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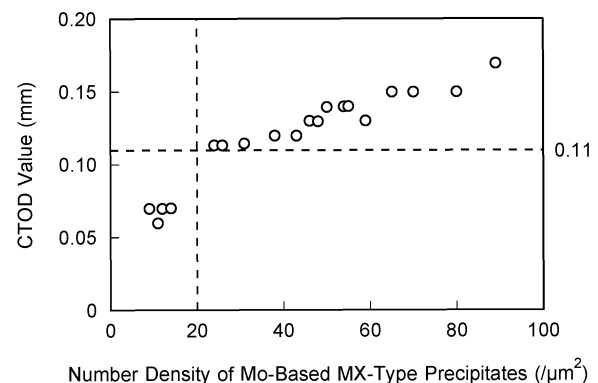
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(54) **STEEL MATERIAL**

(57) A steel material that achieves both high strength and excellent fracture toughness is provided. A steel material according to the present disclosure contains C: 0.10 to 0.45%, Si: 1.00% or less, Mn: 0.01 to 1.00%, Al: 0.001 to 0.100%, Cr: 0.1 to 2.0%, and Mo: 0.20 to 2.00%, contains any one or more elements among Ca: 0.0005 to 0.0200% and Mg: 0.0005 to 0.0200%, contains any one or more elements among Ti: 0.001 to 0.300%, Nb: 0.001 to 0.300%, and V: 0.01 to 0.50%, with the balance being Fe and impurities, and satisfies Formulae (1) and (2) described in the description. The yield strength is 862 MPa or more. A number density of MX-type precipitates which have an equivalent circular diameter of 100 nm or less and in which, when the total content of Mo, Nb, V, and Ti is defined as 100% by mass, the content of Mo is more than 50% by mass is 20 / μm^2 or more.

FIG. 1



Description

TECHNICAL FIELD

- 5 **[0001]** The present disclosure relates to a steel material, and more particularly relates to a steel material which is suitable for use in oil wells.

BACKGROUND ART

- 10 **[0002]** Oil wells and gas wells (hereunder, oil wells and gas wells are collectively referred to as simply "oil wells") are being drilled increasingly deeper, and therefore there is a demand to enhance the strength of oil-well steel materials which are typified by oil-well steel pipes. Specifically, oil-well steel materials of 80 ksi grade (yield strength is 80 to less than 95 ksi, that is, 552 to less than 655 MPa) and 95 ksi grade (yield strength is 95 to less than 110 ksi, that is, 655 to less than 758 MPa) are in widespread use, and recently requests are also starting to be made for oil-well steel materials of 110 ksi grade (yield strength is 758 to less than 862 MPa) and 125 ksi or more (yield strength is 862 MPa or more).

- 15 **[0003]** In addition, in some cases oil wells contain corrosive hydrogen sulfide gas (H₂S) or carbon dioxide gas (CO₂) or the like. Therefore, a steel material for which use as an oil-well steel material is assumed is also required to have excellent corrosion resistance, and not just high strength. Further, in the case of oil-well steel materials, stress is applied to the steel material during use. Therefore, sulfide stress cracking resistance (hereunder, referred to as "SSC resistance") has been used as an index of excellent corrosion resistance of oil-well steel materials.

[0004] Techniques for increasing the strength and SSC resistance of a steel material are proposed in Japanese Patent Application Publication No. 2006-28612 (Patent Literature 1), International Application Publication No. WO2008/123422 (Patent Literature 2), and Japanese Patent Application Publication No. 2017-166060 (Patent Literature 3).

- 25 **[0005]** Patent Literature 1 discloses a steel material that is a steel for pipes, consisting of, in mass%, C: 0.2 to 0.7%, Si: 0.01 to 0.8%, Mn: 0.1 to 1.5%, S: 0.005% or less, P: 0.03% or less, Al: 0.0005 to 0.1%, Ti: 0.005 to 0.05%, Ca: 0.0004 to 0.005%, N: 0.007% or less, Cr: 0.1 to 1.5%, and Mo: 0.2 to 1.0%, with the balance being Fe and impurities. In this steel material, in addition, among inclusions of non-metallic inclusions which contain Ca, Al, Ti, N, O, and S, (Ca %)/(Al %) is 0.55 to 1.72 and (Ca %)/(Ti %) is 0.7 to 19. It is disclosed in Patent Literature 1 that this steel material has a high yield strength of more than 758 MPa and has excellent SSC resistance.

- 30 **[0006]** Patent Literature 2 discloses a steel material that is a low-alloy steel containing, in mass%, C: 0.10 to 0.20%, Si: 0.05 to 1.0%, Mn: 0.05 to 1.5%, Cr: 1.0 to 2.0%, Mo: 0.05 to 2.0%, Al: 0.10% or less, and Ti: 0.002 to 0.05%, with $C_{eq} (= C + (Mn/6) + (Cr + Mo + V)/5)$ being 0.65 or more, and the balance being Fe and impurities, in which, among the impurities, P is 0.025% or less, S is 0.010% or less, N is 0.007% or less, and B is less than 0.0003%. In this steel material, in addition, the number density of M₂₃C₆-type precipitates having a grain size of 1 μm or more is 0.1 /mm² or less. It is disclosed in Patent Literature 2 that this steel material has a yield strength of 654 to 793 MPa and has excellent SSC resistance even in highpressure hydrogen sulfide environments.

- 35 **[0007]** Patent Literature 3 discloses a steel material that is a starting material for high-strength oil-well steel pipes which consists of, in mass%, C: 0.20 to 0.45%, Si: 0.05 to 0.40%, Mn: 0.3 to 0.9%, P: 0.015% or less, S: 0.005% or less, Al: 0.005 to 0.10%, N: 0.001 to 0.006%, Cr: 0.1 to 0.8%, Mo: 0.1 to 1.6%, V: 0.02 to 0.2%, Nb: 0.001 to 0.04%, B: 0.0003 to 0.0030%, and O (oxygen): 0.0030% or less, with the balance being Fe and unavoidable impurities. In addition, in this steel material, the Rockwell hardness HRC satisfies the formula $(15.6 \times [\%C] + 29.2 \leq HRC < 60.5 \times [\%C] + 31.1)$. It is disclosed in Patent Literature 3 that according to this steel material, a steel pipe having a yield strength of 758 to less than 862 MPa and excellent SSC resistance can be obtained.

- 45 CITATION LIST

PATENT LITERATURE

[0008]

- 50 Patent Literature 1: Japanese Patent Application Publication No. 2006-28612
 Patent Literature 2: International Application Publication No. WO2008/123422
 Patent Literature 3: Japanese Patent Application Publication No. 2017-166060

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SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009] In this connection, in the case of an oil-well steel material, minute scratches may be formed on the surface of the steel material during transportation or during drilling. Furthermore, as mentioned above, in the case of an oil-well steel material, stress is applied to the steel material during use. Therefore, when stress is applied to a steel material on the surface on which minute scratches have been formed, there is a possibility that the minute scratches will become the starting points of cracks and that the cracks will propagate. Thus, oil-well steel materials are required to have resistance to fractures even when minute scratches have been formed on the oil-well steel materials.

[0010] In the present description, having high resistance to fractures in a case where minute scratches are formed on a steel material and stress is applied thereto is referred to as "having excellent fracture toughness". That is, the more excellent the fracture toughness is, the more difficult it is for a fracture to occur even when stress is applied to a steel material on which minute scratches have been formed. On the other hand, in general, there is a tendency for the fracture toughness to decrease as the yield strength of a steel material increases. Therefore, there is a need for oil-well steel materials to compatibly achieve both a high yield strength and excellent fracture toughness. However, in each of the aforementioned Patent Literatures 1 to 3, the fracture toughness of the steel material is not investigated.

[0011] An objective of the present disclosure is to provide a steel material that achieves both high strength and excellent fracture toughness.

SOLUTION TO PROBLEM

[0012] A steel material according to the present disclosure consisting of, in mass%,

C: 0.10 to 0.45%,
Si: 1.00% or less,
Mn: 0.01 to 1.00%,
P: 0.050% or less,

S: 0.0050% or less,
Al: 0.001 to 0.100%,
Cr: 0.1 to 2.0%,
Mo: 0.20 to 2.00%,
N: 0.010% or less,

W: 0 to 0.50%,
Co: 0 to 0.50%,
Ni: 0 to 0.50%,
rare earth metal: 0 to 0.020%,
Cu: 0 to 0.50%, and
B: 0 to 0.0100%,

further contains one or more elements selected from a group consisting of:

Ca: 0.0005 to 0.0200%, and
Mg: 0.0005 to 0.0200%,

further contains one or more elements selected from a group consisting of:

Ti: 0.001 to 0.300%,
Nb: 0.001 to 0.300%, and
V: 0.01 to 0.50%,

with the balance being Fe and impurities, and
satisfies Formula (1) and Formula (2),
wherein:

a yield strength is 862 MPa or more; and
in the steel material,

a number density of MX-type precipitates which have an equivalent circular diameter of 100 nm or less and in which, when a total content of Mo, Nb, V, and Ti is defined as 100% by mass, a content of Mo is more than 50% by mass is 20 / μm^2 or more:

$$\text{Mn} \times \text{Sp} \leq 12.0 \quad (1)$$

$$0.05 \leq 7 \times \text{Ti} + 2 \times \text{Nb} + 3 \times \text{V} \leq 0.80 \quad (2)$$

where, in Formula (1), a content of Mn in percent by mass is substituted for "Mn", and a content of S in ppm is substituted for "Sp". A content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (2). Note that, when a corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

ADVANTAGEOUS EFFECT OF INVENTION

[0013] The steel material according to the present disclosure can achieve both high strength and excellent fracture toughness.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

[FIG. 1] FIG. 1 is a view illustrating the relation between the number density ($/\mu\text{m}^2$) of Mo-based MX-type precipitates (MX-type precipitates which have an equivalent circular diameter of 100 nm or less and in which, when the total content of Mo, Nb, V, and Ti is defined as 100% by mass, the content of Mo is more than 50% by mass) and a CTOD value (mm) that is an index of fracture toughness in the present Examples.

[FIG. 2A] FIG. 2A is a schematic diagram of a single edge notched bend (SENB) test specimen that is used in a CTOD test for evaluating the fracture toughness of a steel material in the present embodiment.

[FIG. 2B] FIG. 2B is an enlarged view of a region 10 in FIG. 2A.

