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(54) HIGH-MN STEEL AND METHOD FOR MANUFACTURING SAME

(57) Provided is high-Mn steel having high strength, and excellent low-temperature toughness and ductility, the high-Mn steel having a chemical composition containing, in mass%, C:0.10-0.70%, Si:0.10-0.90%, Mn:20-30%, P:0.030% or less, S:0.0070% or less, Al:0.01—0.07%, Cr:1.8—7.0%, Ni:0.01% or more and less than 1.0%, Ca:0.0005-0.010% or less, N:0.0050-0.0500%, O:0.0050% or less, Ti:0.0050% or less and Nb:0.0050% or less, satisfying $Ca/S \geq 1.0$, with the balance being Fe and inevitable impurities; a microstructure containing austenite as a matrix; a yield stress of 400MPa or more; and an average Charpy impact absorbed energy at -196°C of 100J or more for a full-sized test piece and 20J or more for a half-sized test piece.

EP 3 926 057 A1

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Description

TECHNICAL FIELD

[0001] This disclosure relates to high-Mn steel that is suitable for a structure used in a cryogenic environment such as a storage tank of liquefied gas and a manufacturing method therefor.

BACKGROUND

[0002] A structure for a storage tank of liquefied gas is used in a cryogenic environment. Therefore, a steel plate used for this type of structure needs to have high strength and excellent toughness at extremely low temperature. For example, when a hot-rolled steel plate is used for a storage tank of liquefied natural gas, excellent toughness needs to be guaranteed at an extremely low temperature equal to or below the boiling point of the liquefied natural gas, that is, -164 °C or lower. When a steel material has poor low-temperature toughness, the safety as a structure for a cryogenic 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.

[0003] In view of the demand, austenitic stainless steel which has austenite as a primary microstructure of a steel plate, the austenite showing no brittleness at extremely low temperature, 9 % Ni steel, or 5000-series aluminum alloy have been conventionally used. However, the alloy cost and manufacturing cost of these steels and alloy are high, and thus there is a demand for steel materials which are inexpensive and excellent in low-temperature toughness.

[0004] As new steel materials replacing conventional steel for extremely low temperature, JP 2016-084529 A (PTL 1) and JP 2016-196703 A (PTL 2) propose using, as structural steel used in a cryogenic environment, high-Mn steel added with a large amount of Mn which is relatively inexpensive and an austenite-stabilizing element.

[0005] That is, PTL 1 proposes controlling carbide coverage on austenite crystal grain boundaries. Further, PTL 2 proposes controlling austenite crystal grain size by using carbide coated materials and adding Mg, Ca, and REM.

CITATION LIST

Patent Literature

[0006]

PTL 1: JP 2016-84529 A
PTL 2: JP 2016-196703 A

SUMMARY

(Technical Problem)

[0007] Austenite steel used as steel for extremely low temperature described in PTLs 1 and 2, which is highly strain-hardened from the early stage of deformation until maximum stress (tensile strength) is applied upon tensile deformation, has excellent plastic deformability, and thus exhibits excellent ductility until the middle stage of deformation. On the other hand, the deformation performance in the later stage of deformation after the stress measured in a tensile test reaches the maximum (tensile strength) is also an important characteristic for a structural member. This is because the deformation performance in the later stage of deformation is the performance in the final stage leading to the eventual fracture. From this perspective, ductility in the later stage of deformation, particularly, a sufficient reduction of area should be ensured. From the viewpoint of ensuring ductility of high-strength steel, a desirable reduction of area is 50 % or more.

[0008] It could thus be helpful to provide high-Mn steel which has both high strength and excellent low-temperature toughness and exhibits excellent ductility, and a manufacturing method therefor. As used herein, the terms of "high strength" refers to having a yield strength of 400 MPa or more and a tensile strength of 800 MPa or more at room temperature. Further, the terms of "excellent low-temperature toughness" means that when a Charpy impact test in conformity with JIS Z2242 (1998) is performed at —196 °C on a full-sized (10 mm × 10 mm × 55 mm) test piece which is a steel plate having a plate thickness of 10 mm or more, the base metal has a Charpy impact absorbed energy of 100 J or more on average (when using a half-sized test piece of 10 mm × 5 mm × 55 mm which is a steel plate having a plate thickness of less than 10 mm, 20 J or more on a Charpy V notch half size test). Moreover, the terms of "excellent ductility" refers to having a reduction of area of 50 % or more.

(Solution to Problem)

[0009] We made extensive studies on measures to solve the above-mentioned problems on high-Mn steel, and discovered the following.

[0010] That is, we discovered that in high-Mn steel, toughness can be improved and ductility (reduction of area) upon tensile deformation can be guaranteed by controlling the morphology of Ca-based inclusions and for that purpose, it is effective to control the balance between the Ca content and the S content within an appropriate range.

[0011] Further, we found that in manufacturing the high-Mn steel, it is possible to control the crystal grain size and suppress the formation of precipitates, thereby improving low-temperature toughness by limiting steel material heating temperature, rolling finish temperature and average cooling rate from a temperature at or above (the rolling finish temperature - 100 °C) to a temperature range of 300 °C to 650 °C.

[0012] When high-Mn steel contains Cu, Cu has an effect of improving the chloride stress corrosion cracking resistance under an environment with low chloride concentration. However, Cu conversely deteriorates the chloride stress corrosion cracking resistance under an environment with high chloride concentration. To address this issue, we found that high-Mn steel containing Cu, when optimized in the balance between the Cu content and the Ni content and added with Ni, exhibits excellent chloride stress corrosion cracking resistance even in an environment with high chloride concentration. Thus, it is possible to impart excellent chloride stress corrosion cracking resistance to high-Mn steel containing Cu regardless of the chloride concentration.

[0013] In this disclosure, the term of chloride stress corrosion cracking refers to a phenomenon in which, in a corrosive environment specific to high-Mn steel, in particular, in an environment with chloride ions, high-Mn steel leads to cracking or breaking even when tensile stress applied to the high-Mn steel is not greater than the tensile strength of the high-Mn steel. Further, the terms of chloride stress corrosion cracking resistance refer to resistance properties to the chloride stress corrosion cracking.

