | -     | -    | -     | -    | -    | 0.05 | -    | -    | -    | -      | -      | -      |      |
| 28        | 0.37                         | 0.38 | 24.5 | 0.008 | 0.0018 | 0.010 | 3.5 | 0.0033 | 0.0026 | -     | -    | -     | -    | -    | 2.00 | -    | -    | -    | -      | -      | -      |      |
| 29        | 0.48                         | 0.85 | 26.0 | 0.007 | 0.0025 | 0.018 | 8.0 | 0.0055 | 0.0037 | -     | -    | -     | -    | -    | -    | 0.05 | -    | -    | -      | -      | -      |      |
| 30        | 0.29                         | 0.52 | 18.2 | 0.011 | 0.0014 | 0.035 | 0.5 | 0.0028 | 0.0037 | -     | -    | -     | -    | -    | -    | 2.00 | -    | -    | -      | -      | -      |      |
| 31        | 0.48                         | 0.47 | 33.0 | 0.015 | 0.0018 | 0.031 | 4.5 | 0.0300 | 0.0007 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | 0.0005 | -      |      |
| 32        | 0.47                         | 0.39 | 26.5 | 0.009 | 0.0025 | 0.048 | 3.1 | 0.0010 | 0.0050 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | 0.0050 | -      |      |
| 33        | 0.37                         | 0.28 | 21.2 | 0.008 | 0.0004 | 0.043 | 3.7 | 0.0118 | 0.0100 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | 0.0005 | -      |      |
| 34        | 0.64                         | 0.38 | 24.5 | 0.007 | 0.0014 | 0.038 | 4.5 | 0.0225 | 0.0003 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | 0.0100 | -      |      |
| 35        | 0.46                         | 0.85 | 26.9 | 0.011 | 0.0018 | 0.033 | 4.2 | 0.0026 | 0.0026 | 0.030 | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | 0.0010 |      |
| 36        | 0.37                         | 0.38 | 27.3 | 0.015 | 0.0025 | 0.028 | 4.5 | 0.0022 | 0.0026 | 0.003 | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | 0.0200 |      |
| 37        | 0.55                         | 0.08 | 22.8 | 0.012 | 0.0020 | 0.031 | 2.8 | 0.0026 | 0.0020 | -     | 0.10 | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 38        | 0.54                         | 0.39 | 26.5 | 0.012 | 0.0012 | 0.034 | 4.5 | 0.0030 | 0.0037 | -     | 0.01 | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 39        | 0.48                         | 0.39 | 21.2 | 0.014 | 0.0019 | 0.029 | 5.6 | 0.0034 | 0.0007 | -     | -    | 0.04  | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 40        | 0.37                         | 0.39 | 33.0 | 0.014 | 0.0004 | 0.031 | 4.5 | 0.0038 | 0.0050 | -     | -    | 0.003 | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 41        | 0.44                         | 0.33 | 25.5 | 0.009 | 0.0024 | 0.037 | 3.8 | 0.0031 | 0.0098 | -     | -    | -     | -    | -    | -    | -    | -    | -    | -      | -      | -      |      |
| 42        | 0.36                         | 0.39 | 32.8 | 0.014 | 0.0005 | 0.036 | 4.4 | 0.0031 | 0.0037 | -     | -    | -     | 0.21 | -    | -    | -    | -    | -    | -      | -      | -      |      |

Example

Underlines indicate outside range according to present disclosure.

[Table 1](cont'd)