DESCRIPTION OF EMBODIMENTS

[0015] First, the present inventors conducted studies from the viewpoint of the chemical composition with regard to increasing the strength and the fracture toughness of steel materials for which use in oil wells is assumed. As a result, the present inventors considered that if a steel material consists of, in mass%, C: 0.10 to 0.45%, Si: 1.00% or less, Mn: 0.01 to 1.00%, P: 0.050% or less, S: 0.0050% or less, Al: 0.001 to 0.100%, Cr: 0.1 to 2.0%, Mo: 0.20 to 2.00%, N: 0.010% or less, W: 0 to 0.50%, Co: 0 to 0.50%, Ni: 0 to 0.50%, rare earth metal: 0 to 0.020%, Cu: 0 to 0.50%, and B: 0 to 0.0100%, contains one or more elements selected from a group consisting of Ca: 0.0005 to 0.0200% and Mg: 0.0005 to 0.0200%, and contains one or more elements selected from a group consisting of Ti: 0.001 to 0.300%, Nb: 0.001 to 0.300%, and V: 0.01 to 0.50%, and with the balance being Fe and impurities, there is a possibility that a high yield strength of 862 MPa or more (125 ksi or more) and excellent fracture toughness can both be achieved.

[0016] Next, the present inventors focused their attention on Mn sulfides in the steel material. When subjected to hot working, Mn sulfides tend to become elongated and also tend to become coarse. Further, when coarse Mn sulfides are formed in a steel material, the fracture toughness of the steel material is markedly reduced. Therefore, the present inventors considered that if it can be made difficult for coarse Mn sulfides to form in a steel material, the fracture toughness will be increased while maintaining the yield strength of the steel material.

[0017] Therefore, the present inventors investigated various methods for reducing coarse Mn sulfides in a steel material having the chemical composition described above. As a result, it was revealed that in a steel material having the chemical composition described above, if the chemical composition satisfies the following Formula (1), coarse Mn sulfides in the steel material can be reduced:

$$\text{Mn} \times \text{Sp} \leq 12.0 \quad (1)$$

where, in Formula (1), the content of Mn in percent by mass is substituted for "Mn", and the content of S in ppm is substituted for "Sp".

[0018] Let Fn1 be defined as $\text{Fn1} = \text{Mn} \times \text{Sp}$. Fn1 is an index of Mn sulfides in the steel material. If Fn1 is more than 12.0, a large number of coarse Mn sulfides will be formed in the steel material, and the fracture toughness of the steel material will decrease. Therefore, in the steel material according to the present embodiment, on the precondition that the steel material has the chemical composition described above, Fn1 is made 12.0 or less. As a result, on the condition that the other requirements of the present embodiment are satisfied, a yield strength of 862 MPa or more and excellent fracture toughness can both be achieved.

[0019] On the other hand, even when steel materials had the chemical composition described above and also satisfied Formula (1), in some cases both a yield strength of 862 MPa or more and excellent fracture toughness could not be stably achieved. Therefore, the present inventors investigated various techniques for stably increasing fracture toughness while maintaining yield strength with respect to steel materials that had the chemical composition described above and that

[0020] Specifically, the present inventors focused on fine precipitates, and conducted studies with regard to increasing the fracture toughness of the steel material. As a result of the detailed studies of the present inventors it was revealed that in a steel material that has the chemical composition described above and that satisfies Formula (1), if MX-type precipitates in which Mo is concentrated are finely dispersed, excellent fracture toughness is stably increased while maintaining yield

[0021] First, in a steel material having the chemical composition described above, MX-type precipitates mainly consist of precipitates which have an equivalent circular diameter of 100 nm or less, and the number of the MX-type precipitates which have an equivalent circular diameter of more than 100 nm is negligibly small. Therefore, in the present description, MX-type precipitates which have an equivalent circular diameter of 100 nm or less and in which, when the total content of Mo, Nb, V, and Ti is defined as 100% by mass, the content of Mo is more than 50% by mass are also referred to as "Mo-based MX-type precipitates".

[0022] FIG. 1 is a view illustrating the relation between the number density ($/\mu\text{m}^2$) of Mo-based MX-type precipitates and a CTOD value (mm) that is an index of fracture toughness in the present Examples. FIG. 1 was prepared using, with respect to steel materials that had the chemical composition described above and that satisfied Formula (1) among examples that are described later, a number density ($/\mu\text{m}^2$) of Mo-based MX-type precipitates determined by a method to be described later and a CTOD value (mm) obtained by a CTOD test to be described later. Note that, each of the steel materials in FIG. 1 had a yield strength of 862 MPa or more.

[0023] Referring to FIG. 1, it can be confirmed that in steel materials having the chemical composition described above and satisfying Formula (1), and also having a yield strength of 862 MPa or more, if the number density of Mo-based MX-type precipitates is $20 /\mu\text{m}^2$ or more, the CTOD value stably becomes 0.11 mm or more. Therefore, the steel material according to the present embodiment has the chemical composition described above and satisfies Formula (1), and furthermore, the number density of Mo-based MX-type precipitates in the steel material is made $20 /\mu\text{m}^2$ or more. As a result, even though the steel material according to the present embodiment has a yield strength of 862 MPa or more, the steel material has excellent fracture toughness with a CTOD value of 0.11 mm or more.

[0024] Note that, the mechanism by which the fracture toughness is increased while the yield strength of the steel material is maintained as a result of the number density of MX-type precipitates which have an equivalent circular diameter of 100 nm or less and in which, when the total content of Mo, Nb, V, and Ti is defined as 100% by mass, the content of Mo is more than 50% by mass (Mo-based MX-type precipitates) being made a number density of $20 /\mu\text{m}^2$ or more has not been clarified in detail. However, the present inventors surmise that the mechanism is as follows. In the chemical composition described above, almost all of the MX-type precipitates which have an equivalent circular diameter of 100 nm or less are carbides, and mainly consist of MC-type carbides. It is likely for MC-type carbides to be finely dispersed in the steel material. On the other hand, when the dispersed MC-type carbides are too hard, it is difficult to increase the fracture toughness of the steel material. Therefore, when the MC-type carbides are made Mo-based MC-type carbides in which Mo is relatively concentrated, the hardness of the MC-type carbides decreases. That is, MC-type carbides that have an appropriate hardness can be finely dispersed in the steel material. As a result, the fracture toughness can be increased while maintaining the strength of the steel material.

[0025] There is also a possibility that the mechanism by which the fracture toughness of the steel material is increased while maintaining the yield strength of the steel material is different to the above mechanism surmised by the present inventors. However, the fact that a steel material which has the chemical composition described above and which satisfies Formula (1), and in which the number density of Mo-based MX-type precipitates is $20 /\mu\text{m}^2$ or more has excellent fracture toughness while maintaining the yield strength has been proven by examples that are described later.

[0026] As a result of further detailed studies conducted by the present inventors based on the above findings, it was revealed that in addition to having the chemical composition described above and satisfying Formula (1), by the chemical composition also satisfying the following Formula (2), the number density of Mo-based MX-type precipitates is stably increased to $20 /\mu\text{m}^2$ or more:

$$0.05 \leq 7 \times \text{Ti} + 2 \times \text{Nb} + 3 \times \text{V} \leq 0.80 \quad (2)$$

where, the content of the corresponding element in percent by mass is substituted for each symbol of an element in Formula (2). Note that, if the corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

[0027] Let Fn2 be defined as $\text{Fn2} = 7 \times \text{Ti} + 2 \times \text{Nb} + 3 \times \text{V}$. Fn2 is an index relating to the precipitation state of carbides. Ti, Nb, and/or V form MX-type precipitates. If Fn2 is too low, MX-type precipitates themselves cannot be sufficiently formed.

Consequently, the number density of Mo-based MX-type precipitates will decrease. On the other hand, if Fn2 is too high, the content of Mo in the MX-type precipitates will decrease. As a result, the number density of Mo-based MX-type precipitates will decrease. Therefore, in the steel material according to the present embodiment, on the precondition that the steel material has the chemical composition described above and satisfies Formula (1), Fn2 is made 0.05 to 0.80. As a result, the number density of Mo-based MX-type precipitates can be stably increased to 20 / μm^2 or more.

[0028] As described above, the steel material according to the present embodiment has the chemical composition described above, and also satisfies Formulae (1) and (2), and has a yield strength of 862 MPa or more, and in addition, the number density of Mo-based MX-type precipitates in the steel material is 20 / μm^2 or more. As a result, the steel material according to the present embodiment can achieve both high strength and excellent fracture toughness.

[0029] The gist of the steel material according to the present embodiment, which was completed based on the findings described above, is as follows.

[0030]

[1] A steel material consisting of, in mass%,

C: 0.10 to 0.45%,
Si: 1.00% or less,
Mn: 0.01 to 1.00%,
P: 0.050% or less,
S: 0.0050% or less,
Al: 0.001 to 0.100%,
Cr: 0.1 to 2.0%,
Mo: 0.20 to 2.00%,
N: 0.010% or less,
W: 0 to 0.50%,
Co: 0 to 0.50%,
Ni: 0 to 0.50%,
rare earth metal: 0 to 0.020%,
Cu: 0 to 0.50%, and
B: 0 to 0.0100%,
further containing one or more elements selected from a group consisting of:

Ca: 0.0005 to 0.0200%, and
Mg: 0.0005 to 0.0200%,

further containing one element or more selected from a group consisting of:

Ti: 0.001 to 0.300%,
Nb: 0.001 to 0.300%, and
V: 0.01 to 0.50%,
with the balance being Fe and impurities, and
satisfying Formula (1) and Formula (2),
wherein:

a yield strength is 862 MPa or more; and

in the steel material,
a number density of MX-type precipitates which have an equivalent circular diameter of 100 nm or less and in which, when a total content of Mo, Nb, V, and Ti is defined as 100% by mass, a content of Mo is more than 50% by mass is 20 / μm^2 or more:

$$\text{Mn} \times \text{Sp} \leq 12.0 \quad (1)$$

$$0.05 \leq 7 \times \text{Ti} + 2 \times \text{Nb} + 3 \times \text{V} \leq 0.80 \quad (2)$$

where, in Formula (1), a content of Mn in percent by mass is substituted for "Mn", and a content of S in ppm is substituted for "Sp". A content of a corresponding element in percent by mass is substituted for each symbol

of an element in Formula (2). Note that, when a corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

[2] The steel material according to [1], containing one or more elements selected from a group consisting of:

W: 0.01 to 0.50%,
Co: 0.01 to 0.50%,
Ni: 0.01 to 0.50%,
rare earth metal: 0.001 to 0.020%,
Cu: 0.01 to 0.50%, and
B: 0.0001 to 0.0100%.

[3] The steel material according to [1] or [2], wherein:
the steel material is an oil-well steel pipe.

[0031] The shape of the steel material according to the present embodiment is not particularly limited. The steel material according to the present embodiment may be a steel pipe, may be a round steel bar (a solid material), or may be a steel plate. Note that, the term "round steel bar" means a steel bar in which a cross section perpendicular to the axial direction is a circular shape. Further, the steel pipe may be a seamless steel pipe or may be a welded steel pipe.

[0032] In the present description, the oil-well steel pipe may be a steel pipe that is used for oil country tubular goods. The oil country tubular goods are, for example, steel pipes used for casing pipes or tubing pipes. The oil-well steel pipe according to the present embodiment is preferably a seamless steel pipe. When the oil-well steel pipe according to the present embodiment is a seamless steel pipe, even if the wall thickness is 15 mm or more, a yield strength of 862 MPa or more (125 ksi or more) and excellent fracture toughness can both be achieved.

