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

(72) Inventors:
• **KITSUYA Shigeki**
Tokyo 100-0011 (JP)
• **IKEDA Hiroshi**
Tokyo 100-0011 (JP)
• **UEDA Keiji**
Tokyo 100-0011 (JP)

(74) Representative: **Grünecker Patent- und
Rechtsanwälte
PartG mbB
Leopoldstraße 4
80802 München (DE)**

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

(57) Provided is high-Mn steel excellent in excellent in corrosion resistance, in particular corrosion resistance in a salinity corrosive environment, the high-Mn steel including 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 the balance being Fe and inevitable impurities, in which at least 60 % of the contained Cr is solute Cr.

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Description

TECHNICAL FIELD

[0001] This disclosure relates to a steel plate that is suitable for structural steel used in an extremely low-temperature environment such as a storage tank of liquefied gas, in particular, a steel plate excellent in corrosion resistance in a salinity corrosive environment, and a method for manufacturing the same.

BACKGROUND

[0002] In using a hot-rolled steel plate in a structure for a storage tank of liquefied gas, the operating environment is at extremely low temperatures. Therefore, the hot-rolled steel plate needs to have not only high strength but also toughness at extremely low temperatures. For example, for a hot-rolled steel plate used for a storage tank of liquefied natural gas, excellent toughness needs to be guaranteed at the boiling point of liquefied natural gas, that is, -164 °C or lower. When a steel material has poor low-temperature toughness, the safety as a structure for an extremely low-temperature storage tank may not be maintained. Thus, there is a growing demand for steel materials with improved low-temperature toughness that are applied to such a structure. In view of the demand, austenitic stainless steel which has an austenite microstructure exhibiting no brittleness at extremely low temperatures, 9 % Ni steel, or five thousand series aluminum alloys have been conventionally used. However, the alloy cost and manufacturing cost of those metal materials are high, and thus there is a demand for steel plates which are inexpensive and excellent in extremely low-temperature toughness. As new steel plates replacing conventional steel for extremely low temperatures, high-Mn steel added with a large amount of Mn which is a relatively inexpensive austenite-stabilizing element to form an austenite microstructure is considered to be used as a structural steel plate used in an extremely low-temperature environment.

[0003] However, when a steel plate having an austenite microstructure is placed in a corrosive environment, austenite crystal grain boundaries are eroded by corrosion and when a tensile stress is added, stress corrosion cracking easily occurs, which is a problem of high-Mn steel. In manufacturing a structure for a storage tank of liquefied gas and the like, a steel substrate of a steel plate may be exposed, and when the exposed steel material surface contacts with water vapor containing corrosive substances including salinity, water, and oil, the steel material would be corroded. In the corrosion reaction on a steel plate surface, oxide (rust) is formed from iron by an anodic reaction. Meanwhile, hydrogen is generated by a cathodic reaction of water to enter into the steel, causing hydrogen embrittlement. When residual stress generated by bending or welding during manufacturing or load stress in an operating environment is exerted thereon, stress corrosion cracking may be caused, leading to rupture of a structure. Conventional high-Mn steel may be inferior in terms of corrosion resistance to not only austenitic stainless steel but also 9 % Ni steel and normal low-alloy steel. Therefore, from the viewpoint of safety, it is important that the steel material to be used has not only high strength and toughness at extremely low temperatures but also excellent corrosion resistance.

[0004] For example, JP 2015-508452 A (PTL 1) describes a steel material having improved machinability by cutting and Charpy impact properties at -196 °C of a weld heat-affected zone (HAZ) through addition of Mn in an amount of 15 % to 35 %, Cu in an amount of 5 % or less, and C and Cr in a suitable amount.

[0005] JP 2016-84529 A (PTL 2) describes a high-Mn steel material having improved low temperature toughness through addition of C: 0.25 % to 0.75 %; Si: 0.05 % to 1.0 %; Mn: more than 20 % to 35 % or less; Ni: 0.1 % or more and less than 7.0 %; and Cr: 0.1 % or more and less than 8.0 %.

[0006] JP 2016-196703 A (PTL 3) describes a high-Mn steel material having a base metal and a welded portion with improved extremely low-temperature toughness through addition of C in an amount of 0.001 % to 0.80 % and Mn in an amount of 15 % to 35 %, and addition of elements such as Cr, Ti, Si, Al, Mg, Ca, and REM.