| Steel |      | Chemical composition (mass%) |      |       |        |       |     |        |        |       |   |       |      |      |      |      |      |    |        |        | Remarks |
|-------|------|------------------------------|------|-------|--------|-------|-----|--------|--------|-------|---|-------|------|------|------|------|------|----|--------|--------|---------|
| No.   | C    | Si                           | Mn   | P     | S      | Al    | Cr  | N      | B      | Nb    | V | Ti    | Cu   | Ni   | Mo   | W    | Sn   | Sb | Mg     | Ca     |         |
| 43    | 0.76 | 0.52                         | 24.2 | 0.012 | 0.0018 | 0.029 | 2.7 | 0.0039 | 0.0003 | 0.009 | - | -     | 0.05 | -    | 0.10 | -    | -    | -  | -      | -      | -       |
| 44    | 0.14 | 0.65                         | 18.0 | 0.011 | 0.0019 | 0.021 | 7.7 | 0.0033 | 0.0004 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |
| 45    | 0.51 | 0.68                         | 40.2 | 0.014 | 0.0028 | 0.038 | 2.1 | 0.0055 | 0.0003 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | 0.0022 | -       |
| 46    | 0.22 | 0.72                         | 11.0 | 0.011 | 0.0001 | 0.025 | 0.7 | 0.0028 | 0.0003 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |
| 47    | 0.43 | 0.51                         | 24.8 | 0.044 | 0.0058 | 0.019 | 5.6 | 0.0029 | 0.0004 | 0.012 | - | -     | -    | 0.41 | -    | -    | -    | -  | -      | -      | -       |
| 48    | 0.52 | 1.31                         | 27.5 | 0.012 | 0.0040 | 0.027 | 4.7 | 0.0038 | 0.0003 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |
| 49    | 0.47 | 0.63                         | 26.9 | 0.014 | 0.0060 | 0.132 | 3.9 | 0.0029 | 0.0003 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |
| 50    | 0.45 | 0.62                         | 22.8 | 0.012 | 0.0013 | 0.030 | 0.3 | 0.0023 | 0.0003 | -     | - | 0.009 | -    | -    | -    | 0.09 | -    | -  | -      | 0.0018 | -       |
| 51    | 0.57 | 0.33                         | 21.8 | 0.016 | 0.0047 | 0.022 | 4.2 | 0.0392 | 0.0004 | -     | - | -     | -    | -    | -    | -    | 0.10 | -  | -      | -      | -       |
| 52    | 0.48 | 0.39                         | 25.6 | 0.023 | 0.0350 | 0.018 | 6.1 | 0.0029 | 0.0003 | -     | - | -     | -    | -    | 0.13 | -    | -    | -  | 0.0019 | -      | -       |
| 53    | 0.47 | 0.39                         | 27.3 | 0.015 | 0.0036 | 0.033 | 3.2 | 0.0026 | 0.0001 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |
| 54    | 0.36 | 0.03                         | 25.3 | 0.008 | 0.0025 | 0.021 | 3.2 | 0.0025 | 0.0025 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |
| 55    | 0.25 | 0.50                         | 24.2 | 0.010 | 0.0026 | 0.005 | 4.5 | 0.0019 | 0.0023 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |
| 56    | 0.42 | 0.45                         | 23.6 | 0.008 | 0.0036 | 0.019 | 2.9 | 0.0005 | 0.0020 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |
| 57    | 0.56 | 0.55                         | 20.9 | 0.012 | 0.0041 | 0.018 | 4.4 | 0.0036 | 0.0200 | -     | - | -     | -    | -    | -    | -    | -    | -  | -      | -      | -       |

Underlines indicate outside range according to present disclosure.

[Table 2]