[0033] Hereunder, the steel material according to the present embodiment is described in detail. The symbol "%" relating to an element means "mass percent" unless otherwise noted.

[Chemical composition]

[0034] The chemical composition of the steel material according to the present embodiment contains the following elements.

C: 0.10 to 0.45%

[0035] Carbon (C) increases hardenability of the steel material and increases the strength of the steel material. If the content of C is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of C is too high, even if the contents of other elements are within the range of the present embodiment, in some cases quench cracking will easily occur during quenching in the production process. Therefore, the content of C is 0.10 to 0.45%. A preferable lower limit of the content of C is 0.12%, more preferably is 0.15%, and further preferably is 0.20%. A preferable upper limit of the content of C is 0.40%, more preferably is 0.38%, and further preferably is 0.37%.

Si: 1.00% or less

[0036] Silicon (Si) is unavoidably contained. That is, the lower limit of the content of Si is more than 0%. Si deoxidizes the steel. On the other hand, if the content of Si is too high, even if the contents of other elements are within the range of the present embodiment, formation of carbides will be suppressed and the fracture toughness of the steel material will decrease. Therefore, the content of Si is 1.00% or less. A preferable upper limit of the content of Si is 0.90%, more preferably is 0.80%, further preferably is 0.75%, further preferably is 0.60%, and further preferably is 0.50%. A preferable lower limit of the content of Si in order to effectively obtain the aforementioned advantageous effect is 0.05%, more preferably is 0.10%, and further preferably is 0.15%.

Mn: 0.01 to 1.00%

[0037] Manganese (Mn) deoxidizes the steel. Mn also increases hardenability of the steel material and increases the strength of the steel material. If the content of Mn is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Mn is too high, even if the contents of other elements are within the range of the present embodiment, coarse Mn

sulfides will be formed and the fracture toughness of the steel material will decrease. Therefore, the content of Mn is 0.01 to 1.00%. A preferable lower limit of the content of Mn is 0.03%, more preferably is 0.05%, and further preferably is 0.10%. A preferable upper limit of the content of Mn is 0.90%, more preferably is 0.85%, further preferably is 0.80%, and further preferably is 0.75%.

P: 0.050% or less

[0038] Phosphorus (P) is an impurity. That is, the lower limit of the content of P is more than 0%. If the content of P is too high, even if the contents of other elements are within the range of the present embodiment, P will segregate to grain boundaries and the fracture toughness of the steel material will decrease. Therefore, the content of P is 0.050% or less. A preferable upper limit of the content of P is 0.040%, more preferably is 0.030%, further preferably is 0.020%, and further preferably is 0.015%. The content of P is preferably as low as possible. However, excessively reducing the content of P will significantly increase the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of P is 0.001%, more preferably is 0.002%, and further preferably is 0.003%.

S: 0.0050% or less

[0039] Sulfur (S) is an impurity. That is, the lower limit of the content of S is more than 0%. If the content of S is too high, even if the contents of other elements are within the range of the present embodiment, coarse Mn sulfides will be formed and the fracture toughness of the steel material will decrease. Therefore, the content of S is 0.0050% or less. A preferable upper limit of the content of S is 0.0040%, more preferably is 0.0030%, and further preferably is 0.0020%. The content of S is preferably as low as possible. However, excessively reducing the content of S will significantly increase the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of S is 0.0001%, more preferably is 0.0005%, and further preferably is 0.0010%.

Al: 0.001 to 0.100%

[0040] Aluminum (Al) deoxidizes the steel. If the content of Al is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained and corrosion resistance of the steel material will decrease. On the other hand, if the content of Al is too high, even if the contents of other elements are within the range of the present embodiment, coarse oxide-based inclusions will form and corrosion resistance of the steel material will decrease. Therefore, the content of Al is 0.001 to 0.100%. A preferable lower limit of the content of Al is 0.005%, more preferably is 0.010%, further preferably is 0.020%, and further preferably is 0.025%. A preferable upper limit of the content of Al is 0.080%, more preferably is 0.060%, and further preferably is 0.050%. As used in the present description, the content of "Al" means the content of "acid-soluble Al", that is, "sol. Al".

Cr: 0.1 to 2.0%

[0041] Chromium (Cr) increases hardenability of the steel material. Cr also increases temper softening resistance of the steel material and thereby enables high-temperature tempering. As a result, the fracture toughness of the steel material increases. If the content of Cr is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Cr is too high, even if the contents of other elements are within the range of the present embodiment, corrosion resistance of the steel material will decrease. Therefore, the content of Cr is 0.1 to 2.0%. A preferable lower limit of the content of Cr is 0.2%, and more preferably is 0.4%. A preferable upper limit of the content of Cr is 1.9%, more preferably is 1.8%, further preferably is 1.5%, and further preferably is 1.0%.

Mo: 0.20 to 2.00%

[0042] Molybdenum (Mo) increases hardenability of the steel material. Mo also forms Mo-based MX-type precipitates and increases the fracture toughness of the steel material. If the content of Mo is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Mo is too high, the aforementioned advantageous effects will be saturated. Therefore, the content of Mo is 0.20 to 2.00%. A preferable lower limit of the content of Mo is 0.25%, more preferably is 0.30%, and further preferably is 0.50%. A preferable upper limit of the content of Mo is 1.90%, more preferably is 1.80%, further preferably is 1.60%, and further preferably is 1.40%.

N: 0.010% or less

[0043] Nitrogen (N) is unavoidably contained. That is, the lower limit of the content of N is more than 0%. N combines with Ti to form nitrides, and refines the grains of the steel material by the pinning effect. As a result, the strength of the steel material increases. However, if the content of N is too high, even if the contents of other elements are within the range of the present embodiment, coarse nitrides will be formed and the fracture toughness of the steel material will decrease. Therefore, the content of N is 0.010% or less. A preferable upper limit of the content of N is 0.008%, and more preferably is 0.006%. A preferable lower limit of the content of N for more effectively obtaining the aforementioned advantageous effect is 0.001%, more preferably is 0.002%, and further preferably is 0.003%.

[0044] The chemical composition of the steel material according to the present embodiment contains one or more elements selected from the group consisting of Ca and Mg. In other words, in the chemical composition of the steel material according to the present embodiment, the content of either one of Ca and Mg may be 0%. Each of these elements increases hot workability of the steel material.

Ca: 0.0005 to 0.0200%

[0045] Calcium (Ca) immobilizes S in the steel material as a sulfide to make S harmless, and thereby increases corrosion resistance of the steel material. However, if the content of Ca is too high, even if the contents of other elements are within the range of the present embodiment, oxides in the steel material will coarsen and the fracture toughness of the steel material will decrease. Therefore, when contained, the content of Ca is 0.0005 to 0.0200%. A preferable lower limit of the content of Ca is more than 0.0006%, more preferably is 0.0008%, and further preferably is 0.0010%. A preferable upper limit of the content of Ca is 0.0150%, more preferably is 0.0100%, further preferably is 0.0060%, and further preferably is 0.0040%.

Mg: 0.0005 to 0.0200%

[0046] Magnesium (Mg) immobilizes S in the steel material as a sulfide to make S harmless, and thereby increases corrosion resistance of the steel material. However, if the content of Mg is too high, even if the contents of other elements are within the range of the present embodiment, oxides in the steel material will coarsen and the fracture toughness of the steel material will decrease. Therefore, when contained, the content of Mg is 0.0005 to 0.0200%. A preferable lower limit of the content of Mg is more than 0.0006%, more preferably is 0.0008%, and further preferably is 0.0010%. A preferable upper limit of the content of Mg is 0.0150%, more preferably is 0.0100%, further preferably is 0.0060%, and further preferably is 0.0040%.

[0047] The chemical composition of the steel material according to the present embodiment contains one or more elements selected from the group consisting of Ti, Nb, and V. In other words, in the chemical composition of the steel material according to the present embodiment, as long as any one of Ti, Nb, and V is contained, the contents of the other elements among Ti, Nb, and V may be 0%. Each of these elements forms composite MX-type precipitates together with Mo, and thereby increases the fracture toughness of the steel material.

Ti: 0.001 to 0.300%

[0048] Titanium (Ti) forms Mo-based MX-type precipitates together with Mo, and thereby increases the fracture toughness of the steel material. The Mo-based MX-type precipitates containing Ti also refine the grains of the steel material by the pinning effect, and thereby increase the fracture toughness of the steel material. However, if the content of Ti is too high, even if the contents of other elements are within the range of the present embodiment, the content of Ti in the Mo-based MX-type precipitates will become too high and the content of Mo in the Mo-based MX-type precipitates will decrease. As a result, the fracture toughness of the steel material will, on the contrary, decrease. Therefore, when contained, the content of Ti is 0.001 to 0.300%. A preferable lower limit of the content of Ti is 0.002%, more preferably is 0.003%, further preferably is 0.005%, and further preferably is 0.010%. A preferable upper limit of the content of Ti is 0.250%, more preferably is 0.150%, further preferably is 0.100%, further preferably is 0.080%, and further preferably is 0.060%.

Nb: 0.001 to 0.300%

[0049] Niobium (Nb) forms Mo-based MX-type precipitates together with Mo, and thereby increases the fracture toughness of the steel material. The Mo-based MX-type precipitates containing Nb also refine the grains of the steel material by the pinning effect, and thereby increase the fracture toughness of the steel material. In addition, Nb increases the temper softening resistance of the steel material and increases the strength of the steel material. However, if the

content of Nb is too high, even if the contents of other elements are within the range of the present embodiment, the content of Nb in the Mo-based MX-type precipitates will become too high and the content of Mo in the Mo-based MX-type precipitates will decrease. As a result, the fracture toughness of the steel material will, on the contrary, decrease. Therefore, when contained, the content of Nb is 0.001 to 0.300%. A preferable lower limit of the content of Nb is 0.003%, more preferably is 0.005%, and further preferably is 0.010%. A preferable upper limit of the content of Nb is 0.250%, more preferably is 0.150%, further preferably is 0.100%, and further preferably is 0.080%.

V: 0.01 to 0.50%

[0050] Vanadium (V) forms Mo-based MX-type precipitates together with Mo, and thereby increases the fracture toughness of the steel material. The Mo-based MX-type precipitates containing V also refine the grains of the steel material by the pinning effect, and thereby increase the fracture toughness of the steel material. In addition, V increases temper softening resistance of the steel material and increases the strength of the steel material. However, if the content of V is too high, even if the contents of other elements are within the range of the present embodiment, the content of V in the Mo-based MX-type precipitates will become too high and the content of Mo in the Mo-based MX-type precipitates will decrease. As a result, the fracture toughness of the steel material will, on the contrary, decrease. Therefore, when contained, the content of V is 0.01 to 0.50%. A preferable lower limit of the content of V is 0.01%, more preferably is 0.02%, and further preferably is 0.05%. A preferable upper limit of the content of V is 0.40%, more preferably is 0.30%, and further preferably is 0.20%.