[0014] Based on these discoveries, we conducted further investigation which eventually led to the present disclosure. The primary features of the present disclosure are as follows.

1. High-Mn steel comprising:

    a chemical composition containing (consisting of), in mass%,
    C: 0.10 % or more and 0.70 % or less,
    Si: 0.10 % or more and 0.90 % or less,
    Mn: 20 % or more and 30 % or less,
    P: 0.030 % or less,
    S: 0.0070 % or less,
    Al: 0.01 % or more and 0.07 % or less,
    Cr: 1.8 % or more and 7.0 % or less,
    Ni: 0.01 % or more and less than 1.0 %,
    Ca: 0.0005 % or more and 0.010 % or less,
    N: 0.0050 % or more and 0.0500 % or less,
    O: 0.0050 % or less,
    Ti: 0.0050 % or less, and
    Nb: 0.0050 % or less, within a range satisfying the following formula (1), with the balance being Fe and inevitable impurities,

$$\mathrm{Ca/S} \geq 1.0 \qquad (1);$$

    a microstructure containing austenite as a matrix;
    a yield stress of 400 MPa or more; and
    an average Charpy impact absorbed energy at —196 °C of 100 J or more for a full-sized test piece and 20 J or more for a half-sized test piece.

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

    Cu: less than 2.0 %,
    Mo: 2.0 % or less,
    V: 2.0 % or less,

W: 2.0 % or less,
Mg: 0.0005 % or more and 0.0050 % or less, and
REM (rare earth metal): 0.0010 % or more and 0.0200 % or less.

3. A manufacturing method of high-Mn steel, comprising: heating a steel material having the chemical composition according to 1. or 2. to a temperature range of 1100 °C to 1300 °C; then hot rolling the steel material with a rolling finish temperature of 750 °C or higher and lower than 950 °C to obtain a hot-rolled plate; and then subjecting the hot-rolled plate to cooling treatment at an average cooling rate of 0.5 °C/s or more from a temperature at or above (the rolling finish temperature - 100 °C) to a temperature range of 300 °C to 650 °C.

4. High-Mn steel comprising:
a chemical composition containing (consisting of), in mass%,

C: 0.10 % or more and 0.70 % or less,
Si: 0.10 % or more and 0.90 % or less,
Mn: 20 % or more and 30 % or less,
P: 0.030 % or less,
S: 0.0070 % or less,
Al: 0.01 % or more and 0.07 % or less,
Cr: 1.8 % or more and 7.0 % or less,
Cu: 0.2 % or more and less than 2.0 %
Ni: 0.1 % or more and less than 1.0 %,
Ca: 0.0005 % or more and 0.010 % or less,
N: 0.0050 % or more and 0.0500 % or less,
O: 0.0050 % or less,
Ti: 0.0050 % or less and
Nb: 0.0050 % or less, within a range satisfying the following formulas (1) and (2), with the balance being Fe and inevitable impurities,

$$\mathrm{Ca/S} \geq 1.0 \qquad (1),$$

and

$$0 < \mathrm{Cu/Ni} \leq 2 \qquad (2);$$

and
a microstructure containing austenite as a matrix.

5. A manufacturing method of high-Mn steel, comprising: heating a steel material having the chemical composition according to 4. to a temperature range of 1100 °C to 1300 °C; then hot rolling the steel material with a rolling finish temperature of 750 °C or higher and lower than 950 °C to obtain a hot-rolled plate; and then subjecting the hot-rolled plate to cooling treatment at an average cooling rate of 0.5 °C/s or more from a temperature at or above (the rolling finish temperature - 100 °C) to a temperature range of 300 °C to 650 °C.

(Advantageous Effect)

[0015] According to an embodiment of this disclosure, it is possible to provide high-Mn steel which has high strength, excellent low-temperature toughness especially in a cryogenic range and excellent ductility. Therefore, the safety and the service life of a steel structure used in a cryogenic environment such as a storage tank of liquefied gas can be improved by using our high-Mn steel, which provides significant industrial effects.

[0016] Further, according to another embodiment of this disclosure, it is possible to provide high-Mn steel which exhibits excellent chloride stress corrosion cracking resistance regardless of the chloride concentration.

DETAILED DESCRIPTION

[0017] Our high-Mn steel will be described in detail below.

[Chemical composition]

[0018] The chemical composition of our high-Mn steel and the reasons for the limitations thereof are described first. In the description of the chemical composition, "%" denotes "mass%" unless otherwise noted.

C: 0.10 % or more and 0.70 % or less

[0019] C is an inexpensive austenite-stabilizing element, and an important element to obtain austenite. To obtain this effect, the C content needs to be 0.10 % or more. On the other hand, a C content beyond 0.70 % generates excessive Cr carbides, deteriorating low-temperature toughness. Therefore, the C content is set to 0.10 % or more and 0.70 % or less. The C content is preferably 0.20 % or more. The C content is preferably 0.60 % or less. The C content is more preferably 0.20 % or more and 0.60 % or less.

Si: 0.10 % or more and 0.90 % or less

[0020] Si acts as a deoxidizer, is necessary for steelmaking, and is effective at increasing hardness of a steel plate by solid solution strengthening when dissolved in steel. To obtain such effects, the Si content needs to be 0.10 % or more. On the other hand, a Si content beyond 0.9 % deteriorates weldability and also reduces low-temperature toughness, in particular toughness at extremely low temperature. Therefore, the Si content is set to 0.10 % or more and 0.90 % or less. The Si content is preferably 0.12 % or more. The Si content is preferably 0.70 % or less. The Si content is more preferably 0.12 % or more and 0.70 % or less.

Mn: 20 % or more and 30 % or less

[0021] Mn is a relatively inexpensive austenite-stabilizing element. In this disclosure, Mn is an important element for achieving both strength and cryogenic toughness. To obtain such effects, the Mn content needs to be 20 % or more. On the other hand, a Mn content beyond 30 % does not increase the effect of improving low-temperature toughness but increases alloy cost. Further, such a high Mn content deteriorates weldability and cuttability. Therefore, the Mn content is set to 20 % or more and 30 % or less. The Mn content is preferably 23 % or more. The Mn content is preferably 28 % or less. The Mn content is more preferably 23 % or more and 28 % or less.