CITATION LIST

Patent Literature

[0007]

PTL 1: JP 2015-508452 A

PTL 2: JP 2016-84529 A

PTL3: JP 2016-196703 A

SUMMARY

(Technical Problem)

[0008] However, there is room for consideration in the steel materials described in PTL 1, PTL 2, and PTL 3 from the viewpoint of manufacturing cost for obtaining strength and low-temperature toughness and corrosion resistance when the austenite steel material is placed in a salinity corrosive environment.

[0009] It could thus be helpful to provide high-Mn steel excellent in corrosion resistance, in particular corrosion resistance in a salinity corrosive environment.

(Solution to Problem)

[0010] To achieve the aforementioned object, the inventors conducted extensive study on high-Mn steel as to various factors determining the chemical composition and manufacturing conditions to discover the following.

[0011] a. In adding Cr to high-Mn steel, the addition amount of Cr and the amount of dissolved Cr is properly controlled to thereby make it possible to delay an initial corrosion reaction on a steel plate surface in a salinity corrosive environment. In this way, the hydrogen amount entering into steel can be reduced to suppress the stress corrosion cracking of austenite steel.

[0012] b. Further, a measure of improving crystal grain boundary strength is valid for effectively suppressing rupture of austenite originating from crystal grain boundaries. In particular, P is an element which is easily segregated, as with Mn, during a solidification process of a slab and lowers the crystal grain boundary strength of a portion crossing such a segregation portion. Therefore, impurity elements such as P need to be reduced.

[0013] This disclosure is based on the above discoveries and further investigation conducted by the inventors. The primary features of this disclosure are as follows.

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, and

N: 0.0010 % or more and 0.0300 % or less, with the balance being Fe and inevitable impurities, wherein at least 60 % of the contained Cr is solute Cr.

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

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 1. or 2., wherein the chemical composition further contains, in mass %, at least one selected from the group consisting of

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 1., 2., or 3., wherein the chemical composition further contains, in mass %, at least one selected from the group consisting of

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 for manufacturing a steel plate, comprising: heating a steel raw material having the chemical composition according to any of 1. to 4. to 1000 °C or higher and 1300 °C or lower; subsequently hot rolling the steel raw material with a rolling reduction ratio of 3 or more and 30 or less, a finish rolling temperature of 750 °C or higher, and a time

for which a material to be rolled resides within a temperature range of 600 °C to 950 °C of 30 minutes or less to obtain a hot-rolled steel plate; and then, cooling the hot-rolled steel plate at an average cooling rate of 3 °C/s or more within a temperature range of 600 °C to 700 °C.

[0014] In this disclosure, "excellent in corrosion resistance" means a fracture stress of 400 MPa or more when a test in accordance with the Slow Strain Rate Test Method based on NACE Standard TM0111-2011 is performed by immersing in artificial seawater (chloride ion concentration of 18000 ppm) at 23 °C and performing a constant-rate tensile test at a strain rate of 4×10^{-7} inch/s.

(Advantageous Effect)

[0015] According to this disclosure, it is possible to provide a steel plate excellent in corrosion resistance, in particular, corrosion resistance in a salinity corrosive environment. Therefore, when our steel plate is used for a steel structure used in an extremely low-temperature environment such as a tank for a storage tank of liquefied gas, the safety and the service life of the steel structure is significantly improved, thus producing significantly advantageous effects in industrial terms. Further, our steel plate is inexpensive compared with conventional materials, and thus excellent in economic efficiency.

DETAILED DESCRIPTION

[0016] Our steel plate will be described in detail hereinafter. Note that this disclosure is not limited to the following examples.

[Chemical composition]

[0017] The chemical composition of our steel plate and the reasons for the limitations thereof are described first. In this disclosure, to ensure excellent corrosion resistance, the chemical composition of the steel plate is defined as follows. In the description of the chemical composition, "%" denotes "mass%" unless otherwise noted.

C: 0.20 % or more and 0.70 % or less

[0018] C, which is effective for increasing strength and an inexpensive austenite-stabilizing element, is an important element to obtain austenite. To obtain this effect, the C content needs to be 0.20 % or more. On the other hand, a C content beyond 0.70 % promotes excessive precipitation of Cr carbides and Nb, V, and Ti based carbides, and thus lowers low-temperature toughness and becomes a corrosion origin. Therefore, the C content is set to be 0.20 % or more and 0.70 % or less, and preferably 0.25 % or more and 0.60 % or less.