| Sample No. | Steel No. | Raw material length (mm) | Production conditions  |                          |                         |   |              |              |              |       |                                 |                                |                               | Base metal properties | Stress corrosion cracking resistance | Remarks |                                |               |                       |
|------------|-----------|--------------------------|------------------------|--------------------------|-------------------------|---|--------------|--------------|--------------|-------|---------------------------------|--------------------------------|-------------------------------|-----------------------|--------------------------------------|---------|--------------------------------|---------------|-----------------------|
|            |           |                          | Product thickness (mm) | Heating temperature (°C) | Rolling reduction ratio | Residence time in temperature range of 950 to 600°C (min) |              |              |              |       | Rolling finish temperature (°C) | Cooling start temperature (°C) | Cooling stop temperature (°C) |                       |                                      |         | Average cooling rate *1 (°C/s) | Solute Cr (%) | Fracture stress (MPa) |
|            |           |                          |                        |                          |                         | 950 to 900°C  | 900 to 800°C | 800 to 700°C | 700 to 600°C | Total |                                 |                                |                               |                       |                                      |         |                                |               |                       |
| 1          | 1         | 4000                     | 30                     | 1090                     | 5                       | 6.68  | 3.15         | 0.11         | 0.06         | 10    | 850                             | 500                            | 30                            | 85                    | 601                                  |         |                                |               |                       |
| 2          | 2         | 4500                     | 50                     | 1200                     | 3                       | 2.92  | 1.75         | 0.22         | 0.11         | 5     | 900                             | 550                            | 15                            | 95                    | 605                                  |         |                                |               |                       |
| 3          | 3         | 1500                     | 6                      | 1190                     | 30                      | 12.41   | 7.68         | 4.90         | 0.01         | 25    | 760                             | 550                            | 130                           | 75                    | 636                                  |         |                                |               |                       |
| 4          | 4         | 4000                     | 30                     | 1150                     | 7                       | 8.65  | 6.23         | 0.08         | 0.04         | 15    | 850                             | 500                            | 40                            | 80                    | 660                                  |         |                                |               |                       |
| 5          | 5         | 2000                     | 12                     | 1200                     | 15                      | 11.33   | 8.20         | 0.44         | 0.02         | 20    | 850                             | 500                            | 75                            | 90                    | 603                                  |         |                                |               |                       |
| 6          | 6         | 4000                     | 30                     | 1250                     | 6                       | 5.26  | 4.57         | 0.11         | 0.06         | 10    | 850                             | 600                            | 30                            | 75                    | 654                                  |         |                                |               |                       |
| 7          | 7         | 3000                     | 12                     | 1140                     | 10                      | 9.85  | 9.65         | 0.48         | 0.02         | 20    | 850                             | 550                            | 70                            | 85                    | 639                                  |         |                                |               |                       |
| 8          | 8         | 1800                     | 12                     | 1190                     | 15                      | 16.76   | 12.30        | 0.89         | 0.06         | 30    | 900                             | 550                            | 30                            | 70                    | 647                                  |         |                                |               |                       |
| 9          | 9         | 5000                     | 50                     | 1190                     | 4                       | 4.42  | 3.25         | 0.22         | 0.11         | 8     | 900                             | 550                            | 15                            | 90                    | 668                                  |         |                                |               |                       |
| 10         | 10        | 5000                     | 50                     | 1270                     | 3                       | 2.16  | 2.01         | 0.67         | 0.17         | 5     | 900                             | 550                            | 10                            | 75                    | 604                                  |         |                                |               |                       |
| 11         | 11        | 4000                     | 30                     | 1140                     | 5                       | 4.14  | 3.25         | 0.56         | 0.06         | 8     | 800                             | 500                            | 30                            | 85                    | 612                                  |         |                                |               |                       |
| 12         | 12        | 2500                     | 12                     | 1060                     | 15                      | 6.57  | 8.36         | 0.05         | 0.02         | 15    | 750                             | 500                            | 70                            | 80                    | 606                                  |         |                                |               |                       |
| 13         | 13        | 2500                     | 12                     | 1150                     | 10                      | 5.48  | 4.23         | 0.27         | 0.02         | 10    | 800                             | 600                            | 75                            | 85                    | 701                                  |         |                                |               |                       |
| 14         | 14        | 1200                     | 6                      | 1250                     | 25                      | 17.60   | 12.36        | 0.02         | 0.01         | 30    | 750                             | 450                            | 140                           | 65                    | 605                                  |         |                                |               |                       |
| 15         | 15        | 1500                     | 6                      | 1150                     | 20                      | 15.73   | 14.23        | 0.02         | 0.01         | 30    | 750                             | 400                            | 140                           | 70                    | 604                                  |         |                                |               |                       |
| 16         | 16        | 4500                     | 50                     | 1190                     | 4                       | 1.80  | 2.87         | 0.22         | 0.11         | 5     | 950                             | 550                            | 15                            | 90                    | 641                                  |         |                                |               |                       |
| 17         | 17        | 2500                     | 12                     | 1150                     | 10                      | 7.28  | 7.25         | 0.44         | 0.02         | 15    | 800                             | 500                            | 75                            | 80                    | 641                                  |         |                                |               |                       |
| 18         | 18        | 4000                     | 30                     | 1180                     | 20                      | 7.12  | 7.30         | 0.56         | 0.03         | 15    | 830                             | 500                            | 60                            | 85                    | 602                                  |         |                                |               |                       |
| 19         | 19        | 4000                     | 20                     | 1150                     | 10                      | 13.95   | 5.80         | 0.17         | 0.08         | 20    | 840                             | 500                            | 20                            | 80                    | 604                                  |         |                                |               |                       |