P: 0.030 % or less

[0022] When a P content is beyond 0.030 %, P segregates to grain boundaries 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. Therefore, the P content is set to 0.030 % or less. Excessively reducing P, however, involves high refining cost and is economically disadvantageous. Therefore, the P content is desirably set to 0.002 % or more. The P content is preferably 0.005 % or more. The P content is preferably 0.028 % or less, and more preferably 0.024 % or less. Further, the P content is more preferably 0.005 % or more and 0.028 % or less.

S: 0.0070 % or less

[0023] S deteriorates base metal low-temperature toughness and ductility. Therefore, the upper limit of the S content is 0.0070 %, and desirably, the S content is kept as small as possible. Accordingly, the S content is set to 0.0070 % or less. Excessively reducing S, however, involves high refining cost and is economically disadvantageous. Therefore, the S content is preferably set to 0.001 % or more. The S content is preferably 0.0020 % or more. The S content is preferably 0.0060 % or less. The S content is more preferably 0.0020 % or more and 0.0060 % or less.

Al: 0.01 % or more and 0.07 % or less

[0024] Al acts as a deoxidizer and is most commonly used in molten steel deoxidizing processes to obtain a steel plate. To obtain such an effect, the Al content needs to be 0.01 % or more. On the other hand, when the Al content is beyond 0.07 %, Al is mixed into a weld metal portion during welding, deteriorating toughness of the weld metal. Therefore, the Al content is set to 0.07 % or less. Therefore, the Al content is set to 0.01 % or more and 0.07 % or less. The Al content is preferably 0.02 % or more. The Al content is preferably 0.06 % or less. The Al content is more preferably 0.02 % or more and 0.06 % or less.

Cr: 1.8 % or more and 7.0 % or less

[0025] Cr is an element which stabilizes austenite with an appropriate amount of addition and is effective at improving low-temperature toughness and base metal strength. To obtain such effects, the Cr content needs to be 1.8 % or more. On the other hand, a Cr content beyond 7.0 % generates Cr carbides, deteriorating low-temperature toughness and stress corrosion cracking resistance. Therefore, the Cr content is set to 1.8 % or more and 7.0 % or less. The Cr content is preferably 2.0 % or more. The Cr content is preferably 6.7 % or less. The Cr content is more preferably 2.0 % or more and 6.7 % or less. Further, to improve stress corrosion cracking resistance, the Cr content is further preferably 2.0 % or more. The content is further preferably 6.0 % or less.

Ni: 0.01 % or more and less than 1.0 %

[0026] Ni is effective at increasing hardness of a steel plate by solid solution strengthening when dissolved in steel and at improving low-temperature toughness, especially toughness at extremely low temperature. Thus, Ni is contained in an amount of 0.01 % or more. On the other hand, from the perspective of alloy cost, the Ni content is desirably minimized, and thus the addition amount of Ni is set to less than 1.0 %. The Ni content is preferably 0.03 % or more. The Ni content is preferably 0.8 % or less. The Ni content is more preferably 0.03 % or more and 0.8 % or less. Here, stainless steels such as SUS304 and SUS316 as austenite steel which are excellent in low-temperature toughness have optimized Ni equivalent and Cr equivalent as an alloy design for obtaining an austenite microstructure, and thus are added with a large amount of Ni. In contrast with these steels, the steel of this disclosure is an austenitic material which is produced at lower cost by minimizing the need for Ni. The need for Ni is minimized by optimizing the addition amount of Mn.

Ni: 0.1 % or more and less than 1.0 %

[0027] Further, when the high-Mn steel contains a predetermined amount of Cu, the addition of Ni with an appropriate balance between the amount of Cu and the amount of Ni can exhibit excellent chloride stress corrosion cracking resistance regardless of the chloride concentration. From this point of view, in high-Mn steel containing Cu in an amount of 0.2 % or more and less than 2.0 % as described later, the Ni content is set to 0.1 % or more and less than 1.0 %. A Ni content of less than 0.1 % does not produce the effect on stress corrosion cracking. A Ni content of 1.0 % or more incurs cost increase.

Ca: 0.0005 % or more and 0.010 % or less

[0028] Ca improves toughness through morphological control of inclusions described below and effectively acts to ensure ductility (reduction of area) during tensile deformation. To obtain such effects, the Ca content needs to be 0.0005 % or more. On the other hand, addition of Ca in excess of 0.010 % may reduce ductility and toughness instead. Therefore, the Ca content is set to 0.0005 % or more and 0.010 % or less. The Ca content is preferably 0.0010 % or more. The Ca content is preferably 0.0090 % or less. The Ca content is more preferably 0.0010 % or more and 0.0090 % or less.

Ca/S ≥ 1.0

[0029] With the Ca content and S content described above, it is important to control the morphology of Ca-based inclusions by further keeping Ca/S within an appropriate range. That is, setting Ca/S to ≥ 1.0 to promote composite precipitation of MnS using Ca-based inclusions as nuclei in crystal grains is effective at suppressing the precipitation and coarsening of MnS on crystal grain boundaries, thereby improving toughness and ensuring ductility during tensile deformation, specifically, achieving a reduction of area of 50 % or more. To obtain such effects, Ca/S needs to be 1.0 or more. Ca/S is preferably 1.7 or more.

N: 0.0050 % or more and 0.0500 % or less

[0030] N is an austenite-stabilizing element and an element which is effective at improving low-temperature toughness. To obtain such an effect, the N content needs to be 0.0050 % or more. On the other hand, the N content beyond 0.0500 % coarsens nitrides or carbonitrides, deteriorating toughness. Therefore, the N content is set to 0.0050 % or more and 0.0500 % or less. The N content is preferably 0.0060 % or more. The N content is preferably 0.0400 % or less. The N content is more preferably 0.0060 % or more and 0.0400 % or less.