Si: 0.05 % or more and 1.00 % or less

[0019] Si acts as a deoxidizer, is necessary for steelmaking, and is effective at increasing the strength of a steel plate by solid solution strengthening when dissolved in steel. To obtain such an effect, the Si content needs to be 0.05 % or more. On the other hand, a Si content beyond 1.00 % may deteriorate weldability and surface characteristics, lowering stress corrosion cracking resistance. Therefore, the Si content is set to 0.05 % or more and 1.00 % or less, and preferably 0.07 % or more and 0.50 % or less.

Mn: 15.0 % or more and 35.0 % or less

[0020] Mn is a relatively inexpensive austenite-stabilizing element. In this disclosure, Mn is an important element for achieving both high strength and extremely low-temperature toughness. To obtain those effects, the Mn content needs to be 15.0 % or more. On the other hand, the Mn content beyond 35.0 % causes saturation of the effect of improving the extremely low-temperature toughness, increasing alloy costs. Further, such a high Mn content deteriorates weldability and cuttability, and further promotes segregation as well as the occurrence of stress corrosion cracking. Therefore, the Mn content is set to 15.0 % or more and 35.0 % or less, and preferably 18.0 % or more and 28.0 % or less.

P: 0.030 % or less

[0021] When the P content is beyond 0.030 %, P segregates to grain boundaries to lower grain boundary strength and becomes an origin of stress corrosion cracking. Therefore, the upper limit of the P content is 0.030 %, and desirably,

the P content is kept as small as possible. Properties are improved as the P content is lower, and thus, the P content is preferably set to 0.024 % or less, and more preferably 0.020 % or less. On the other hand, reducing the P content to less than 0.001 % involves high steelmaking costs and impairs economic efficiency. Thus, the content of 0.001 % or more is allowable.

S: 0.0200 % or less

[0022] S deteriorates the low-temperature toughness and ductility of the base metal. Therefore, the upper limit of the S content is 0.0200 %, and desirably, the S content is kept as small as possible. Therefore, the S content is set to 0.0200 % or less, and preferably 0.0180 % or less. On the other hand, reducing the S content to less than 0.0001 % involves high steelmaking costs and impairs economic efficiency. Thus, the content of 0.0001 % or more is allowable.

Al: 0.010 % or more and 0.100 % or less

[0023] Al acts as a deoxidizer and is used most commonly in molten steel deoxidizing processes to obtain a steel plate. Al also has an effect of fixing solute N in steel to form AlN, thus suppressing coarsening of crystal grains. Additionally, Al has an effect of suppressing deterioration of toughness caused by decrease in solute N. To obtain such an effect, the Al content needs to be 0.010 % or more. On the other hand, a Al content beyond 0.100 % may form coarse nitrides which would become an origin of corrosion and fracture, thus lowering stress corrosion cracking resistance. Further, Al diffuses to a weld metal portion during welding to deteriorate toughness of the weld metal. Thus, the Al content is set to 0.100 % or less, and preferably 0.020 % or more and 0.070 % or less.

Cr of 0.5 % or more and 8.0 % or less and at least 60 % of the contained Cr being solute Cr

[0024] Cr is an important element because it is contained in a suitable amount to thereby produce an effect of delaying an initial corrosion reaction on a steel plate surface in a salinity corrosive environment to decrease the amount of hydrogen entering a steel plate and improve stress corrosion cracking resistance. When the Cr content is increased, corrosion resistance can be improved. On the other hand, Cr inevitably precipitates in the form of, for example, a nitride, a carbide, or a carbonitride during rolling and those precipitates may become an origin of corrosion and fracture to deteriorate stress corrosion cracking resistance. Therefore, the Cr content is set to 0.5 % or more and 8.0 % or less.

[0025] Examining in detail the Cr effect which delays an initial corrosion reaction on a steel plate surface in a salinity corrosive environment, it has been found that the amount of solute Cr is important to ensure this effect, and when Cr exists in a solid solution state in an amount of 0.3 % or more, the effect is surely exhibited. On the other hand, it is necessary to devise manufacturing conditions to make Cr solid solution state and since the lower limit of Cr solid dissolution ratio which can be stably ensured by a minor change of manufacturing conditions is 60 %, the Cr content needs to be at least 0.5 % to obtain solute Cr in an amount of 0.3 % or more. The amount of solute Cr is preferably 1.0 % or more and 6.0 % or less, and more preferably 1.2 % or more and 5.5 % or less. The solid solution state refers to a state in which solute atoms exist as atoms without forming precipitates.