(continued)

| Sample No. | Steel No. | Raw material length (mm) | Production conditions  |                          |                         |   |              |              |              |       |                                 |                                |                               |                                 | Base metal properties | Stress corrosion resistance | Remarks |               |                       |
|------------|-----------|--------------------------|------------------------|--------------------------|-------------------------|---|--------------|--------------|--------------|-------|---------------------------------|--------------------------------|-------------------------------|---------------------------------|-----------------------|-----------------------------|---------|---------------|-----------------------|
|            |           |                          | Product thickness (mm) | Heating temperature (°C) | Rolling reduction ratio | Residence time in temperature range of 950 to 600°C (min) |              |              |              |       | Rolling finish temperature (°C) | Cooling start temperature (°C) | Cooling stop temperature (°C) | Average cooling rate * 1 (°C/s) |                       |                             |         | Solute Cr (%) | Fracture stress (MPa) |
|            |           |                          |                        |                          |                         | 950 to 900°C  | 900 to 800°C | 800 to 700°C | 700 to 600°C | Total |                                 |                                |                               |                                 |                       |                             |         |               |                       |
| 20         | 20        | 3000                     | 30                     | 1190                     | 7                       | 9.93  | 4.73         | 0.22         | 0.11         | 15    | 890                             | 860                            | 550                           | 15                              | 85                    | 603                         | Example |               |                       |
| 21         | 21        | 4000                     | 25                     | 1270                     | 8                       | 7.72  | 6.50         | 0.67         | 0.11         | 15    | 760                             | 730                            | 450                           | 15                              | 85                    | 638                         |         |               |                       |
| 22         | 22        | 4000                     | 15                     | 1140                     | 13                      | 19.03   | 5.80         | 0.11         | 0.06         | 25    | 840                             | 810                            | 500                           | 30                              | 75                    | 630                         |         |               |                       |
| 23         | 23        | 4000                     | 20                     | 1060                     | 10                      | 15.00   | 4.75         | 0.17         | 0.08         | 20    | 840                             | 810                            | 550                           | 20                              | 80                    | 634                         |         |               |                       |
| 24         | 24        | 4000                     | 15                     | 1150                     | 13                      | 21.03   | 3.80         | 0.11         | 0.06         | 25    | 840                             | 810                            | 450                           | 30                              | 75                    | 630                         |         |               |                       |
| 25         | 25        | 4000                     | 10                     | 1200                     | 20                      | 19.58   | 5.30         | 0.08         | 0.04         | 25    | 840                             | 810                            | 500                           | 40                              | 75                    | 630                         |         |               |                       |
| 26         | 26        | 4000                     | 25                     | 1150                     | 8                       | 8.87  | 5.80         | 0.22         | 0.11         | 15    | 890                             | 860                            | 500                           | 15                              | 85                    | 638                         |         |               |                       |
| 27         | 27        | 4000                     | 20                     | 1190                     | 10                      | 15.15   | 4.60         | 0.17         | 0.08         | 20    | 890                             | 860                            | 500                           | 20                              | 80                    | 634                         |         |               |                       |
| 28         | 28        | 3000                     | 30                     | 1150                     | 7                       | 9.87  | 3.80         | 0.22         | 0.11         | 14    | 890                             | 860                            | 550                           | 15                              | 85                    | 638                         |         |               |                       |
| 29         | 29        | 3000                     | 40                     | 1090                     | 5                       | 4.99  | 4.23         | 0.67         | 0.11         | 10    | 790                             | 760                            | 450                           | 15                              | 85                    | 638                         |         |               |                       |
| 30         | 30        | 4000                     | 20                     | 1130                     | 10                      | 10.77   | 8.65         | 0.50         | 0.08         | 20    | 760                             | 730                            | 500                           | 20                              | 80                    | 634                         |         |               |                       |
| 31         | 31        | 4000                     | 15                     | 1150                     | 13                      | 12.60   | 12.01        | 0.33         | 0.06         | 25    | 790                             | 760                            | 500                           | 30                              | 75                    | 630                         |         |               |                       |
| 32         | 32        | 4000                     | 20                     | 1080                     | 10                      | 10.86   | 8.56         | 0.50         | 0.08         | 20    | 760                             | 730                            | 550                           | 20                              | 80                    | 634                         |         |               |                       |
| 33         | 33        | 4000                     | 15                     | 1120                     | 13                      | 10.38   | 14.23        | 0.33         | 0.06         | 25    | 770                             | 740                            | 450                           | 30                              | 75                    | 630                         |         |               |                       |
| 34         | 34        | 4000                     | 20                     | 1100                     | 10                      | 15.15   | 4.60         | 0.17         | 0.08         | 20    | 940                             | 910                            | 500                           | 20                              | 80                    | 601                         |         |               |                       |
| 35         | 35        | 4000                     | 15                     | 1110                     | 13                      | 12.25   | 12.36        | 0.33         | 0.06         | 25    | 790                             | 760                            | 500                           | 30                              | 75                    | 630                         |         |               |                       |
| 36         | 36        | 4000                     | 20                     | 1090                     | 10                      | 9.47  | 9.95         | 0.50         | 0.08         | 20    | 820                             | 790                            | 550                           | 20                              | 80                    | 634                         |         |               |                       |
| 37         | 37        | 4000                     | 25                     | 1120                     | 8                       | 7.22  | 7.45         | 0.22         | 0.11         | 15    | 830                             | 800                            | 500                           | 15                              | 80                    | 634                         |         |               |                       |