O: 0.0050 % or less

[0031] O deteriorates low-temperature toughness through the formation of oxides. Therefore, the O content is set to 0.0050 % or less. The O content is preferably 0.0045 % or less. Excessive reducing the O content involves high refining cost and is economically disadvantageous. Therefore, the O content is desirably 0.0003 % or more.

Ti: 0.0050 % or less and Nb: 0.0050 % or less

[0032] Ti and Nb form carbonitrides with a high melting point in steel to prevent coarsening of crystal grains, then becoming an origin of fracture and a propagation path of cracks. In particular, in high-Mn steel, Ti and Nb hinder microstructural control for enhancing low-temperature toughness and improving ductility, and thus, need to be intentionally limited. Specifically, Ti and Nb are components which are inevitably introduced with raw materials and other sources, and Ti of more than 0.005 % and 0.010 % or less and Nb of more than 0.005 % and 0.010 % or less are typically introduced into steel. Thus, according to the method described below, it is necessary to avoid inevitable introduction of Ti and Nb and limit the content of each of Ti and Nb to 0.0050 % or less. By limiting the content of each of Ti and Nb to 0.0050 % or less, the adverse effect of carbonitrides can be eliminated, and excellent low-temperature toughness and ductility can be guaranteed. The content of each of Ti and Nb is preferably set to less than 0.0050 %, and more preferably 0.003 % or less.

Cu: 0.2 % or more and less than 2.0 %

[0033] Cu has an effect of improving chloride stress corrosion cracking resistance under an environment with low chloride concentration. From this point of view, a Cu content of 0.2 % or more is effective. On the other hand, Cu conversely deteriorates chloride stress corrosion cracking resistance under an environment with high chloride concentration. Therefore, when Cu is contained, the Cu content is set to less than 2.0 %. A Cu content of less than 0.2 % does not produce an effect on stress corrosion cracking properties, and a Cu content of 2.0 % or more causes the above problem and incurs cost increase. The Cu content is preferably 0.3 % or more. The Cu content is preferably 0.8 % or less. The Cu content is more preferably 0.3 % or more and 0.8 % or less.

$0 < \mathrm{Cu/Ni} \leq 2$

[0034] Here, in high Mn steel containing Cu and Ni, in order to ensure excellent chloride corrosion cracking resistance regardless of the chloride concentration, it is important to control the Cu and Ni contents within the range described above and additionally optimize the balance between the Cu content and the Ni content so as to satisfy $0 < \mathrm{Cu/Ni} \leq 2$. In the case of $\mathrm{Cu/Ni} > 2$, the Ni content is excessively small relative to the Cu content and excellent chloride stress corrosion cracking resistance cannot be achieved under an environment with high chloride concentration.

[0035] The balance other than the aforementioned essential components is Fe and inevitable impurities. The inevitable impurities include H, and a total content of 0.01 % or less may be allowed.

[0036] In this disclosure, in order to further improve strength and low-temperature toughness, the following elements can be contained as necessary in addition to the above essential components:
at least one selected from the group consisting of Mo: 2.0 % or less, V: 2.0 % or less, W: 2.0 % or less, Mg: 0.0005 % or more and 0.0050 % or less, REM: 0.0010 % or more and 0.0200 % or less.

Mo: 2.0 % or less, V: 2.0 % or less, W: 2.0 % or less

[0037] Mo, V, and W stabilize austenite and improve base metal strength. To obtain such effects, Mo, V, and/or W is preferably contained in an amount of 0.001 % or more. On the other hand, when the content of each added element is beyond 2.0 %, coarse carbonitrides are generated, which may become an origin of fracture, and additionally increase manufacturing cost. Therefore, when any of these alloying elements is/are added, the content of each added element is preferably 2.0 % or less. The content of each added element is more preferably 0.003 % or more. The content of each added element is preferably 1.7 % or less, and more preferably 1.5 % or less. Further, the content of each added element is preferably 0.003 % or more and 1.7 % or less, and more preferably 0.003 % or more and 1.5 % or less.

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

[0038] Mg and REM are elements useful for morphological control of inclusions and can be contained as necessary. The morphological control of inclusions means granulating elongated sulfide inclusions. The morphological control of inclusions improves ductility, toughness, and sulfide stress corrosion cracking resistance. To obtain such effects, Mg is 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. Therefore, when Mg are contained, the Mg content is preferably 0.0005 % or more. The Mg content is preferably 0.0050 % or less. When REM is contained, the REM content is preferably 0.0010 % or more. The REM content is preferably 0.0200 % or less. The Mg content is more preferably 0.0010 % or more. The Mg content is more preferably 0.0040 % or less. The Mg content is further preferably 0.0010 % or more and 0.0040 % or less. The REM content is more preferably 0.0020 % or more. The REM content is more preferably 0.0150 % or less. The REM content is further preferably 0.0020 % or more and 0.0150 % or less.

[Microstructure]

Microstructure containing austenite as a matrix

[0039] When a steel material has a body centered cubic (bcc) crystal structure, the steel material may cause brittle fracture in a low-temperature environment, and thus, is not suitable for use in a low-temperature environment. When the steel material is assumed to be used in a low-temperature environment, the steel material is required to have, as a matrix, an austenite microstructure, which has a face centered cubic (fcc) crystal structure. As used herein, the terms of "containing austenite as a matrix" means that the area ratio of austenite phase is 90 % or more. The remainder besides the austenite phase is ferrite or martensite phase. Of course, the area ratio of the austenite phase may be 100 %.

[Manufacturing method]

[0040] The manufacturing method of high-Mn steel of this disclosure comprises: heating a steel material having the aforementioned chemical composition; hot rolling the heated steel material to obtain a hot-rolled plate; and subjecting the hot-rolled plate to cooling treatment. Further, in the manufacturing method of high-Mn steel of this disclosure, the temperature range in the heating of the steel material is 1100 °C to 1300 °C, the rolling finish temperature in the hot rolling is 750 °C or higher and lower than 950 °C, and the average cooling rate from a temperature at or above (the rolling finish temperature - 100 °C) to a temperature range of 300 °C to 650 °C in the cooling treatment is 0.5 °C/s or more.