N: 0.0010 % or more and 0.0300 % or less

[0026] N is an austenite-stabilizing element and an element which is effective for improving extremely low-temperature toughness. Further, N has an effect of bonding with Nb, V, and Ti to finely precipitate as nitrides or carbonitrides and serving as a diffusible hydrogen trapping site to suppress stress corrosion cracking. To obtain such an effect, the N content needs to be 0.0010 % or more. On the other hand, a N content beyond 0.0300 % promotes the formation of excessive nitrides or carbonitrides to reduce the solute element amount, lowering not only corrosion resistance but also toughness. Therefore, the N content is set to 0.0010 % or more and 0.0300 % or less, and preferably 0.0020 % or more and 0.0150 % or less.

[0027] In this disclosure, to further improve corrosion resistance, in addition to the above essential elements, the following elements can be contained as necessary:

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

Nb: 0.003 % or more and 0.030 % or less

[0028] Nb precipitates as carbonitrides and the formed carbonitrides serve as a diffusible hydrogen trapping site. Thus, Nb is an element which has an effect of suppressing stress corrosion cracking. To obtain such an effect, Nb is preferably contained in an amount of 0.003 % or more. On the other hand, when the Nb content is more than 0.030 %, coarse

carbonitrides may precipitate to become an origin of fracture. Further, the precipitates may be coarsened to deteriorate base metal toughness. Therefore, when Nb is contained, the Nb content is preferably set to 0.003 % or more and 0.030 % or less, 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 precipitates as carbonitrides and the formed carbonitrides serve as a diffusible hydrogen trapping site. Thus, V is an element which has an effect of suppressing stress corrosion cracking. To obtain such an effect, V is preferably contained in an amount of 0.01 % or more. On the other hand, when the V content is more than 0.10 %, coarse carbonitrides may precipitate to become an origin of fracture. Further, the precipitates may be coarsened to deteriorate base metal toughness. Therefore, when V is contained, the V content is preferably set to 0.01 % or more and 0.10 % or less, 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 precipitates as nitrides or carbonitrides and the formed nitrides or carbonitrides serve as a diffusible hydrogen trapping site. Thus, Ti is an element which has an effect of suppressing stress corrosion cracking. To obtain such an effect, Ti is preferably contained in an amount of 0.003 % or more. On the other hand, when the Ti content is more than 0.0040 %, the precipitates may be coarsened to deteriorate base metal toughness. Further, coarse carbonitrides may precipitate to become an origin of fracture. When Ti is contained, the Ti content is preferably set to 0.003 % or more and 0.040 % or less, more preferably 0.005 % or more and 0.035 % or less, and further preferably 0.007 % or more and 0.032 % or less.

[0031] In this disclosure, to further improve corrosion resistance, the chemical composition may optionally contain at least one selected from the group of 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.

[0032] Cu, Ni, Sn, Sb, Mo, and W are elements which are added with Cr to thereby improve corrosion resistance of high-Mn steel in a salinity corrosive environment. Cu, Sn, and Sb have an effect of increasing hydrogen overvoltage in a steel material to thereby suppress a hydrogen evolution reaction corresponding to the cathodic reaction. Ni forms a precipitation layer on a steel material surface and physically suppresses permeation of corrosive anions such as Cl⁻ into a steel substrate. Further, Cu, Ni, Sn, Sb, Mo, and W are liberated as a metal ion from a steel material surface during corrosion and densify corrosion products, thereby suppressing permeation of corrosive anions into a steel interface (interface between a rust layer and a steel substrate). Mo and W are liberated as MO₄²⁻ and WO₄²⁻, respectively, and adsorbed in the corrosive products or to the steel plate surface, thereby imparting cation selective permeability and electrically suppressing permeation of corrosive anions into the steel substrate.

[0033] The above effects become apparent when those elements coexist with Cr in high-Mn steel and are exerted when those elements are contained in an amount not lower than the respective lower limits listed above. However, large contents of those elements deteriorate weldability and toughness and are disadvantageous in terms of costs.