(continued)

| Sample No.             | Steel No.                | Raw material length (mm) | Production conditions  |                          |                         |  |              |              |              |       |                                 |                                |                               | Base metal properties          | Stress corrosion cracking resistance | Remarks               |                                |               |                       |
|------------------------|--------------------------|--------------------------|------------------------|--------------------------|-------------------------|--|--------------|--------------|--------------|-------|---------------------------------|--------------------------------|-------------------------------|--------------------------------|--------------------------------------|-----------------------|--------------------------------|---------------|-----------------------|
|                        |                          |                          | Product thickness (mm) | Heating temperature (°C) | Rolling reduction ratio | Residence time in temperature range of 950 to 600°C (min)  |              |              |              |       | Rolling finish temperature (°C) | Cooling start temperature (°C) | Cooling stop temperature (°C) |                                |                                      |                       | Average cooling rate *1 (°C/s) | Solute Cr (%) | Fracture stress (MPa) |
|                        |                          |                          |                        |                          |                         | 950 to 900°C   | 900 to 800°C | 800 to 700°C | 700 to 600°C | Total |                                 |                                |                               |                                |                                      |                       |                                |               |                       |
| 38                     | 38                       | 4000                     | 10                     | 1100                     | 20                      | 19.58  | 5.30         | 0.08         | 0.04         | 25    | 880                             | 850                            | 550                           | 40                             | 75                                   | 630                   |                                |               |                       |
| 39                     | 39                       | 4000                     | 25                     | 1200                     | 8                       | 7.46   | 7.21         | 0.22         | 0.11         | 15    | 760                             | 730                            | 450                           | 15                             | 80                                   | 602                   |                                |               |                       |
| 40                     | 40                       | 4000                     | 20                     | 1150                     | 10                      | 10.39  | 9.36         | 0.17         | 0.08         | 20    | 830                             | 800                            | 500                           | 20                             | 80                                   | 634                   |                                |               |                       |
| 41                     | 41                       | 4000                     | 30                     | 1180                     | 20                      | 7.61   | 7.20         | 0.17         | 0.03         | 15    | 830                             | 760                            | 500                           | 60                             | 80                                   | 723                   |                                |               |                       |
| 42                     | 42                       | 2000                     | 20                     | 1200                     | 10                      | 27.83  | 1.67         | 0.33         | 0.17         | 30    | 900                             | 850                            | 550                           | 10                             | 60                                   | 610                   |                                |               |                       |
| Product thickness (mm) | Heating temperature (°C) | Rolling reduction ratio  | 950 to 900°C           | 900 to 800°C             | 800 to 700°C            | Residence time in temperature range of 950 to 600°C (min.) |              |              |              |       | Rolling finish temperature (°C) | Cooling start temperature (°C) | Cooling stop temperature (°C) | Average cooling rate *1 (°C/s) | Solute Cr (%)                        | Fracture stress (MPa) |                                |               |                       |
|                        |                          |                          |                        |                          |                         | 700 to 600°C   | Total        |              |              |       |                                 |                                |                               |                                |                                      |                       |                                |               |                       |
|                        |                          |                          |                        |                          |                         | 17.57  | 12.36        | 0.05         | 0.02         | 30    |                                 |                                |                               |                                |                                      |                       |                                |               |                       |
| 43                     | 43                       | 1000                     | 6                      | 1050                     | 30                      | 17.57  | 12.36        | 0.05         | 0.02         | 30    | 800                             | 700                            | 500                           | 70                             | 60                                   | 385                   |                                |               |                       |
| 44                     | 44                       | 2000                     | 12                     | 1050                     | 15                      | **   | **           | **           | **           | **    | 750                             | 700                            | 500                           | 70                             | **                                   | **                    |                                |               |                       |
| 45                     | 45                       | 5000                     | 50                     | 1280                     | 4                       | 627  | 823          | 0.33         | 0.17         | 15    | 850                             | 800                            | 600                           | 10                             | 90                                   | 430                   |                                |               |                       |
| 46                     | 46                       | 2000                     | 12                     | 1100                     | 15                      | **   | **           | **           | **           | **    | 800                             | 750                            | 550                           | 65                             | **                                   | **                    |                                |               |                       |
| 47                     | 47                       | 3000                     | 30                     | 1200                     | 5                       | 10.60  | 923          | 0.11         | 0.06         | 20    | 850                             | 800                            | 550                           | 30                             | 85                                   | 401                   |                                |               |                       |
| 48                     | 48                       | 1000                     | 6                      | 1100                     | 30                      | 14.70  | 1523         | 0.05         | 0.02         | 30    | 750                             | 700                            | 450                           | 70                             | 60                                   | 355                   |                                |               |                       |
| 49                     | 49                       | 2000                     | 12                     | 1050                     | 15                      | 11.60  | 823          | 0.14         | 0.02         | 20    | 800                             | 750                            | 500                           | 70                             | 85                                   | 428                   |                                |               |                       |
| 50                     | 50                       | 1000                     | 6                      | 1200                     | 30                      | 12.60  | 12.36        | 0.03         | 0.01         | 25    | 800                             | 700                            | 500                           | 130                            | 65                                   | 408                   |                                |               |                       |
| 51                     | 51                       | 2000                     | 12                     | 1100                     | 15                      | 11.92  | 1225         | 0.78         | 0.06         | 25    | 800                             | 750                            | 550                           | 30                             | 50                                   | 379                   |                                |               |                       |
| 52                     | 52                       | 2000                     | 12                     | 1150                     | 15                      | 10.50  | 9.36         | 0.10         | 0.05         | 20    | 750                             | 700                            | 500                           | 35                             | 70                                   | 395                   |                                |               |                       |