[0041] In manufacturing the high-Mn steel of this disclosure, the steel material can be obtained from molten steel having the aforementioned chemical composition which is prepared by steelmaking using a publicly-known method such as using a converter or an electric heating furnace. In addition, the high-Mn steel may also be subjected to secondary refinement in a vacuum degassing furnace. During the secondary refinement, to limit the contents of Ti and Nb which hinder suitable microstructural control within the aforementioned range, it is necessary to prevent Ti and Nb from being inevitably introduced with raw materials and other sources so as to reduce the contents of Ti and Nb. For example, by reducing the basicity of slag during the refining stage, these alloy elements are concentrated in the slag to be discharged, thus reducing Ti and Nb concentrations in a final slab product. Alternatively, the molten steel can be oxidized by blowing in oxygen, and the Ti and Nb alloys can be suspended and separated during reflux. Subsequently, it is preferable to make the steel into a steel material such as a slab having a determined size by a publicly-known steelmaking method such as continuous casting or ingot casting. The slab after continuous casting may be subjected to blooming to obtain a steel material.

[0042] Further, manufacturing conditions are specifically defined below to make the aforementioned steel material into a steel material exhibiting high strength, excellent low-temperature toughness and ductility.

Heating temperature of a steel material: 1100 °C or higher and 1300 °C or lower

[0043] To coarsen the crystal grain size in the microstructure of the steel material, the heating temperature before hot rolling is set to 1100 °C or higher. However, the heating temperature beyond 1300 °C may trigger local melting. Thus, the upper limit of the heating temperature is set to 1300 °C. The temperature is controlled based on a surface temperature of the steel material.

Rolling finish temperature: 750 °C or higher and lower than 950 °C

[0044] The steel material (steel ingot or a billet) is heated and subsequently subjected to hot rolling. To make coarse crystal grains, it is preferable to increase the accumulated rolling reduction ratio at high temperature. That is, hot rolling at low temperature refines the microstructure and excessively introduces working strain, thus deteriorating low-temperature toughness. Therefore, the lower limit of the rolling finishing temperature in the hot rolling is set to 750 °C in terms of a surface temperature of the steel plate. On the other hand, finishing of rolling in a temperature range of 950 °C or higher will result in excessively coarse grain size, and thus desired yield stress cannot be obtained. Therefore, final finish rolling needs to be performed in one pass or more at lower than 950 °C.

[0045] Average cooling rate from a temperature at or above (the rolling finish temperature - 100 °C) to a temperature range of 300 °C to 650 °C: 0.5 °C/s or more
After the hot rolling, cooling is immediately performed. Slowly cooling the steel plate after the hot rolling promotes formation of precipitates, thus deteriorating low-temperature toughness. Cooling the steel plate at a cooling rate of 0.5 °C/s or more in a predetermined temperature range can prevent formation of these precipitates. Further, excessive cooling distorts the steel plate, deteriorating productivity. Therefore, the upper limit of the cooling start temperature can be set at 900 °C. Further, the lower limit of the cooling start temperature is set at (the rolling finish temperature - 100 °C). Starting the cooling from a temperature lower than this temperature promotes formation of precipitates after the hot rolling, thus deteriorating low-temperature toughness. Further, the cooling end temperature is within a temperature range of 300 °C to 650 °C. This is because cooling to the above temperature range can suppress the precipitation of carbides which lower toughness. For the aforementioned reasons, in the cooling after the hot rolling, the average cooling rate at a surface of the steel plate from a temperature at or above (the rolling finish temperature - 100 °C) in terms of a surface temperature of the steel plate to a temperature range of 300 °C to 650 °C is set to 0.5 °C/s or more. On the other hand, from the viewpoint of industrial production, the average cooling rate is preferably 200 °C/s or less. The cooling rate is calculated as an average cooling rate of the steel plate by simulation calculation based on the temperature change of its surface.

[0046] Furthermore, in the aforementioned casting process, during the cooling, the cooling time in the temperature range of 1400 °C to 1300 °C in terms of a surface temperature of the steel is preferably controlled to 100 s or less. Controlling the cooling time in the casting process as described above promotes composite precipitation of MnS containing Ca-based inclusions such as Ca(O,S) as nucleus and the number of (Ca,Mn)S is increased. As a result, MnS does not grow at crystal grain boundaries or within crystal grains and thus the ratio of elongated MnS is lowered. Through such morphological control of Ca-based inclusions, high-Mn steel having a good reduction of area as high as 51 % or more can be obtained.

EXAMPLES

[0047] This disclosure will be described in further detail below by way of Examples. Note that this disclosure is not limited to the following examples.

[0048] Steel slabs having the chemical compositions listed in Table 1 were made as steel materials by a process for refining with converter and ladle and continuous casting. Next, the obtained steel slabs were subjected to blooming and hot rolling to obtain steel plates having a thickness up to 32 mm under the conditions listed in Table 2. Tensile properties, toughness, and microstructures of the steel plates were evaluated as described below.

(1) Tensile test properties

[0049] JIS NO. 4 tensile test pieces were collected from the obtained steel plates having a plate thickness of more than 15 mm. Round bar tensile test pieces having a parallel portion diameter of 6 mm and a gauge length of 25 mm were collected from the obtained steel plates having a plate thickness of less than 15 mm. Then, the test pieces were subjected to a tensile test to investigate tensile test properties. In this disclosure, when a test piece had a yield stress of 400 MPa or more and a tensile strength of 800 MPa or more, the corresponding steel plate was determined to have excellent tensile properties and high strength. Further, when a test piece had a reduction of area of 50 % or more, the corresponding steel plate was determined to have excellent ductility.