[0034] Therefore, preferred contents are: a Cu content of 0.01 % or more and 0.50 % or less; a Ni content of 0.01 % or more and 0.50 % or less; a Sn content of 0.01 % or more and 0.30 % or less; a Sb content of 0.01 % or more and 0.30 % or less; a Mo content of 0.01 % or more and 2.0 % or less; and a W content of 0.01 % or more and 2.0 % or less.

[0035] More preferred contents are: a Cu content of 0.02 % or more and 0.40 % or less; a Ni content of 0.02 % or more and 0.40 % or less; a Sn content of 0.02 % or more and 0.25 % or less; a Sb content of 0.02 % or more and 0.25 % or less; a Mo content of 0.02 % or more and 1.9 % or less; and a W content of 0.02 % or more and 1.9 % or less.

[0036] Similarly, in this disclosure, to further improve corrosion resistance, the chemical composition may optionally contain at least one selected from the group of 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.

[0037] Ca, Mg, and REM are elements useful for morphological control of inclusions and can be contained as necessary. As used herein, the morphological control of inclusions means granulating elongated sulfide-based inclusions. The morphological control of inclusions improves ductility, toughness, and sulfide stress corrosion cracking resistance. To obtain such effects, Ca and Mg are preferably contained in an amount of 0.0005 % or more and REM is preferably contained in an amount of 0.0010 % or more. On the other hand, when these elements are contained in a large amount, not only the amount of nonmetallic inclusions may be increased, ending up deteriorating ductility, toughness, and sulfide stress corrosion cracking resistance, but also an economic disadvantage may be entailed.

[0038] Therefore, when Ca is contained, the Ca content is preferably set to 0.0005 % or more and 0.0050 % or less, when Mg is contained, the Mg content is preferably set to 0.0005 % or more and 0.0100 % or less, and when REM is contained, the REM content is preferably set to 0.0010 % or more and 0.0200 % or less. A Ca content of 0.0010 % or

more and 0.0040 % or less, a Mg content of 0.0010 % or more and 0.0040 % or less, and a REM content is 0.0020 % or more and 0.0150 % or less are more preferable.

[0039] The following describes manufacturing conditions in this disclosure. In the following description, temperatures (°C) refer to the temperature of the mid-thickness part of a steel plate.

[Reheating temperature of a steel raw material: 1000 °C or higher and 1300 °C or lower]

[0040] Heating a steel raw material to 1000 °C or higher is for dissolving carbonitrides in the microstructure to make the crystal grain size and the like uniform. Specifically, when the heating temperature is lower than 1000 °C, carbonitrides are not sufficiently dissolved and thus desired properties cannot be obtained. Further, heating at a temperature higher than 1300 °C deteriorates material properties due to coarsening of crystal grain size and needs excessive energy, lowering productivity. Thus, the upper limit of the heating temperature is set to 1300 °C, preferably 1050 °C or higher and 1250 °C or lower, and more preferably 1070 °C or higher and 1250 °C or lower.

[Rolling reduction ratio: 3 or more and 30 or less]

[0041] Since in hot rolling with a rolling reduction ratio of less than 3, an effect of promoting recrystallization and homogenizing a grain size cannot be obtained, coarse austenite grains remain and a part having the coarse austenite grains is preferentially oxidized, thereby deteriorating corrosion resistance. Therefore, the rolling reduction ratio in hot rolling is limited to 3 or more. On the other hand, the upper limit of the rolling reduction ratio needs to be 30 for the reasons given below. As used herein, the rolling reduction ratio is defined by a plate thickness of a material to be rolled / a plate thickness of a steel plate after hot rolling.

[Finish rolling temperature: 750 °C or higher]

[0042] When the finish rolling temperature is lower than 750 °C, the amount of carbide precipitates during rolling is significantly increased, and even when the time for which a material to be rolled resides within a temperature range of 600 °C to 950 °C is 30 minutes or less, a sufficient amount of solute Cr may not be obtained, lowering corrosion resistance. Further, when rolling is performed at a temperature of lower than 750 °C, deformation resistance is increased to apply an excessive load to a manufacturing apparatus. Thus, the finish rolling temperature is set to 750 °C or higher. From the viewpoint of suppressing significant coarsening of crystal grain size, the upper limit of the finish rolling temperature is preferably 1050 °C or lower.