[0051] The balance of the chemical composition of the steel material according to the present embodiment is Fe and impurities. Here, the term "impurities" refers to substances which, when industrially producing the steel material, are mixed in from ore or scrap used as the raw material or from the production environment or the like, and which are allowed within a range that does not adversely affect the steel material according to the present embodiment.

[Optional elements]

[0052] The chemical composition of the steel material described above may further contain one or more elements selected from the group consisting of W, Co, Ni, and rare earth metal in lieu of a part of Fe. Each of these elements increases corrosion resistance of the steel material.

W: 0 to 0.50%

[0053] Tungsten (W) is an optional element, and does not have to be contained. That is, the content of W may be 0%. When contained, W forms a protective corrosion coating in a corrosive environment and suppresses penetration of hydrogen into the steel material. As a result, corrosion resistance of the steel material is increased. If even a small amount of W is contained, the aforementioned advantageous effect will be obtained to a certain extent. However, if the content of W is too high, even if the contents of other elements are within the range of the present embodiment, coarse carbides will form in the steel material, and corrosion resistance of the steel material will decrease. Therefore, the content of W is 0 to 0.50%. A preferable lower limit of the content of W is more than 0%, and more preferably is 0.01%. A preferable upper limit of the content of W is 0.40%, more preferably is 0.30%, further preferably is 0.20%, and further preferably is 0.10%.

Co: 0 to 0.50%

[0054] Cobalt (Co) is an optional element, and does not have to be contained. That is, the content of Co may be 0%. When contained, Co forms a protective corrosion coating in a corrosive environment and suppresses penetration of hydrogen into the steel material. As a result, corrosion resistance of the steel material is increased. If even a small amount of Co is contained, the aforementioned advantageous effect will be obtained to a certain extent. However, if the content of Co is too high, even if the contents of other elements are within the range of the present embodiment, hardenability of the steel material will decrease and the strength of the steel material will decrease. Therefore, the content of Co is 0 to 0.50%. A preferable lower limit of the content of Co is more than 0%, more preferably is 0.01%, and further preferably is 0.02%. A preferable upper limit of the content of Co is 0.40%, more preferably is 0.30%, and further preferably is 0.20%.

Ni: 0 to 0.50%

[0055] Nickel (Ni) is an optional element, and does not have to be contained. That is, the content of Ni may be 0%. When contained, Ni dissolves in the steel and increases corrosion resistance of the steel material. If even a small amount of Ni is contained, these advantageous effects will be obtained to a certain extent. However, if the content of Ni is too high, even if the contents of other elements are within the range of the present

embodiment, local corrosion will be promoted and corrosion resistance of the steel material will decrease. Therefore, the content of Ni is 0 to 0.50%. A preferable lower limit of the content of Ni is more than 0%, more preferably is 0.01%, and further preferably is 0.02%. A preferable upper limit of the content of Ni is 0.40%, more preferably is 0.30%, further preferably is 0.20%, and further preferably is 0.15%.

Rare earth metal (REM): 0 to 0.020%

[0056] Rare earth metal (REM) is an optional element, and does not have to be contained. That is, the content of REM may be 0%. When contained, REM immobilizes S in the steel material as a sulfide to make S harmless, and thereby increases corrosion resistance of the steel material. If even a small amount of REM is contained, the aforementioned advantageous effect will be obtained to a certain extent. However, if the content of REM is too high, even if the contents of other elements are within the range of the present embodiment, oxides in the steel material will coarsen and corrosion resistance of the steel material will decrease. Therefore, the content of REM is 0 to 0.020%. A preferable lower limit of the content of REM is more than 0%, more preferably is 0.001%, further preferably is 0.003%, and further preferably is 0.005%. A preferable upper limit of the content of REM is 0.018%, and more preferably is 0.015%.

[0057] Note that, in the present description the term "REM" means one or more types of element selected from the group consisting of scandium (Sc) which is the element with atomic number 21, yttrium (Y) which is the element with atomic number 39, and the elements from lanthanum (La) with atomic number 57 to lutetium (Lu) with atomic number 71 that are lanthanoids. In the present description, the term "content of REM" means the total content of these elements.

[0058] The chemical composition of the steel material described above may further contain one or more elements selected from the group consisting of Cu and B in lieu of a part of Fe. Each of these elements increases hardenability of the steel material and increases the strength of the steel material.

Cu: 0 to 0.50%

[0059] Copper (Cu) is an optional element, and does not have to be contained. That is, the content of Cu may be 0%. When contained, Cu increases hardenability of the steel material and increases the strength of the steel material. If even a small amount of Cu is contained, the aforementioned advantageous effects will be obtained to a certain extent. However, if the content of Cu is too high, even if the contents of other elements are within the range of the present embodiment, hardenability of the steel material will become too high and corrosion resistance of the steel material will decrease. Therefore, the content of Cu is 0 to 0.50%. A preferable lower limit of the content of Cu is more than 0%, more preferably is 0.01%, further preferably is 0.02%, and further preferably is 0.05%. A preferable upper limit of the content of Cu is 0.35%, more preferably is 0.25%, and further preferably is 0.15%.

B: 0 to 0.0100%

[0060] Boron (B) is an optional element, and does not have to be contained. That is, the content of B may be 0%. When contained, B increases hardenability of the steel material and increases the strength of the steel material. If even a small amount of B is contained, the aforementioned advantageous effects will be obtained to a certain extent. However, if the content of B is too high, even if the contents of other elements are within the range of the present embodiment, coarse nitrides will form and corrosion resistance of the steel material will decrease. Therefore, the content of B is 0 to 0.0100%. A preferable lower limit of the content of B is more than 0%, more preferably is 0.0001%, further preferably is 0.0003%, and further preferably is 0.0005%. A preferable upper limit of the content of B is 0.0080%, and more preferably is 0.0060%.

[Formula (1)]

[0061] On the precondition that the steel material according to the present embodiment has the chemical composition described above, the steel material satisfies the following Formula (1). As a result, on the condition that the other requirements of the present embodiment are satisfied, the steel material according to the present embodiment can achieve both a yield strength of 862 MPa or more and excellent fracture toughness.

$$Mn \times Sp \leq 12.0 \quad (1)$$

where, in Formula (1), the content of Mn in percent by mass is substituted for "Mn", and the content of S in ppm is substituted for "Sp".

[0062] Fn1 (= Mn × Sp) is an index of Mn sulfides in the steel material. If Fn1 is more than 12.0, a large number of coarse Mn sulfides will form in the steel material, and the fracture toughness of the steel material will decrease. Therefore, in the

steel material according to the present embodiment, on the precondition that the steel material has the chemical composition described above, Fn1 is made 12.0 or less. As a result, on the condition that the other requirements of the present embodiment are satisfied, a yield strength of 862 MPa or more and excellent fracture toughness can both be achieved.

[0063] A more preferable upper limit of Fn1 is 11.5, further preferably is 11.0, and further preferably is 10.0. Note that, the lower limit of Fn1 is not particularly limited, and for example may be 0.1. However, when taking industrial production into consideration, a preferable lower limit of Fn1 is 0.3, and more preferably is 0.5.

[Formula (2)]

[0064] On the precondition that the steel material according to the present embodiment has the chemical composition described above and satisfies Formula (1), the steel material satisfies the following Formula (2). As a result, on the condition that the other requirements of the present embodiment are satisfied, the steel material according to the present embodiment can achieve both a yield strength of 862 MPa or more and excellent fracture toughness.

$$0.05 \leq 7 \times \text{Ti} + 2 \times \text{Nb} + 3 \times \text{V} \leq 0.80 \quad (2)$$

where, the content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (2). Note that, when a corresponding element is not contained, "0" is substituted for the symbol of the relevant element.

[0065] Fn2 ($= 7 \times \text{Ti} + 2 \times \text{Nb} + 3 \times \text{V}$) is an index relating to the precipitation state of carbides. Ti, Nb, and/or V form MX-type precipitates. If Fn2 is too low, the MX-type precipitates themselves cannot be sufficiently formed. Consequently, the number density of Mo-based MX-type precipitates will decrease. On the other hand, if Fn2 is too high, the content of Mo in the MX-type precipitates will decrease. As a result, the number density of Mo-based MX-type precipitates will decrease. Therefore, in the steel material according to the present embodiment, on the precondition that the steel material has the chemical composition described above and satisfies Formula (1), Fn2 is made 0.05 to 0.80. As a result, the number density of Mo-based MX-type precipitates can be stably increased to 20 / μm^2 or more.

[0066] A preferable lower limit of Fn2 is 0.08, more preferably is 0.10, and further preferably is 0.15. A preferable upper limit of Fn2 is 0.75, more preferably is 0.70, and further preferably is 0.60.

[Yield strength]

[0067] The steel material according to the present embodiment has the chemical composition described above, and also satisfies Formulae (1) and (2), and in addition, the number density of Mo-based MX-type precipitates in the steel material is made 20 / μm^2 or more. As a result, even though the yield strength is 862 MPa or more, the steel material according to the present embodiment has excellent fracture toughness. In short, the yield strength of the steel material according to the present embodiment is 862 MPa or more. In the present embodiment, although an upper limit of the yield strength is not particularly limited, and for example, the upper limit of the yield strength is 965 MPa. As used herein, the term "yield strength" means 0.6% total elongation proof stress (MPa) obtained by a tensile test conducted at normal temperature ($24 \pm 3^\circ\text{C}$) in accordance with ASTM E8/E8M (2021) that is described hereunder.

[0068] Specifically, in the present embodiment, the yield strength of the steel material is determined by the following method. First, a tensile test specimen is prepared from the steel material according to the present embodiment. The size of the tensile test specimen is not particularly limited. For example, a round bar tensile test specimen in which the diameter of the parallel portion is 6 mm and the gage length is 30 mm is used as the tensile test specimen. If the steel material is a steel pipe, the tensile test specimen is prepared from the center position of the wall thickness. In this case, the longitudinal direction of the tensile test specimen is to be made parallel to the axial direction of the steel pipe. If the steel material is a round steel bar, the tensile test specimen is prepared from an R/2 position. Note that, in the present description, the term "R/2 position" of a round steel bar means the center position of a radius R in a cross section perpendicular to the axial direction of the round steel bar. Further, in this case, the longitudinal direction of the tensile test specimen is to be made parallel to the axial direction of the round steel bar. If the steel material is a steel plate, the tensile test specimen is prepared from the center position of the thickness. In this case, the longitudinal direction of the tensile test specimen is to be made parallel to the rolling elongation direction of the steel plate. A tensile test is carried out in air at normal temperature ($24 \pm 3^\circ\text{C}$) in accordance with ASTM E8/E8M (2021) using the prepared tensile test specimen, and the 0.6% total elongation proof stress (MPa) is determined. The determined 0.6% total elongation proof stress is defined as the yield strength (MPa).