(2) Low-temperature toughness

[0050] Charpy V-notch full-sized test pieces were taken from the direction parallel to the rolling direction at a position from the steel plate surface to a depth of 1/4 of the plate thickness (hereinafter, referred to as 1/4 position of the plate thickness) of each steel plate over 20 mm in thickness, or at a position from the steel plate surface to a depth of 1/2 of the plate thickness (hereinafter, referred to as 1/2 position of the plate thickness) of each steel plate not over 20 mm in thickness, in conformity with JIS Z 2202 (1998). Then, the test pieces were subjected to the Charpy impact test in conformity with JIS Z 2242 (1998), where three test pieces were used for each steel plate, to determine absorbed energy at -196 °C and evaluate base metal toughness. In this disclosure, when the three test pieces had an average absorbed energy (vE_{-196}) of 100 J or more, the corresponding steel plate was determined to have excellent base metal low-temperature toughness. For steel plates having a plate thickness of less than 10 mm, Charpy V-notch half-sized test pieces were collected from the steel plates and similarly subjected to the Charpy impact test. For steel plates having a plate thickness of less than 10 mm, when the test pieces had an average absorbed energy of 20 J or more, the corresponding steel plate was determined to have excellent base metal low-temperature toughness.

(3) Stress corrosion cracking test

[0051] Stress corrosion cracking resistance of samples 32 and 33 was evaluated in a boiling magnesium chloride solution in conformity with ASTM G36 (herein, it may be referred to "Boiling magnesium chloride solution test"). As the test piece, a U-bending test piece in conformity with ASTM G30 Example a was used. A test piece of 2.5 mm thick × 20 mm wide × 80 mm long was taken in the C-direction from a position of 1 mm below the surface of each steel plate. The test piece was bent at the center thereof in the longitudinal direction with 5R and subjected to the test.

[0052] The test time was 400 hours. After the test, test pieces with no cracks observed on the surface thereof was judged to have excellent chloride stress corrosion cracking resistance. In Table 3, cases where no cracks were visually observed on the surface are indicated as "good", and cases where cracks were visually observed on the surface as "poor".

[0053] High-Mn steel of this disclosure was confirmed to satisfy the aforementioned desired performance (a base metal yield stress of 400 MPa or more, a reduction of area of 50 % or more, an average absorbed energy (vE_{-196}) of 100 J or more (20 J or more for a half-sized test piece) for low-temperature toughness). On the other hand, the comparative examples out of the scope of this disclosure did not satisfy the aforementioned desired performance in terms of one or more of yield stress, reduction of area, and low-temperature toughness.

[0054] Further, sample 32, in which Cu and Ni were contained so that Cu/Ni was within the predetermined range. exhibited excellent chloride stress corrosion cracking resistance. On the other hand, in sample 33 where Cu/Ni was outside the predetermined range, sufficient chloride stress corrosion cracking resistance could not be confirmed.

[Table 1]

Steel No.	Chemical composition (mass%)																				Remarks
	C	Si	Mn	P	S	Al	Cr	O	N	Nb	Ti	V	Cu	Ni	Mo	W	Ca	Mg	REM	Ca/S	Cu/Ni	
A	0.189	0.44	28.5	0.015	0.0030	0.042	4.01	0.0020	0.0205	0.002	0.003	-	-	0.04	-	-	0.0041	-	-	1.4	-	Example
B	0.652	0.18	22.4	0.011	0.0048	0.031	2.52	0.0041	0.0374	0.001	0.001	-	-	0.05	-	-	0.0072	-	-	1.5	-	Example
C	0.435	0.38	24.1	0.023	0.0038	0.027	4.50	0.0022	0.0241	0.002	0.001	-	0.31	0.07	-	-	0.0080	-	-	2.1	4.4	Example
D	0.339	0.76	20.4	0.019	0.0062	0.042	3.04	0.0031	0.0185	0.002	0.002	0.04	-	0.02	0.41	-	0.0075	-	-	1.2	-	Example
E	0.285	0.35	28.2	0.024	0.0021	0.067	1.85	0.0023	0.0255	0.001	0.003	-	-	0.01	-	0.07	0.0023	-	-	1.1	-	Example
F	0.463	0.31	26.8	0.017	0.0045	0.038	6.52	0.0040	0.0375	0.003	0.001	-	-	0.06	-	-	0.0063	-	-	1.4	-	Example
G	0.342	0.38	22.8	0.021	0.0019	0.047	2.52	0.0030	0.0201	0.002	0.001	-	0.45	0.08	-	-	0.0040	0.0011	-	2.1	5.6	Example
H	0.412	0.18	20.4	0.017	0.0015	0.030	2.05	0.0029	0.0075	0.002	0.001	-	-	0.09	-	-	0.0024	-	0.0027	1.6	-	Example
I	0.325	0.14	25.2	0.020	0.0028	0.042	5.21	0.0024	0.0152	0.003	0.002	-	-	0.03	-	-	0.0031	-	-	1.1	-	Example
J	0.420	0.37	23.7	0.014	0.0012	0.035	4.22	0.0023	0.0214	0.002	0.004	-	0.62	0.07	-	-	0.0042	-	-	3.5	8.9	Example
K	0.572	0.32	26.1	0.016	0.0029	0.032	4.04	0.0021	0.0099	0.001	0.003	-	-	0.05	-	-	0.0056	-	-	1.9	-	Example
L	0.945	0.42	20.3	0.003	0.0026	0.034	4.00	0.0039	0.0311	0.003	0.004	-	-	0.01	-	-	0.0029	-	-	1.1	-	Comparative Example
M	0.109	0.04	23.9	0.019	0.0032	0.042	5.23	0.0012	0.0275	0.002	0.001	-	-	-	-	-	0.0042	-	-	1.3	-	Comparative Example
N	0.132	0.52	15.8	0.005	0.0045	0.042	2.32	0.0034	0.0455	0.003	0.003	-	-	0.03	-	-	0.0052	-	-	1.2	-	Comparative Example
O	0.226	0.47	23.2	0.047	0.0063	0.050	1.85	0.0041	0.0336	0.001	0.003	-	-	0.01	-	-	0.0068	-	-	1.1	-	Comparative Example
P	0.327	0.28	27.4	0.028	0.0095	0.021	1.99	0.0032	0.0074	0.001	0.003	-	-	0.02	-	-	0.0097	-	-	1.0	-	Comparative Example
R	0.280	0.41	26.8	0.017	0.0039	0.052	7.84	0.0028	0.0195	0.003	0.001	-	-	0.01	-	-	0.0048	-	-	1.2	-	Comparative Example
S	0.427	0.28	25.7	0.024	0.0033	0.047	6.07	0.0075	0.0205	0.003	0.002	-	-	0.02	-	-	0.0040	-	-	1.2	-	Comparative Example
T	0.353	0.11	24.9	0.027	0.0045	0.032	3.31	0.0028	0.0769	0.003	0.002	-	-	0.03	-	-	0.0051	-	-	1.1	-	Comparative Example
U	0.462	0.55	25.3	0.022	0.0043	0.027	4.22	0.0021	0.0255	0.003	0.003	-	-	0.01	-	-	0.0029	-	-	0.7	-	Comparative Example
V	0.440	0.29	24.5	0.019	0.0037	0.034	4.34	0.0027	0.0224	0.001	0.002	-	-	0.08	-	-	0.0038	-	-	1.0	-	Example
W	0.384	0.82	20.9	0.027	0.0004	0.045	3.22	0.0033	0.0205	0.001	0.003	-	-	0.03	-	-	0.0004	-	-	1.0	-	Comparative Example
X	0.587	0.44	25.8	0.022	0.0025	0.019	3.97	0.0024	0.0128	0.002	0.001	-	-	0.01	0.14	-	0.0023	-	-	0.9	-	Comparative Example
Y	0.602	0.25	23.3	0.025	0.0020	0.034	2.62	0.0032	0.0246	0.004	0.011	-	-	0.02	-	0.20	0.0029	-	-	1.5	-	Comparative Example
Z	0.080	0.36	20.4	0.019	0.0046	0.042	3.85	0.0021	0.0237	0.003	0.004	-	-	0.02	-	-	0.0048	-	-	1.0	-	Comparative Example
AA	0.290	0.39	27.6	0.012	0.0030	0.042	4.20	0.0020	0.0190	0.002	0.003	-	0.40	0.30	-	-	0.0033	-	-	1.1	1.3	Example
BB	0.280	0.39	27.8	0.012	0.0030	0.042	4.20	0.0020	0.0210	0.002	0.003	-	0.40	0.05	-	-	0.0033	-	-	1.1	8.0	Reference Example