[Time for which a material to be rolled resides within a temperature range of 600 °C to 950 °C: 30 minutes or less]

[0043] In hot rolling, if the time for which a material to be rolled resides within a temperature range of 600 °C to 950 °C (residence time) is more than 30 minutes, a large amount of carbonitrides and carbides precipitate during rolling and the necessary amount of solute Cr cannot be obtained, lowering corrosion resistance and extremely-low temperature toughness. Therefore, the time for which a material to be rolled resides within a temperature range of 600 °C to 950 °C is limited to 30 minutes or less. The time for which a material to be rolled resides within a temperature range of 600 °C to 950 °C is preferable as short as possible, and thus, no lower limit is placed thereon.

[0044] To set the time for which a material to be rolled resides within a temperature range of 600 °C to 950 °C to 30 minutes or less, the length of the material to be rolled is made to be 5000 mm or less and the rolling reduction ratio of the material to be rolled is limited to 30 or less as described above. This is because when the length of the material to be rolled is more than 5000 mm or the rolling reduction ratio is more than 30, the rolling time becomes long and as a result, the time for which a material to be rolled resides within a temperature range of 600 °C to 950 °C exceeds 30 minutes.

[Average cooling rate within a temperature range of 600 °C to 700 °C: 3 °C/s or more]

[0045] Since when the average cooling rate within a temperature range of 600 °C to 700 °C is less than 3 °C/s, a large amount of precipitates such as Cr carbides are formed, the average cooling rate is limited to 3 °C/s or more. The average cooling rate is preferable as fast as possible, and thus, no upper limit is placed thereon.

EXAMPLES

[0046] Steels of Nos. 1 to 28 listed in Table 1 were produced by steelmaking to obtain slabs, subsequently the slabs were formed into steel plates of sample Nos. 1 to 34 having a plate thickness of 6 mm to 50 mm under the manufacturing conditions listed in Table 2, and the steel plates were subjected to the following test.

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[0047] The corrosion resistance test was performed in accordance with the Slow Strain Rate Test Method based on NACE Standard TM0111-2011 (hereinafter, referred to as "SSRT test"). Test pieces having a shape of notched Type A round bar were used. The test pieces were immersed in artificial seawater (having chloride ion concentration of 18000 ppm) at 23 °C and subjected to a constant-rate tensile test at a strain rate of 4×10^{-7} inch/s. In this disclosure, a test piece having a fracture stress of 400 MPa or more was considered as having excellent stress corrosion cracking resistance. The results thus obtained are listed in Table 2.