[Mo-based MX-type precipitates]

[0069] The steel material according to the present embodiment has the chemical composition described above, and satisfies Formulae (1) and (2), and in addition, the number density of MX-type precipitates which have an equivalent

circular diameter of 100 nm or less and in which, when the total content of Mo, Nb, V, and Ti is defined as 100% by mass, the content of Mo is more than 50% by mass is $20/\mu\text{m}^2$ or more. As a result, the steel material according to the present embodiment has excellent fracture toughness even though the yield strength is 862 MPa or more. As mentioned above, in the present description, MX-type precipitates which have an equivalent circular diameter of 100 nm or less and in which, when the total content of Mo, Nb, V, and Ti is defined as 100% by mass, the content of Mo is more than 50% by mass are also referred to as "Mo-based MX-type precipitates".

[0070] Here, most MX-type precipitates that have an equivalent circular diameter of 100 nm or less are MC-type carbides. Further, it is likely for MC-type carbides to be finely dispersed in the steel material. On the other hand, depending on the elements that constitute the MC-type carbides, in some cases the hardness of MC-type carbides will be too high. In such a case, it is difficult to increase the fracture toughness while maintaining the strength of the steel material. Therefore, in the present embodiment, MC-type carbides that contain Nb and/or V and/or Ti are made into MC-type carbides in which Mo is concentrated (Mo-based MX-type precipitates) as composite carbides with Mo. Furthermore, in the present embodiment, the number density of the Mo-based MX-type precipitates is raised. As a result, precipitates that have an appropriate hardness are finely dispersed in the steel material, and thus the fracture toughness of the steel material can be increased while maintaining the yield strength of the steel material.

[0071] Therefore, in the present embodiment, the steel material has the chemical composition described above, satisfies Formulae (1) and (2), and the number density of Mo-based MX-type precipitates in the steel material is $20/\mu\text{m}^2$ or more. A preferable lower limit of the number density of Mo-based MX-type precipitates is $21/\mu\text{m}^2$, more preferably is $23/\mu\text{m}^2$, and further preferably is $25/\mu\text{m}^2$. The upper limit of the number density of Mo-based MX-type precipitates is not particularly limited, and for example is $200/\mu\text{m}^2$.

[0072] In the present embodiment, the number density of Mo-based MX-type precipitates is determined by the following method. First, a micro test specimen for preparing an extraction replica is prepared from the steel material according to the present embodiment. If the steel material is a steel pipe, the micro test specimen is taken from the center position of the wall thickness. If the steel material is a round steel bar, the micro test specimen is taken from the R/2 position. If the steel material is a steel plate, the micro test specimen is taken from the center position of the thickness. The size of the micro test specimen is, for example, $10\text{ mm} \times 10\text{ mm}$. The surface of the micro test specimen is mirror-polished, and thereafter the micro test specimen is immersed for 10 minutes in a 3% nital etching reagent to etch the surface. The etched surface is then covered with a carbon deposited film. The micro test specimen whose surface is covered with the deposited film is immersed for 20 minutes in a 5% nital etching reagent. The deposited film is thereby peeled off from the immersed micro test specimen. The deposited film that peeled off from the micro test specimen is cleaned with ethanol, and thereafter is scooped up with a sheet mesh and dried. Note that, in the present embodiment, a copper (Cu) sheet mesh is used.

[0073] The deposited film (replica film) is observed using a transmission electron microscope (TEM). Specifically, arbitrary locations are specified on the deposited film, and the specified locations are observed at an observation magnification of $\times 100000$ with an acceleration voltage of 200 kV. Note that, the size of the observation visual field is, for example, $2.0\text{ }\mu\text{m} \times 3.0\text{ }\mu\text{m}$. In each observation visual field, particles having an equivalent circular diameter of 100 nm or less are identified. Note that, it is possible to identify the particles based on the contrast. In the present description, the term "particles" is not limited to circular (spherical) small matters, and may be small matters that have an angular shape, or may be particles that have an elongated elliptical shape. Further, the equivalent circular diameter of precipitates can be determined by performing image analysis of an observation image in TEM observation. Note that, in the present embodiment, the lower limit of the equivalent circular diameter of the identified particles having an equivalent circular diameter of 100 nm or less is set as 10 nm. That is, in the present embodiment, particles having an equivalent circular diameter of 10 to 100 nm are identified.

[0074] The identified particles are subjected to point analysis by energy dispersive X-ray spectrometry (EDS). The contents of the elements contained in each particle are determined by the EDS point analysis. In the EDS point analysis, the acceleration voltage is set to 200 kV. Further, the point analysis is conducted for quantification of Mo, Nb, V, and Ti as elements to be analyzed. Here, when the total content of Mo, Nb, V, and Ti is defined as 100% by mass, precipitates in which the content of Mo is more than 70% by mass tend to be M_2X -type precipitates. Therefore, in the present embodiment, when the total content of Mo, Nb, V, and Ti is defined as 100% by mass, precipitates in which the content of Mo is 70% by mass or less are identified as MX-type precipitates. Thus, in the present embodiment, when the total content of Mo, Nb, V, and Ti which was quantified by EDS point analysis is defined as 100% by mass, particles in which the content of Mo is in the range of more than 50% to 70% by mass are identified as Mo-based MX-type precipitates.

[0075] The number density ($1/\mu\text{m}^2$) of Mo-based MX-type precipitates is determined based on the total number of the Mo-based MX-type precipitates identified in the respective observation visual fields and the total area of the observation visual fields. Note that, in the present embodiment, a value obtained by rounding off decimals of the obtained numerical value is determined as the number density of Mo-based MX-type precipitates.

[Fracture toughness]

[0076] The steel material according to the present embodiment has the chemical composition described above, and also satisfies Formulae (1) and (2), and in addition, the number density of Mo-based MX-type precipitates in the steel material is made $20 / \mu\text{m}^2$ or more. As a result, the steel material according to the present embodiment has excellent fracture toughness even though the yield strength is 862 MPa or more. As used herein, the phrase "excellent fracture toughness" means that a CTOD value obtained by a CTOD test conducted at normal temperature (25°C) in accordance with ISO 12135 (2021) that is described hereunder is 0.11 mm or more.

[0077] Specifically, in the present embodiment, the fracture toughness of the steel material is evaluated by the following method. First, a single edge notched bend (SENB) test specimen that is illustrated in FIG. 2A and FIG. 2B is prepared from the steel material according to the present embodiment. FIG. 2A is a schematic diagram of the SENB test specimen used in a CTOD test for evaluating the fracture toughness of the steel material in the present embodiment. FIG. 2B is an enlarged view of a region 10 in FIG. 2A. Referring to FIG. 2A, the SENB test specimen is prepared in a size having a thickness B of 10 mm, a width W of 20 mm, and a length L of 100 mm. If the steel material is a steel pipe, the SENB test specimen is prepared from the center position of the wall thickness. In this case, the longitudinal direction of the SENB test specimen is to be parallel to the axial direction of the steel pipe. If the steel material is a round steel bar, the SENB test specimen is prepared from an R/2 position. In this case, the longitudinal direction of the SENB test specimen is to be parallel to the axial direction of the round steel bar. If the steel material is a steel plate, the SENB test specimen is prepared from the center position of the thickness. In this case, the longitudinal direction of the SENB test specimen is to be parallel to the rolling elongation direction of the steel plate.

[0078] Referring to FIG. 2A, a notch in the width W direction is formed at the center position in the length L direction in the SENB test specimen. The notch of the SENB test specimen is formed by machining. Further, referring to FIG. 2B, the notch of the SENB test specimen is formed so as to have a width of 2 mm and a depth of 8 mm. The prepared SENB test specimen is subjected to a fatigue test to introduce a pre-crack. In the present embodiment, an initial relative crack length a_0/W is 0.50. Specifically, the fatigue test is carried out at normal temperature (25°C) so that a fatigue pre-crack introduced at the tip of the notch is 2 mm.

[0079] The SENB test specimen into which the fatigue pre-crack has been introduced is subjected to a CTOD test conducted at normal temperature (25°C) in accordance with ISO 12135 (2021). The CTOD value (mm) is determined based on ISO 12135 (2021), based on the breaking load in a load-displacement curve obtained by the CTOD test, and a plastic component of the clip gage opening displacement. Note that, the same test is conducted three times, and the smallest CTOD value (mm) is defined as the CTOD value (mm) of the steel material. In the present embodiment, a value determined by rounding off to the second decimal place of the obtained numerical value is adopted as the CTOD value of the steel material.

[Microstructure]

[0080] In the microstructure of the steel material according to the present embodiment, the total of the volume ratios of tempered martensite and tempered bainite is 90% or more. The balance of the microstructure is, for example, ferrite or pearlite. When the total of the volume ratios of tempered martensite and tempered bainite contained in the microstructure of a steel material having the chemical composition described above is 90% or more, on the condition that the other requirements of the present embodiment are satisfied, the steel material exhibits a yield strength of 125 ksi or more (862 MPa or more). That is, in the present embodiment, if the yield strength of the steel material is 125 ksi or more, it is determined that the total of the volume ratios of tempered martensite and tempered bainite in the microstructure of the steel material is 90% or more.

[0081] Note that, when determining the volume ratios of tempered martensite and tempered bainite by observation, the volume ratios can be determined by the following method. First, a test specimen is prepared from the steel material. If the steel material is a steel pipe, a test specimen having an observation surface with dimensions of 10 mm in the pipe axis direction and 8 mm in the wall thickness (pipe radius) direction is prepared from the center position of the wall thickness. Note that, in a case where the wall thickness of the steel pipe is less than 10 mm, a test specimen having an observation surface with dimensions of 10 mm in the pipe axis direction and the wall thickness of the steel pipe in the pipe radius direction is prepared. If the steel material is a round steel bar, a test specimen having an observation surface with dimensions of 10 mm in the axial direction and 8 mm in the radial direction of a cross section and which includes the R/2 position at the center thereof is prepared. Note that, in a case where the diameter of a cross section of the round steel bar is less than 10 mm, a test specimen having an observation surface with dimensions of 10 mm in the axial direction and the diameter of the round steel bar in the radial direction of the cross section and which includes the R/2 position is prepared. If the steel material is a steel plate, a test specimen having an observation surface with dimensions of 10 mm in the rolling elongation direction and 10 mm in the thickness direction is prepared from the center position of the thickness. Note that, if the thickness of the steel plate is less than 10 mm, a test specimen having an observation surface with dimensions of 10

mm in the rolling elongation direction and the thickness of the steel plate in the thickness direction is prepared.

[0082] After polishing the observation surface of the test specimen to obtain a mirror surface, the test specimen is immersed for about 10 seconds in a nital etching reagent to reveal the microstructure by etching. The etched observation surface is observed by means of a secondary electron image obtained using a scanning electron microscope (SEM), and observation is performed in 10 visual fields. The area of each visual field is, for example, 10000 μm^2 (magnification of $\times 1000$). In each visual field, tempered martensite and tempered bainite are identified based on the contrast. The area fractions of the identified tempered martensite and tempered bainite are determined. The method for determining the area fractions is not particularly limited, and a well-known method can be used. For example, the area fractions of tempered martensite and tempered bainite can be determined by image analysis. In the present embodiment, the arithmetic average value of the area fractions of tempered martensite and tempered bainite determined in all of the visual fields is defined as the volume ratio of tempered martensite and tempered bainite.