[Table 2]

Sample No.	Steel No.	Cooling time from 1400 °C to 1300 °C during casting	Plate thickness	Hot rolling method				Remarks
				Heating temperature of steel material	Rolling finish temperature	Cooling start temperature	Average cooling rate to temperature range of 300 °C to 650 °C	
		(s)	(mm)	(°C)	(°C)	(°C)	(°C/s)	
1	A	20	32	1160	863	836	8	Example
2	B	50	23	1180	825	795	11	Example
3	C	60	12	1150	781	726	13	Example
4	D	80	21	1120	792	760	10	Example
5	E	20	24	1130	860	830	9	Example
6	F	30	14	1130	842	787	11	Example
7	G	30	8	1260	885	821	15	Example
8	H	40	9	1200	832	773	12	Example
9	I	50	14	1140	828	772	4	Example
10	J	70	29	1160	858	831	0.9	Example
11	K	30	11	1110	755	705	11	Example
12	J	20	12	1150	775	723	11	Example
13	L	30	19	1230	765	733	8	Comparative Example
14	M	50	30	1180	885	858	7	Comparative Example
15	N	30	13	1100	820	765	11	Comparative Example
16	O	40	24	1130	853	823	9	Comparative Example
17	P	50	20	1190	804	761	6	Comparative Example
18	R	20	20	1150	801	764	9	Comparative Example

(continued)

Sample No.	Steel No.	Cooling time from 1400 °C to 1300 °C during casting	Plate thickness	Hot rolling method				Remarks
				Heating temperature of steel material	Rolling finish temperature	Cooling start temperature	Average cooling rate to temperature range of 300 °C to 650 °C	
		(s)	(mm)	(°C)	(°C)	(°C)	(°C/s)	
19	S	40	14	1110	814	758	11	Comparative Example
20	T	30	28	1150	852	828	2	Comparative Example
21	C	50	11	1170	669	614	10	Comparative Example
22	D	20	18	1220	807	775	0.3	Comparative Example
23	E	30	24	1020	853	823	10	Comparative Example
24	U	50	10	1120	760	713	11	Comparative Example
25	V	30	12	1180	805	742	12	Example
26	W	20	22	1150	773	738	10	Comparative Example
27	X	30	10	1090	741	693	12	Comparative Example
28	A	50	30	1290	984	952	8	Comparative Example
29	Y	20	8	1130	852	796	12	Comparative Example
30	Z	30	28	1150	821	788	9	Comparative Example
31	A	300	32	1160	863	836	8	Example
32	AA	20	30	1100	900	850	10	Example

(continued)

Sample No.	Steel No.	Cooling time from 1400 °C to 1300 °C during casting	Plate thickness	Hot rolling method				Remarks
				Heating temperature of steel material	Rolling finish temperature	Cooling start temperature	Average cooling rate to temperature range of 300 °C to 650 °C	
		(s)	(mm)	(°C)	(°C)	(°C)	(°C/s)	
33	BB	30	30	1100	900	850	10	Reference Example

[Table 3]

Sample No.	Steel No.	Yield stress (MPa)	Tensile strength (MPa)	Reduction of area (%)	Absorbed energy at —196 °C (VE$_{-196}$) (J)	Boiling magnesium chloride solution test	Remarks
1	A	421	854	55	137	-	Example
2	B	548	940	57	121	-	Example
3	C	568	970	60	119	-	Example
4	D	562	956	53	116	-	Example
5	E	483	885	52	137	-	Example
6	F	455	855	55	141	-	Example
7	G	421	940	59	62*	-	Example
8	H	506	967	57	54*	-	Example
9	I	449	850	51	127	-	Example
10	J	404	842	64	133	-	Example
11	K	569	969	56	116	-	Example
12	J	559	953	61	127	-	Example
13	L	625	974	51	58	-	Comparative Example
14	M	357	817	55	127	-	Comparative Example
15	N	445	869	51	36	-	Comparative Example
16	O	450	882	54	72	-	Comparative Example
17	P	523	939	50	79	-	Comparative Example
18	R	521	939	53	48	-	Comparative Example
19	S	449	849	52	83	-	Comparative Example
20	T	419	854	52	75	-	Comparative Example
21	C	670	1061	54	42	-	Comparative Example
22	D	541	942	54	67	-	Comparative Example
23	E	479	879	53	69	-	Comparative Example
24	U	553	942	44	108	-	Comparative Example
25	V	553	962	51	126	-	Example
26	W	583	960	48	108	-	Comparative Example