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Table 1

Material No.		Chemical Composition (mass%)																	Remarks		
		C	Si	Mn	P	S	Cr	Al	N	Ni	Ti	Cu	Mo	V	W	Nb	Sn	Sb	Mg	Ca	REM
	1	0.47	0.39	27.3	0.015	0.0036	3.2	0.033	0.0026	-	-	-	-	-	-	-	-	-	-	-	-
	2	0.45	0.35	26.5	0.010	0.0020	7.0	0.035	0.0028	-	-	-	-	-	-	-	-	-	-	-	-
	3	0.43	0.31	24.5	0.008	0.0028	0.5	0.038	0.0034	-	-	-	-	-	-	-	-	-	-	-	-
	4	0.54	0.50	22.8	0.007	0.0012	5.3	0.028	0.0031	-	-	-	-	-	-	-	-	-	-	-	-
	5	0.48	0.45	25.4	0.011	0.0020	5.1	0.036	0.0125	-	0.008	-	-	-	-	-	-	-	-	-	-
	6	0.37	0.39	21.1	0.015	0.0036	7.6	0.031	0.0026	-	-	-	-	-	-	0.012	-	-	-	-	-
	7	0.48	0.52	24.3	0.012	0.0040	4.7	0.037	0.0090	-	-	-	-	-	-	-	-	-	-	-	-
	9	0.48	0.48	24.8	0.012	0.0030	4.9	0.036	0.0105	-	0.008	-	-	0.04	-	-	-	-	-	-	-
	8	0.37	0.39	33.0	0.014	0.0004	4.5	0.036	0.0031	-	-	0.21	-	-	-	-	-	-	-	-	-
	10	0.65	0.28	26.0	0.015	0.0036	5.0	0.033	0.0026	0.22	-	-	-	-	-	-	-	-	-	-	-
	11	0.46	0.39	26.5	0.013	0.0015	2.7	0.028	0.0022	-	-	-	-	-	-	-	0.06	-	-	-	-
	12	0.43	0.85	21.0	0.010	0.0014	4.0	0.031	0.0026	-	-	-	-	-	-	-	-	0.11	-	-	-
	13	0.47	0.38	24.5	0.015	0.0018	4.7	0.032	0.0029	-	-	-	0.01	-	-	-	-	-	-	-	-
	14	0.55	0.08	26.0	0.009	0.0023	5.5	0.033	0.0026	-	-	-	-	-	0.05	-	-	-	-	-	-
	15	0.54	0.15	18.2	0.011	0.0020	5.2	0.018	0.0118	-	-	-	-	-	-	-	-	-	-	0.0021	-
	16	0.48	0.45	24.4	0.008	0.0012	4.7	0.035	0.0048	-	-	-	-	-	-	-	-	-	0.002	-	-
	17	0.26	0.55	26.1	0.022	0.0019	1.9	0.031	0.0031	-	-	-	-	-	-	-	-	-	-	-	0.0015
	18	0.75	0.51	24.3	0.012	0.0018	2.8	0.029	0.0039	-	-	0.05	0.10	-	-	0.009	-	-	-	-	-
	19	0.15	0.65	18.0	0.011	0.0030	7.8	0.022	0.0033	-	-	-	-	-	-	-	-	-	-	-	-
	20	0.50	0.68	40.1	0.014	0.0028	2.1	0.038	0.0055	-	-	-	-	-	-	-	-	-	-	0.0023	-
	21	0.22	0.72	12.0	0.011	0.0001	0.6	0.003	0.0029	-	-	-	-	-	-	-	-	-	-	-	-
	22	0.43	0.51	24.8	0.044	0.0058	5.6	0.019	0.0029	0.41	-	-	-	-	-	0.012	-	-	-	-	-
	23	0.52	1.29	27.5	0.012	0.0040	4.8	0.029	0.0038	-	-	-	-	-	-	-	-	-	-	-	-
	24	0.46	0.63	26.9	0.013	0.0060	3.9	0.132	0.0029	-	-	-	-	-	-	-	-	-	-	-	-
	25	0.52	0.37	27.3	0.011	0.0073	9.2	0.049	0.0031	-	-	-	0.08	-	-	-	-	-	-	-	0.0055
	26	0.45	0.62	22.8	0.012	0.0013	0.3	0.030	0.0023	-	0.009	-	-	-	0.09	-	-	-	-	0.0018	-
	27	0.57	0.32	21.8	0.016	0.0047	4.2	0.022	0.0392	-	-	-	-	-	-	-	0.1	-	-	-	-
	28	0.48	0.39	25.6	0.023	0.0350	6.1	0.018	0.0029	-	-	-	0.13	-	-	-	-	-	0.0019	-	-

Note: Underlines represent out of the scope of this disclosure.

Table 2

Sample No.	Material No.	Material length (mm)	Manufacturing conditions								Base metal properties	Stress corrosion cracking resistance	Remarks
			Product thickness (mm)	Heating temperature (°C)	Rolling reduction ratio	Finish rolling temperature (°C)	Cooling start (°C)	Cooling stop (°C)	Average cooling rate* 1 (°C/s)	Residence time (min)			
1	1	4500	30	1100	5	850	800	500	30	10	85	559	Example
2	2	5000	50	1200	3	900	850	550	15	5	95	529	
3	3	1200	6	1200	30	760	700	550	130	25	75	518	
4	4	4000	30	1150	7	850	800	500	40	15	80	573	
5	5	2000	12	1200	15	850	750	500	75	20	90	580	
6	6	4000	30	1250	6	850	800	600	30	10	75	554	
7	7	3000	12	1150	10	850	780	550	70	20	85	569	
9	9	1800	12	1200	15	900	750	550	30	30	70	502	
8	8	5000	50	1200	4	900	800	550	15	8	90	581	
10	10	5000	50	1280	3	900	750	550	10	5	75	503	
11	11	4000	30	1150	5	800	750	500	30	8	85	495	
12	12	2000	12	1050	15	750	700	500	70	15	80	481	
13	13	2500	12	1150	10	800	750	600	75	10	85	590	
14	14	1200	6	1250	25	750	700	450	140	30	65	483	
15	15	1500	6	1150	20	750	700	400	140	30	70	521	
16	16	5000	50	1200	4	950	900	550	15	5	90	546	
17	17	2500	12	1150	10	800	750	500	75	15	80	536	
18	18	1000	6	1050	30	800	700	500	70	30	60	335	
19	19	2000	12	1050	15	750	700	500	70	*2	*2	*2	
20	20	5000	50	1280	4	850	800	600	10	15	90	380	