[Production method]

[0083] A method for producing the steel material according to the present embodiment will now be described. Hereunder, a method for producing a seamless steel pipe as one example of the steel material according to the present embodiment is described. The method for producing a seamless steel pipe includes a process of preparing a hollow shell (preparation process), and a process of subjecting the hollow shell to quenching and tempering to form a seamless steel pipe (quenching process and tempering process). Note that, a production method according to the present embodiment is not limited to the production method described below. Hereunder, each process is described in detail.

[Preparation process]

[0084] In the preparation process, an intermediate steel material having the chemical composition described above is prepared. A method for producing the intermediate steel material is not particularly limited as long as the intermediate steel material has the chemical composition described above. Here, the intermediate steel material is a plate-shaped steel material in a case where the end product is a steel plate, and is a hollow shell in a case where the end product is a steel pipe.

[0085] The preparation process may include a process of preparing a starting material (starting material preparation process), and a process of subjecting the starting material to hot working to produce an intermediate steel material (hot working process). Hereunder, a case where the preparation process includes the starting material preparation process and the hot working process is described in detail.

[Starting material preparation process]

[0086] In the starting material preparation process, a starting material is produced using a molten steel having the chemical composition described above. The method for producing the starting material is not particularly limited, and it suffices to use a well-known method. Specifically, a cast piece (a slab, a bloom, or a billet) may be produced by a continuous casting process using the molten steel. An ingot may also be produced by an ingot-making process using the molten steel. As necessary, the slab, bloom, or ingot may be subjected to blooming to produce a billet. A starting material (a slab, a bloom, or a billet) is produced by the above process.

[Hot working process]

[0087] In the hot working process, the prepared starting material is subjected to hot working to produce an intermediate steel material. If the steel material is a seamless steel pipe, the intermediate steel material corresponds to a hollow shell. First, a billet is heated in a heating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. After taking out the billet from the heating furnace, the billet is subjected to hot working to produce a hollow shell (seamless steel pipe). The method of hot working is not particularly limited, and it suffices to use a well-known method.

[0088] For example, the Mannesmann process may be performed as hot working to produce a hollow shell. In this case, a round billet is subjected to piercing-rolling using a piercing machine. When performing piercing-rolling, although not particularly limited, for example, the piercing ratio is 1.0 to 4.0. The round billet that was subjected to piercing-rolling is further subjected to hot rolling with a mandrel mill, a stretch reducing mill, a sizing mill or the like to produce a hollow shell. The cumulative reduction of area in the hot working process is, for example, 20 to 70%.

[0089] A hollow shell may be produced from the billet by performing the other hot working methods. For example, in a case where the steel material is a heavy-wall steel material of a short length such as a coupling, a hollow shell may be produced by forging by the Ehrhardt process or the like. A hollow shell is produced by the above process. Although not particularly limited, the wall thickness of the hollow shell is, for example, 9 to 60 mm.

[0090] If the steel material is a round steel bar, first, the starting material is heated in a heating furnace. Although not

particularly limited, the heating temperature is, for example, 1100 to 1300°C. After being taken out from the heating furnace, the starting material is subjected to hot working to produce an intermediate steel material in which a cross section perpendicular to the axial direction is a circular shape. The hot working is, for example, blooming performed using a blooming mill or hot rolling performed using a continuous mill. In a continuous mill, a horizontal stand having a pair of grooved rolls arranged one on the other in the vertical direction, and a vertical stand having a pair of grooved rolls arranged side by side in the horizontal direction are alternately arranged.

[0091] If the steel material is a steel plate, first, the starting material is heated in a heating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. After being taken out from the heating furnace, the starting material is subjected to hot rolling using a blooming mill and a continuous mill to produce an intermediate steel material in the shape of a steel plate.

[0092] The hollow shell produced by hot working may be air-cooled (as-rolled). The hollow shell produced by hot working may be subjected to direct quenching after the hot working without being cooled to normal temperature, or may be subjected to quenching after undergoing supplementary heating (reheating) after the hot working.

[0093] In the case of performing direct quenching after the hot working, or performing quenching after supplementary heating, cooling may be stopped midway through the quenching process or slow cooling may be performed. In this case, the occurrence of quench cracking in the hollow shell can be suppressed. In addition, in the case of performing direct quenching after hot working or performing quenching after supplementary heating, stress relief annealing (SR) may be performed at a time that is after quenching and before the heat treatment of the next process. In this case, residual stress of the hollow shell is eliminated.

[0094] As described above, an intermediate steel material is prepared in the preparation process. The intermediate steel material may be produced by the aforementioned preferable process, or may be an intermediate steel material that was produced by a third party, or an intermediate steel material may be prepared that was produced in another factory other than the factory in which a quenching process and a tempering process to be described later are performed or that was produced at different works. Hereunder, the quenching process is described in detail.

[Quenching process]

[0095] In the quenching process, the prepared intermediate steel material (hollow shell) is subjected to quenching. As used herein, the term "quenching" means rapidly cooling the intermediate steel material which is at a temperature not lower than the A_3 point. In the present description, the temperature of the intermediate steel material immediately prior to rapid cooling when performing quenching is also referred to as a "quenching temperature". Here, in the quenching process according to the present embodiment, after heating at an intermediate temperature is performed, heating at a high temperature is performed, and thereafter the intermediate steel material is rapidly cooled. That is, the quenching process according to the present embodiment includes an intermediate temperature heating process, a high temperature heating process, and a rapid cooling process. Hereunder, each process is described in detail.

[Intermediate temperature heating process]

[0096] In the intermediate temperature heating process, the prepared intermediate steel material (hollow shell) is heated from a room temperature to a heating temperature, and is then held at the heating temperature. In this way, in the intermediate temperature heating process, fine Mo-based MX-type precipitates are caused to precipitate in the intermediate steel material. Specifically, a preferable heating temperature in the intermediate temperature heating process is 400 to less than 600°C. If the heating temperature is too low, the amount of Mo-based MX-type precipitates that are precipitated in the intermediate temperature heating process will decrease. As a result, the number density of Mo-based MX-type precipitates in the produced steel material will decrease. On the other hand, if the heating temperature is too high, the Mo-based MX-type precipitates will grow too much and the Mo-based MX-type precipitates will coarsen in the intermediate temperature heating process, and consequently the number density of Mo-based MX-type precipitates in the produced steel material will decrease.

[0097] Therefore, in the intermediate temperature heating process according to the present embodiment, a preferable heating temperature is 400 to less than 600°C. A more preferable lower limit of the heating temperature in the intermediate temperature heating process is 410°C, further preferably is 420°C, and further preferably is 430°C. A more preferable upper limit of the heating temperature in the intermediate temperature heating process is 590°C, further preferably is 580°C, and further preferably is 570°C.

[0098] A preferable holding time in the intermediate temperature heating process is 20 to 120 minutes. If the holding time is too short, the amount of Mo-based MX-type precipitates that are precipitated in the intermediate temperature heating process will decrease. As a result, the number density of Mo-based MX-type precipitates in the produced steel material will decrease. On the other hand, if the holding time is too long, the Mo-based MX-type precipitates will grow too much, and the Mo-based MX-type precipitates will coarsen in the intermediate temperature heating process. As a result, the number

density of Mo-based MX-type precipitates in the produced steel material will decrease.

[0099] Therefore, in the intermediate temperature heating process according to the present embodiment, a preferable holding time is 20 to 120 minutes. A more preferable lower limit of the holding time in the intermediate temperature heating process is 25 minutes. A more preferable upper limit of the holding time in the intermediate temperature heating process is 100 minutes, and further preferably is 90 minutes.

[High temperature heating process]

[0100] In the high temperature heating process, the intermediate steel material (hollow shell) that was heated in the intermediate temperature heating process is heated from the heating temperature of the intermediate temperature heating process to the heating temperature of the high temperature heating process, and is then held at the heating temperature of the high temperature heating process. In this way, in the high temperature heating process, the microstructure of the steel material is transformed to an austenite single phase. As a result, by carrying out the subsequent rapid cooling process, quenching of the intermediate steel material can be performed. Specifically, a preferable heating temperature in the high temperature heating process is 880 to 1000°C. If the heating temperature is too low, the microstructure of the intermediate steel material will not be sufficiently transformed, and the effect of quenching will not be sufficiently obtained. As a result, in the produced steel material, the mechanical property defined in the present embodiment will not be obtained. On the other hand, if the heating temperature is too high, austenite grains will coarsen. In addition, if the heating temperature is too high, most of the fine Mo-based MX-type precipitates that precipitated in the intermediate temperature heating process will dissolve. As a result, the fracture toughness of the produced steel material will decrease.

[0101] Therefore, in the high temperature heating process according to the present embodiment, a preferable heating temperature is 880 to 1000°C. A more preferable lower limit of the heating temperature in the high temperature heating process is 890°C, and further preferably is 900°C. A more preferable upper limit of the heating temperature in the high temperature heating process is 990°C, and further preferably is 980°C.

[0102] A preferable holding time in the high temperature heating process is 10 to 90 minutes. If the holding time is too short, the microstructure of the intermediate steel material will not sufficiently transform, and the effect of the quenching will not be sufficiently obtained. As a result, in the produced steel material, the mechanical property defined in the present embodiment will not be obtained. On the other hand, if the holding time is overly long, the aforementioned advantageous effect will be saturated.

[0103] Therefore, in the high temperature heating process according to the present embodiment, a preferable holding time is 10 to 90 minutes. A more preferable lower limit of the holding time in the high temperature heating process is 15 minutes. A more preferable upper limit of the holding time in the high temperature heating process is 80 minutes, and further preferably is 60 minutes.

[Rapid cooling process]

[0104] In the rapid cooling process, the intermediate steel material (hollow shell) that was heated in the high temperature heating process is rapidly cooled. In the rapid cooling process, the intermediate steel material (hollow shell) is continuously cooled to continuously decrease the surface temperature of the hollow shell. The method of performing the continuous cooling treatment is not particularly limited, and a well-known method can be used. The method of performing the continuous cooling treatment is, for example, a method that cools the hollow shell by immersing the hollow shell in a water bath, or a method that subjects the hollow shell to accelerated cooling by shower water cooling or mist cooling.

[0105] If the cooling rate during quenching is too slow, the microstructure will not become a microstructure principally composed of martensite and bainite, and the mechanical property defined in the present embodiment will not be obtained. Here, in the rapid cooling process according to the present embodiment, the average cooling rate when the surface temperature of the intermediate steel material (hollow shell) is within the range of 800 to 500°C during quenching is defined as "cooling rate during quenching $CR_{800-500}$ ". Specifically, the cooling rate during quenching $CR_{800-500}$ is determined based on a temperature measured at a region that is most slowly cooled within a cross-section of the intermediate steel material that is being quenched (for example, in the case of forcedly cooling both surfaces, the cooling rate is measured at the center portion of the thickness of the intermediate steel material).