(continued)

Sample No.	Steel No.	Yield stress (MPa)	Tensile strength (MPa)	Reduction of area (%)	Absorbed energy at —196 °C (VE_{-196}) (J)	Boiling magnesium chloride solution test	Remarks
27	X	579	982	45	112	-	Comparative Example
28	A	369	847	54	139	-	Comparative Example
29	Y	501	994	55	17*	-	Comparative Example
30	Z	428	848	50	35	-	Comparative Example
31	A	421	854	50	112	-	Example
32	AA	435	851	55	105	good	Example
33	BB	437	853	60	120	poor	Reference Example

* half-sized test piece

Claims

1. High-Mn steel comprising:

a chemical composition containing, in mass%,
C: 0.10 % or more and 0.70 % or less,
Si: 0.10 % or more and 0.90 % or less,
Mn: 20 % or more and 30 % or less,
P: 0.030 % or less,
S: 0.0070 % or less,
Al: 0.01 % or more and 0.07 % or less,
Cr: 1.8 % or more and 7.0 % or less,
Ni: 0.01 % or more and less than 1.0 %,
Ca: 0.0005 % or more and 0.010 % or less,
N: 0.0050 % or more and 0.0500 % or less,
O: 0.0050 % or less,
Ti: 0.0050 % or less, and
Nb: 0.0050 % or less, within a range satisfying the following formula (1), with the balance being Fe and inevitable impurities,

$$Ca/S \geq 1.0 \qquad (1);$$

a microstructure containing austenite as a matrix;
a yield stress of 400 MPa or more; and
an average Charpy impact absorbed energy at -196 °C of 100 J or more for a full-sized test piece and 20 J or more for a half-sized test piece.

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

Cu: less than 2.0 %,
Mo: 2.0 % or less,

V: 2.0 % or less,
W: 2.0 % or less,
Mg: 0.0005 % or more and 0.0050 % or less, and
REM: 0.0010 % or more and 0.0200 % or less.

3. A manufacturing method of high-Mn steel, comprising: heating a steel material having the chemical composition according to claim 1 or 2 to a temperature range of 1100 °C to 1300 °C; then hot rolling the steel material with a rolling finish temperature of 750 °C or higher and lower than 950 °C to obtain a hot-rolled plate; and then subjecting the hot-rolled plate to cooling treatment at an average cooling rate of 0.5 °C/s or more from a temperature at or above (the rolling finish temperature - 100 °C) to a temperature range of 300 °C to 650 °C.

4. High-Mn steel comprising:
a chemical composition containing, in mass%,

C: 0.10 % or more and 0.70 % or less,
Si: 0.10 % or more and 0.90 % or less,
Mn: 20 % or more and 30 % or less,
P: 0.030 % or less,
S: 0.0070 % or less,
Al: 0.01 % or more and 0.07 % or less,
Cr: 1.8 % or more and 7.0 % or less,
Cu: 0.2 % or more and less than 2.0 %
Ni: 0.1 % or more and less than 1.0 %,
Ca: 0.0005 % or more and 0.010 % or less,
N: 0.0050 % or more and 0.0500 % or less,
O: 0.0050 % or less,
Ti: 0.0050 % or less and
Nb: 0.0050 % or less, within a range satisfying the following formulas (1) and (2), with the balance being Fe and inevitable impurities,

$$\mathrm{Ca/S} \geq 1.0 \qquad (1),$$

and

$$0 < \mathrm{Cu/Ni} \leq 2 \qquad (2);$$

and
a microstructure containing austenite as a matrix.

5. A manufacturing method of high-Mn steel, comprising: heating a steel material having the chemical composition according to claim 4 to a temperature range of 1100 °C to 1300 °C; then hot rolling the steel material with a rolling finish temperature of 750 °C or higher and lower than 950 °C to obtain a hot-rolled plate; and then subjecting the hot-rolled plate to cooling treatment at an average cooling rate of 0.5 °C/s or more from a temperature at or above (the rolling finish temperature - 100 °C) to a temperature range of 300 °C to 650 °C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/005017

A. CLASSIFICATION OF SUBJECT MATTER
C21D 8/02(2006.01)i; C22C 38/00(2006.01)i; C22C 38/58(2006.01)i
FI: C22C38/00 302A; C22C38/58; C21D8/02 D

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C21D8/02; C22C38/00-38/60

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2018/199145 A1 (JFE STEEL CORPORATION) 01.11.2018 (2018-11-01) paragraphs [0009]-[0050]	1-5
X	JP 2017-155300 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 07.09.2017 (2017-09-07) paragraphs [0009]-[0050]	1-5
X	JP 2016-084529 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 19.05.2016 (2016-05-19) paragraphs [0009]-[0051]	1-5
X	JP 2016-196703 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 24.11.2016 (2016-11-24) paragraphs [0007]-[0050]	1-5

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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"&"	document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/005017

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2018/105510 A1 (JFE STEEL CORPORATION) 14.06.2018 (2018-06-14) paragraphs [0009]-[0077]	1-3
A	JP 51-018913 A (NIPPON STEEL CORP.) 14.02.1976 (1976-02-14) entire text, all drawings	1-5

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2020/005017

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
WO 2018/199145 A1	01 Nov. 2018	CN 110573642 A paragraphs [0009]-[0110]	
JP 2017-155300 A	07 Sep. 2017	(Family: none)	
JP 2016-084529 A	19 May 2016	(Family: none)	
JP 2016-196703 A	24 Nov. 2016	(Family: none)	
WO 2018/105510 A1	14 Jun. 2018	EP 3553195 A1 paragraphs [0009]-[0075]	
JP 51-018913 A	14 Feb. 1976	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2016084529 A **[0004] [0006]**
- JP 2016196703 A **[0004] [0006]**