(continued)

Sample No.	Material No.	Material length (mm)	Manufacturing conditions								Base metal properties	Stress corrosion cracking resistance	Remarks
			Product thickness (mm)	Heating temperature (°C)	Rolling reduction ratio	Finish rolling temperature (°C)	Cooling start (°C)	Cooling stop (°C)	Average cooling rate* 1 (°C/s)	Residence time (min)			
21	<u>21</u>	2000	12	1100	15	800	750	550	65	<u>*2</u>	<u>*2</u>	Comparative Example	
22	<u>22</u>	3000	30	1200	5	850	800	550	30	20	85		
23	<u>23</u>	1000	6	1100	30	750	700	450	70	30	60		
24	<u>24</u>	2000	12	1050	15	800	750	500	70	20	85		
25	<u>25</u>	1200	6	1150	30	900	850	550	35	30	60		
26	<u>26</u>	1000	6	1200	30	800	700	500	130	25	65		
27	<u>27</u>	2000	12	1100	15	800	750	550	30	25	50		
28	<u>28</u>	2000	12	1150	15	750	700	500	35	20	70		
29	9	4000	30	<u>975</u>	6	850	800	600	35	10	45		
30	9	2000	12	<u>1200</u>	15	<u>600</u>	500	400	-	30	50		
31	9	2000	6	1200	30	800	naturally cooled	naturally cooled	2	50	40		
32	9	2000	6	1100	40	800	750	500	5	40	40		
33	9	5000	50	1200	3	850	800	600	15	45	45		
34	9	<u>5500</u>	30	1200	7	850	800	600	30	40	45		
Note: Underlines represent out of the scope of this disclosure.													
*1 indicates an average cooling rate within a temperature range of700 °C to 600 °C.													
*2 Measurement was omitted because an austenite microstructure was not obtained.													

[0048] Examples (sample Nos. 1 to 17) according to this disclosure were confirmed to have corrosion resistance satisfying 400 MPa or more for the fracture stress of the SSRT test. In contrast, comparative examples (sample Nos. 18 to 34) outside the scope of this disclosure did not satisfy the above-described target performance in terms of 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, and
N: 0.0010 % or more and 0.0300 % or less, with the balance being Fe and inevitable impurities,
wherein at least 60 % of the contained Cr is solute Cr.
2. The steel plate according to claim 1, wherein the chemical composition further contains, in mass%, at least one selected from the group consisting of
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 %, at least one selected from the group consisting of
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 claim 1, 2, or 3, wherein the chemical composition further contains, in mass %, at least one selected from the group consisting of
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 for manufacturing a steel plate, comprising:
heating a steel raw material having the chemical composition according to any of claims 1 to 4 to 1000 °C or higher and 1300 °C or lower; subsequently hot rolling the steel raw material with a rolling reduction ratio of 3 or more and 30 or less, a finish rolling temperature of 750 °C or higher, and a time for which a material to be rolled resides within a temperature range of 600 °C to 950 °C of 30 minutes or less to obtain a hot-rolled steel plate; and then, cooling the hot-rolled steel plate at an average cooling rate of 3 °C/s or more within a temperature range of 600 °C to 700 °C.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/034011

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C38/00 (2006.01) i, C21D8/02 (2006.01) i, C22C38/38 (2006.01) i,
C22C38/60 (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. C22C1/00-49/14, C21D8/02

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2016-196703 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 24 November 2016, claims, paragraphs [0017], [0039], [0041], steel no. 38-42, 45-48, 51, 54, 56, 59-61, 63 of tables 1-2, steel no. 66-71, 78-80, 82-87 of tables 1-3 (Family: none)	4-5 1-3
A	JP 2017-071817 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 13 April 2017 (Family: none)	1-5



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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

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

"&" document member of the same patent family

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Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2015508452 A [0004] [0007]
- JP 2016084529 A [0005] [0007]
- JP 2016196703 A [0006] [0007]