(continued)

| Product thickness (mm)  | Heating temperature (°C) | Rolling reduction ratio |    |      |    | Residence time in temperature range of 950 to 600°C (min.) |              |              |              | Rolling finish temperature (°C) | Cooling start temperature (°C) | Cooling stop temperature (°C) | Average cooling rate *1 (°C/s) | Solute Cr (%) | Fracture stress (MPa) |     |                     |
|---|--------------------------|-------------------------|----|------|----|--|--------------|--------------|--------------|---------------------------------|--------------------------------|-------------------------------|--------------------------------|---------------|-----------------------|-----|---------------------|
|   |                          |                         |    |      |    | 950 to 900°C   | 900 to 800°C | 800 to 700°C | 700 to 600°C |                                 |                                |                               |                                |               |                       |     | Total               |
| 53  | 53                       | 4000                    | 30 | 1180 | 20 | 7.08   | 725          | 0.63         | 0.04         | 15                              | 830                            | 760                           | 500                            | 40            | 80                    | 555 | Comparative Example |
| 54  | 54                       | 4000                    | 20 | 1200 | 10 | 10.35  | 8.32         | 1.25         | 0.08         | 20                              | 800                            | 750                           | 500                            | 20            | 60                    | 396 |                     |
| 55  | 55                       | 4000                    | 20 | 1150 | 10 | 6.77   | 6.45         | 1.67         | 0.11         | 15                              | 780                            | 730                           | 500                            | 15            | 60                    | 389 |                     |
| 56  | 56                       | 4000                    | 20 | 1130 | 10 | 9.11   | 9.56         | 1.25         | 0.08         | 20                              | 820                            | 770                           | 500                            | 20            | 60                    | 391 |                     |
| 57  | 57                       | 4000                    | 20 | 1180 | 10 | 6.95   | 6.27         | 1.67         | 0.11         | 15                              | 800                            | 750                           | 500                            | 15            | 60                    | 397 |                     |
| 58  | 9                        | 4000                    | 30 | 975  | 6  | 5.63   | 4.23         | 0.10         | 0.05         | 10                              | 850                            | 800                           | 600                            | 35            | 45                    | 353 |                     |
| 59  | 9                        | 2000                    | 12 | 1200 | 15 | 5.23   | 8.36         | 7.48         | 8.93         | 30                              | 600                            | 500                           | 400                            | -             | 50                    | 344 |                     |
| 60  | 9                        | 2000                    | 12 | 1200 | 15 | 15.60  | 14.23        | 0.11         | 0.06         | 30                              | 850                            | 600                           | 450                            | 30            | 50                    | 325 |                     |
| 61  | 9                        | 2000                    | 6  | 1200 | 30 | 23.11  | 23.56        | 2.22         | 1.11         | 50                              | 800                            | Natural cooling               | Natural cooling                | 2             | 40                    | 335 |                     |