[0106] In the rapid cooling process according to the present embodiment, a preferable cooling rate during quenching $CR_{800-500}$ is 300°C/min or more. A more preferable lower limit of the cooling rate during quenching $CR_{800-500}$ is 450°C/min, and further preferably is 600°C/min. Although an upper limit of the cooling rate during quenching $CR_{800-500}$ is not particularly defined, the upper limit is, for example, 60000°C/min.

[0107] The quenching process according to the present embodiment can be carried out by the above process. Note that, in the quenching process according to the present embodiment, quenching may also be performed after performing heating of the intermediate steel material in the austenite zone a plurality of times. However, in such a case the intermediate temperature heating process, the high temperature heating process, and the rapid cooling process are

to be performed at the first time that quenching is performed. That is, it is preferable not to perform the intermediate temperature heating process at the second and subsequent times that quenching is performed. If the intermediate temperature heating process is also performed at the second and subsequent times that quenching is performed, in some cases the Mo-based MX-type precipitates will coarsen in the second and subsequent intermediate temperature heating processes. As a result, in some cases the number density of Mo-based MX-type precipitates in the produced steel material will decrease. Therefore, when performing quenching two or more times, it is preferable that when quenching is performed for the second time and subsequent times, the high temperature heating process and the rapid cooling process are performed. Hereunder, the tempering process is described in detail.

[Tempering process]

[0108] The tempering process is carried out by performing tempering after performing the quenching that is described above. In the present description, the term "tempering" means reheating the intermediate steel material after quenching to a temperature that is equal to or less than the A_{c1} point, and holding the intermediate steel material at that temperature. The tempering temperature is appropriately adjusted in accordance with the chemical composition of the steel material and the yield strength to be obtained. That is, with respect to an intermediate steel material (hollow shell) having the chemical composition of the present embodiment, the tempering temperature is adjusted so as to adjust the yield strength of the steel material to be, for example, 125 ksi or more (862 MPa or more). Here, the tempering temperature corresponds to the temperature of the heat treatment furnace when the intermediate steel material after quenching is heated and held at the relevant temperature. The term "tempering time" means the period of time from when the temperature of the intermediate steel material reaches a predetermined tempering temperature until the intermediate steel material is taken out from the heat treatment furnace.

[0109] The tempering temperature is appropriately adjusted according to the chemical composition of the steel material and the yield strength to be obtained. That is, with respect to an intermediate steel material (hollow shell) having the chemical composition of the present embodiment, the tempering temperature is adjusted so as to adjust the yield strength of the steel material to be 862 MPa or more. In the tempering process according to the present embodiment, a preferable tempering temperature is 650 to 700°C. A more preferable lower limit of the tempering temperature is 655°C. A more preferable upper limit of the tempering temperature is 695°C.

[0110] If the tempering time is too short, in some cases a microstructure that is principally composed of tempered martensite and tempered bainite will not be obtained. On the other hand, if the tempering time is too long, the aforementioned advantageous effect will be saturated. Therefore, in the tempering process of the present embodiment, preferably the tempering time is set within the range of 20 to 180 minutes. A more preferable lower limit of the tempering time is 30 minutes. A more preferable upper limit of the tempering time is 150 minutes, and further preferably is 120 minutes.

[0111] The steel material according to the present embodiment can be produced by the production method described above. Note that, in the above description of the production method, a method for producing a steel pipe has been described as one example. However, the steel material according to the present embodiment may also be a steel plate or the other shapes. A method for producing a steel plate or a steel material of the other shapes also includes, for example, a preparation process, a quenching process, and a tempering process, similarly to the production method described above. Further, the production method described above is an example, and the steel material may also be produced by the other production methods.

[0112] Hereunder, the present invention is described more specifically by way of examples.

EXAMPLES

[0113] Molten steels which had the chemical compositions shown in Table 1-1 and Table 1-2 and which each had a weight of 180 kg were produced. Note that, the symbol "-" in Table 1-1 and Table 1-2 means that the content of the corresponding element was at the level of an impurity. Specifically, the symbol "-" means that the content of V, the content of W, the content of Co, the content of Ni, and the content of Cu of steel R were each 0% when rounded off to the second decimal place. Similarly, the symbol "-" means that the content of Ti, the content of Nb, and the content of rare earth metal (REM) of steel R were each 0% when rounded off to the third decimal place. Similarly, the symbol "-" means that the content of Ca of steel C, the content of Mg of steel R, and the content of B of steel R were each 0% when rounded off to the fourth decimal place. Further, Fn1 and Fn2 which were determined based on the respective chemical compositions described in Table 1 and the definitions described above are shown in Table 2.

[Table 1-1]

[0114]

EP 4 506 472 A1

TABLE 1-1

Steel	Chemical Composition (unit is mass%; balance is Fe and impurities)									
	C	Si	Mn	P	S	Al	Cr	Mo	N	Ca
A	0.27	0.32	0.44	0.007	0.0007	0.041	0.5	0.70	0.001	0.0011
B	0.27	0.32	0.42	0.009	0.0008	0.041	0.7	0.70	0.002	0.0011
C	0.28	0.29	0.44	0.007	0.0009	0.042	0.5	0.71	0.001	-
D	0.35	0.34	0.33	0.009	0.0009	0.034	1.0	1.30	0.003	0.0012
E	0.27	0.28	0.13	0.007	0.0010	0.033	0.7	0.91	0.003	0.0008
F	0.22	0.32	0.64	0.008	0.0010	0.044	0.7	0.61	0.001	0.0013
G	0.26	0.24	0.41	0.008	0.0011	0.030	1.0	0.72	0.004	0.0011
H	0.28	0.29	0.22	0.010	0.0012	0.036	0.5	0.73	0.002	0.0019
I	0.27	0.32	0.44	0.007	0.0007	0.035	0.5	0.70	0.002	0.0010
J	0.30	0.27	0.47	0.009	0.0009	0.038	1.9	0.50	0.001	-
K	0.35	0.29	0.30	0.007	0.0009	0.034	0.2	0.47	0.003	0.0008
L	0.33	0.34	0.44	0.009	0.0008	0.040	0.9	1.88	0.002	-
M	0.20	0.28	0.36	0.008	0.0007	0.034	0.9	0.32	0.002	0.0012
N	0.28	0.29	0.81	0.010	0.0013	0.036	0.5	0.50	0.002	0.0019
O	0.26	0.78	0.43	0.011	0.0011	0.034	1.0	0.55	0.007	0.0036
P	0.19	0.50	0.22	0.010	0.0012	0.028	1.3	0.73	0.002	-
Q	0.27	0.32	0.44	0.007	0.0020	0.035	0.5	0.33	0.002	-
R	0.11	0.30	0.45	0.010	0.0011	0.033	0.5	0.42	0.001	0.0011
S	0.30	0.31	0.50	0.009	0.0010	0.035	0.7	0.01	0.001	0.0012
T	0.32	0.41	1.21	0.014	0.0020	0.034	0.3	0.40	0.002	0.0013
U	0.27	0.31	0.41	0.020	0.0030	0.037	0.3	0.42	0.002	0.0018

[Table 1-2]

[0115]

TABLE 1-2

Steel	Chemical Composition (unit is mass%; balance is Fe and impurities)									
	Mg	Ti	Nb	V	W	Co	Ni	REM	Cu	B
A	-	0.012	0.012	0.09	-	-	-	-	-	-
B	-	0.016	0.031	-	0.01	-	-	-	-	-
C	0.0010	0.014	-	-	-	0.02	-	-	-	-
D	0.0012	0.002	0.072	0.05	-	-	0.02	-	-	-
E	-	0.004	0.025	0.08	-	-	-	0.009	-	-
F	-	0.011	-	0.11	-	-	-	-	0.02	-
G	-	0.012	0.028	0.10	-	-	-	-	-	0.0011
H	-	0.035	0.043	0.15	-	-	-	-	-	-
I	-	0.009	-	-	-	-	0.02	-	0.02	0.0011
J	0.0013	0.020	-	0.08	-	-	-	-	-	-
K	-	0.015	-	0.09	0.01	-	-	-	-	0.0013

EP 4 506 472 A1

(continued)

Steel	Chemical Composition (unit is mass%; balance is Fe and impurities)									
	Mg	Ti	Nb	V	W	Co	Ni	REM	Cu	B
L	0.0013	0.013	-	0.10	-	-	-	-	-	-
M	-	0.012	0.012	0.09	-	-	-	-	-	-
N	-	0.035	0.043	0.15	-	-	-	-	-	-
O	0.0037	0.054	-	-	-	0.12	0.10	-	-	-
P	0.0015	0.007	-	0.20	-	-	-	-	0.11	0.0056
Q	0.0011	0.057	-	0.20	-	-	-	-	-	-
R	-	-	-	-	-	-	-	-	-	-
S	-	0.013	-	-	-	-	-	-	-	0.0012
T	-	0.023	-	-	-	-	0.02	-	0.02	-
U	-	0.030	-	-	-	-	-	-	0.02	-

[Table 2]

[0116]

TABLE 2

Test Number	Steel	Fn1	Fn2	Quenching Process			Tempering Process	
				Intermediate Temperature Heating Process		High Temperature Heating Process	Tempering Temperature (°C)	Holding Time (min)
				Heating Temperature (°C)	Holding Time (min)	Heating Temperature (°C)		
1	A	3.1	0.38	500	50	900	680	60
2	B	3.4	0.17	500	50	920	670	100
3	C	4.0	0.10	550	60	920	680	60
4	D	3.0	0.31	550	30	920	680	60
5	E	1.3	0.32	500	50	920	680	60
6	F	6.4	0.41	500	60	900	670	80
7	G	4.5	0.44	450	90	920	690	60
8	H	2.6	0.78	500	30	950	680	80
9	I	3.1	0.06	500	30	920	680	60
10	J	4.2	0.38	450	30	920	690	60
11	K	2.7	0.38	450	20	920	670	90
12	L	3.5	0.39	500	20	920	670	80
13	M	2.5	0.38	500	50	900	680	60
14	N	10.5	0.78	450	30	950	680	60
15	O	4.7	0.38	500	50	980	690	120
16	P	2.6	0.65	500	60	920	670	100
17	F	6.4	0.41	580	5	900	670	80

EP 4 506 472 A1

(continued)

Test Number	Steel	Fn1	Fn2	Quenching Process			Tempering Process	
				Intermediate Temperature Heating Process		High Temperature Heating Process	Tempering Temperature (°C)	Holding Time (min)
				Heating Temperature (°C)	Holding Time (min)	Heating Temperature (°C)		
18	F	6.4	0.41	250	60	900	670	80
19	J	4.2	0.38	920	120	920	680	60
20	Q	8.8	1.00	500	30	920	690	120
21	R	5.0	0.00	500	30	920	680	80
22	S	5.0	0.09	580	20	920	670	60
23	T	24.2	0.16	450	30	900	670	90
24	U	12.3	0.21	450	30	900	680	80

[0117] Ingots were produced using the molten steels described above. Each ingot was subjected to hot rolling to produce a steel plate having a thickness of 20 mm. After hot rolling, the steel plate of each test number that had been cooled to normal temperature was subjected to quenching and tempering. In the quenching process, after performing the intermediate temperature heating process and the high temperature heating process, the rapid cooling process was performed. Specifically, the steel plate of each test number was held at a heating temperature (°C) for a holding time (min) which are each described in the column "Intermediate Temperature Heating Process" in Table 2. In addition, the steel plate of each test number was held for 20 minutes at a heating temperature (°C) described in the column "High Temperature Heating Process" in Table 2, and thereafter was subjected to rapid cooling by shower water cooling. Note that, for each test number the cooling rate during quenching $CR_{800-500}$ was within the range of 300 to 800°C/min. Further, the temperature (°C) of the heat treatment furnace that heated the steel plate was adopted as the heating temperature (°C) that is described in Table 2. In addition, the time (min) for which the steel plate was held at the heating temperature was adopted as the holding time (min) that is described in Table 2.