| 62  | 9                        | 5000                    | 50 | 1200 | 3  | 22.08  | 22.59        | 0.22         | 0.11         | 45                              | 850                            | 800                           | 600                            | 15            | 45                    | 342 |                     |
| 63  | 9                        | 5500                    | 30 | 1200 | 7  | 21.27  | 18.56        | 0.11         | 0.06         | 40                              | 850                            | 800                           | 600                            | 30            | 45                    | 372 |                     |
| 64  | 9                        | 5000                    | 6  | 1150 | 35 | 15.21  | 18.01        | 1.67         | 0.11         | 35                              | 850                            | 770                           | 580                            | 15            | 55                    | 356 |                     |
| 65  | 9                        | 2000                    | 20 | 1200 | 10 | 33.00  | 1.67         | 0.33         | 0.17         | 35                              | 900                            | 850                           | 550                            | 10            | 55                    | 505 |                     |
| Underlines indicate outside range according to present disclosure.            |                          |                         |    |      |    |  |              |              |              |                                 |                                |                               |                                |               |                       |     |                     |
| *1) Average cooling rate from 700 to 600°C.                                   |                          |                         |    |      |    |  |              |              |              |                                 |                                |                               |                                |               |                       |     |                     |
| ** Measurement was omitted because austenite microstructure was not obtained. |                          |                         |    |      |    |  |              |              |              |                                 |                                |                               |                                |               |                       |     |                     |

**[0050]** Each steel plate (samples No. 1 to No. 42) according to the present disclosure had corrosion resistance satisfying a fracture stress of 600 MPa or more in the SSRT test. Each Comparative Example (samples No. 43 to No. 65) outside the range according to the present disclosure failed to satisfy the foregoing target performance in stress corrosion cracking resistance.

## Claims

### 1. A steel plate comprising:

a chemical composition containing, in mass%,  
 C: 0.20 % or more and 0.70 % or less,  
 Si: 0.05 % or more and 1.00 % or less,  
 Mn: 15.0 % or more and 35.0 % or less,  
 P: 0.030 % or less,  
 S: 0.0200 % or less,  
 Al: 0.010 % or more and 0.100 % or less,  
 Cr: 0.5 % or more and 8.0 % or less,  
 N: 0.0010 % or more and 0.0300 % or less, and  
 B: 0.0003 % or more and 0.0100 % or less,  
 with a balance consisting of Fe and inevitable impurities,  
 wherein 60 % or more of the Cr is solute Cr.

### 2. The steel plate according to claim 1, wherein the chemical composition further contains, in mass%, one or more selected from

Nb: 0.003 % or more and 0.030 % or less,  
 V: 0.01 % or more and 0.10 % or less, and  
 Ti: 0.003 % or more and 0.040 % or less.

### 3. The steel plate according to claim 1 or 2, wherein the chemical composition further contains, in mass%, one or more selected from

Cu: 0.01 % or more and 0.50 % or less,  
 Ni: 0.01 % or more and 0.50 % or less,  
 Sn: 0.01 % or more and 0.30 % or less,  
 Sb: 0.01 % or more and 0.30 % or less,  
 Mo: 0.01 % or more and 2.0 % or less, and  
 W: 0.01 % or more and 2.0 % or less.

### 4. The steel plate according to any one of claims 1 to 3, wherein the chemical composition further contains, in mass%, one or more selected from

Ca: 0.0005 % or more and 0.0050 % or less,  
 Mg: 0.0005 % or more and 0.0100 % or less, and  
 REM: 0.0010 % or more and 0.0200 % or less.

### 5. A method of producing a steel plate, the method comprising:

heating a steel raw material having the chemical composition according to any one of claims 1 to 4 to 1000 °C or more and 1300 °C or less;  
 thereafter subjecting the steel raw material to hot rolling at a rolling finish temperature of 750 °C or more with a residence time of the steel raw material in a temperature range of 950 °C or less and 600 °C or more being 30 minutes or less; and  
 thereafter cooling at an average cooling rate of 3 °C/s or more in a temperature range of 700 °C or less and 600 °C or more.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/030769

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C38/00 (2006.01) i, C21D8/02 (2006.01) i, C22C38/58 (2006.01) i

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C22C38/00, C21D8/02, C22C38/58

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2019

Registered utility model specifications of Japan 1996-2019

Published registered utility model applications of Japan 1994-2019

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|-----------|---|-----------------------|
| X<br>A    | WO 2018/104984 A1 (JFE STEEL CORPORATION) 14 June 2018, claims 1, 4, paragraphs [0049], [0054], [0056]-[0060], table 1 (steel no. 1-11, 20-21), table 2 (steel no. 1-11, 20-21) & EP 3553195 A1, claims 1, 4, paragraphs [0051], [0056], [0059]-[0063], table 1-1 (steel no. 1-11, 20-21), table 2-1 (steel no. 1-11, 20-21) & CN 110050082 A & TW 201825694 A & KR 10-2019-0077470 A | 3-5<br>1-2            |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search  
17 October 2019 (17.10.2019)Date of mailing of the international search report  
05 November 2019 (05.11.2019)Name and mailing address of the ISA/  
Japan Patent Office  
3-4-3, Kasumigaseki, Chiyoda-ku,  
Tokyo 100-8915, Japan

Authorized officer

Telephone No.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/030769

| C (Continuation). | DOCUMENTS CONSIDERED TO BE RELEVANT   |                       |
|-------------------|---|-----------------------|
| Category*         | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
| X<br>A            | JP 2015-508452 A (POSCO) 19 March 2015, claims 1, 5, 6, paragraphs [0038]-[0042], table 1-1 (inventive examples A1, A3, A4), table 2-1 (inventive examples A1, A3, A4) & EP 2799571 A1, claims 1, 5, 6, paragraphs [0038]-[0042], table 1 (inventive examples A1, A3, A4), table 2 (inventive examples A1, A3, A4) & US 2015/0020928 A1 & CN 104220617 A & KR 10-2013-0075565 A & WO 2013/100614 A1 | 3, 5<br>1-2, 4        |
| X<br>A            | JP 2017-507249 A (POSCO) 16 March 2017, claims 1, 3, paragraphs [0039]-[0045], table 1 (inventive example 4), table 2 (inventive example 4) & EP 3088555 A1, claims 1, 3, paragraphs [0039]-[0045], table 1 (inventive example 4), table 2 (inventive example 4) & US 2016/0319407 A1 & CN 105849302 A & KR 10-2015-0075315 A & WO 2015/099363 A1   | 3, 5<br>1-2, 4        |
| X<br>A            | JP 2017-155300 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 07 September 2017, claims 1, 3, paragraphs [0032], [0039]-[0045], table 1 (steel no. A2, A12, A16-A18, A26, B14), table 2 (steel no. A2, A12, A16-A18, A26, B14), fig. 7 (Family: none)  | 3-5<br>1-2            |
| X<br>A            | JP 2016-196703 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 24 November 2016, claim 1, paragraphs [0038]-[0042], table 1 (steel no. 17, 53), table 2 (steel no. 17, 53) (Family: none)   | 4-5<br>1-3            |
| P, A              | WO 2019/059095 A1 (JFE STEEL CORPORATION) 28 March 2019, entire text (Family: none)   | 1-5                   |

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- JP 2015508452 A [0005] [0008]
- JP 2016084529 A [0006] [0008]
- JP 2016196703 A [0007] [0008]