[0118] The obtained steel plate of each test number was subjected to tempering. Specifically, the steel plate of each test number was subjected to tempering in which the steel plate was held at a tempering temperature (°C) for a holding time (min) which are each described in the column "Tempering Process" in Table 2. Here, the temperature (°C) of the tempering furnace that heated the steel plate was adopted as the tempering temperature (°C) that is described in Table 2. Further, the time (min) for which the steel plate was held at the tempering temperature was adopted as the holding time (min) that is described in Table 2. The steel plate of each test number was obtained by the production process described above.

[Evaluation tests]

[0119] The obtained steel plate of each test number was subjected to a tensile test, a test to measure the number density of Mo-based MX-type precipitates, and a fracture toughness test that are described hereunder.

[Tensile test]

[0120] The steel plate of each test number was subjected to a tensile test, and the yield strength and tensile strength were determined. The tensile test was carried out in accordance with ASTM E8/E8M (2021). Specifically, a round bar tensile test specimen having a parallel portion diameter of 6 mm and a gage length of 30 mm was prepared from the center position of the thickness of the steel plate of each test number. The longitudinal direction of the round bar tensile test specimen was parallel to the rolling elongation direction of the steel plate. The tensile test was carried out in air at normal temperature (25°C) using the prepared round bar tensile test specimens, and the yield strength (MPa) of the steel plate of each test number was determined. Note that, in the present Examples, the 0.6% total elongation proof stress obtained in the tensile test was defined as the yield strength. Further, the maximum stress during uniform elongation was defined as the tensile strength (MPa). For each test number, the obtained yield strength is shown as "YS (MPa)" and the obtained tensile strength is shown as "TS (MPa)" in Table 3.

[Table 3]

[0121]

TABLE 3

Test Number	YS (MPa)	TS (MPa)	Mo-based MX-type Precipitates Number Density (/μm ²)	CTOD Value (mm)
1	886	963	70	0.15
2	893	967	89	0.17
3	892	970	55	0.14
4	928	1007	48	0.13
5	901	965	65	0.15
6	911	980	46	0.13
7	876	964	80	0.15
8	925	995	26	0.11
9	913	992	31	0.11
10	907	975	54	0.14
11	920	1000	38	0.12
12	901	979	50	0.14
13	903	982	26	0.11
14	907	985	24	0.11
15	942	1031	59	0.13
16	895	986	43	0.12
17	917	974	9	0.07
18	910	978	14	0.07
19	894	961	11	0.06
20	916	998	12	0.07
21	889	967	4	0.06
22	914	979	3	0.06
23	932	1007	25	0.09
24	938	993	21	0.08

[Test to measure number density of Mo-based MX-type precipitates]

[0122] The steel plate of each test number was subjected to a test to measure the number density of Mo-based MX-type precipitates, and the number density of Mo-based MX-type precipitates was thereby determined. Specifically, a micro test specimen was prepared from the center position of the thickness of the steel plate of each test number. The obtained micro test specimen was used to prepare a replica film by the method described above, and the replica film was observed with a TEM. As the conditions for the TEM observation, the observation magnification was set to $\times 100000$, the acceleration voltage was set to 200 kV, and the size of each observation visual field was set to $2.0\ \mu\text{m} \times 3.0\ \mu\text{m}$. In the observation visual fields, particles having an equivalent circular diameter of 100 nm or less were identified by the method described above. The identified particles having an equivalent circular diameter of 100 nm or less were subjected to EDS point analysis by the method described above. When the total content of Mo, Nb, V, and Ti which was quantified by the EDS point analysis was defined as 100% by mass, those particles in which the content of Mo was in the range of more than 50% to 70% by mass were defined as Mo-based MX-type precipitates. The number density (/μm²) of Mo-based MX-type precipitates was determined based on the total number of Mo-based MX-type precipitates identified in the respective observation visual fields and the total area of the observation visual fields. For each test number, the obtained number density (/μm²) of Mo-

based MX-type precipitates is shown in Table 3.

[Fracture toughness test]

[0123] The steel plate of each test number was subjected to a fracture toughness test, and a CTOD value was determined. Specifically, a SENB test specimen illustrated in FIG. 2A was prepared from the center position of the thickness of the steel plate of each test number. The longitudinal direction of the SENB test specimen was parallel to the rolling elongation direction of the steel plate. A width W direction of the SENB test specimen was parallel to the width direction of the steel plate. As illustrated in FIG. 2A and FIG. 2B, a notch having a depth of 8 mm in the width W direction had been formed in the SENB test specimen by machining. A fatigue pre-crack of 2 mm was introduced into the tip of the notch of the SENB test specimen. At such time, a fatigue test was carried out at room temperature ($24 \pm 3^\circ\text{C}$).

[0124] The SENB test specimen into which the fatigue pre-crack had been introduced was subjected to a CTOD test at normal temperature (25°C) in accordance with ISO 12135 (2021). A CTOD value (mm) was determined based on ISO 12135 (2021), based on the breaking load in a load-displacement curve obtained by the CTOD test, and a plastic component of the clip gage opening displacement. In the present Examples, the load application rate in the CTOD test was set to 20.94 kN/min, and Young's modulus was set to 212000 MPa. Note that, the same test was conducted three times, and the smallest CTOD value (mm) was defined as the CTOD value (mm) of the steel material. For each test number, the obtained CTOD value (mm) is shown in Table 3.

[Test results]

[0125] The test results are shown in Table 3.

[0126] Referring to Table 1-1, Table 1-2, Table 2, and Table 3, for each of the steel plates of Test Nos. 1 to 16, the chemical composition was appropriate and the yield strength was 862 MPa or more (125 ksi or more). In addition, for each of these steel plates, Fn1 was 12.0 or less, and Fn2 was 0.05 to 0.80. Furthermore, for each of these steel plates, the number density of Mo-based MX-type precipitates was $20/\mu\text{m}^2$ or more. As a result, for each of these steel plates the CTOD value was 0.11 mm or more, and thus excellent fracture toughness was exhibited.

[0127] On the other hand, for the steel plate of Test No. 17, the holding time in the intermediate temperature heating process was too short. Consequently, in this steel plate the number density of Mo-based MX-type precipitates was less than $20/\mu\text{m}^2$. As a result, for this steel plate the CTOD value was less than 0.11 mm, and thus excellent fracture toughness was not exhibited.

[0128] For the steel plate of Test No. 18, the heating temperature in the intermediate temperature heating process was too low. Consequently, in this steel plate the number density of Mo-based MX-type precipitates was less than $20/\mu\text{m}^2$. As a result, for this steel plate the CTOD value was less than 0.11 mm, and thus excellent fracture toughness was not exhibited.

[0129] For the steel plate of Test No. 19, the heating temperature in the intermediate temperature heating process was too high. Consequently, in this steel plate the number density of Mo-based MX-type precipitates was less than $20/\mu\text{m}^2$. As a result, for this steel plate the CTOD value was less than 0.11 mm, and thus excellent fracture toughness was not exhibited.

[0130] For the steel plate of Test No. 20, Fn2 was too high. Consequently, in this steel plate the number density of Mo-based MX-type precipitates was less than $20/\mu\text{m}^2$. As a result, for this steel plate the CTOD value was less than 0.11 mm, and thus excellent fracture toughness was not exhibited.

[0131] The steel plate of Test No. 21 did not contain any of Ti, Nb, and V, and furthermore the value of Fn2 was too low. Consequently, in this steel plate the number density of Mo-based MX-type precipitates was less than $20/\mu\text{m}^2$. As a result, for this steel plate the CTOD value was less than 0.11 mm, and thus excellent fracture toughness was not exhibited.

[0132] In the steel plate of Test No. 22, the content of Mo was too low. Consequently, in this steel plate the number density of Mo-based MX-type precipitates was less than $20/\mu\text{m}^2$. As a result, for this steel plate the CTOD value was less than 0.11 mm, and thus excellent fracture toughness was not exhibited.

[0133] In the steel plate of Test No. 23, the content of Mn was too high, and Fn1 was too high. As a result, for this steel plate the CTOD value was less than 0.11 mm, and thus excellent fracture toughness was not exhibited.

[0134] In the steel plate of Test No. 24, Fn1 was too high. As a result, for this steel plate the CTOD value was less than 0.11 mm, and thus excellent fracture toughness was not exhibited.

[0135] An embodiment of the present disclosure has been described above. However, the embodiment described above is merely an example for carrying out the present disclosure. Therefore, the present disclosure is not limited to the above-described embodiment, and can be implemented by appropriately modifying the above-described embodiment within a range not departing from the gist thereof.

Claims

1. A steel material consisting of, in mass%,

C: 0.10 to 0.45%,
 Si: 1.00% or less,
 Mn: 0.01 to 1.00%,
 P: 0.050% or less,
 S: 0.0050% or less,
 Al: 0.001 to 0.100%,
 Cr: 0.1 to 2.0%,
 Mo: 0.20 to 2.00%,
 N: 0.010% or less,
 W: 0 to 0.50%,
 Co: 0 to 0.50%,
 Ni: 0 to 0.50%,
 rare earth metal: 0 to 0.020%,
 Cu: 0 to 0.50%, and
 B: 0 to 0.0100%,
 further containing one or more elements selected from a group consisting of:

Ca: 0.0005 to 0.0200%, and
 Mg: 0.0005 to 0.0200%,

further containing one or more elements selected from a group consisting of:

Ti: 0.001 to 0.300%,
 Nb: 0.001 to 0.300%, and
 V: 0.01 to 0.50%,

with the balance being Fe and impurities, and
 satisfying Formula (1) and Formula (2),
 wherein:

a yield strength is 862 MPa or more; and
 in the steel material,
 a number density of MX-type precipitates which have an equivalent circular diameter of 100 nm or less
 and in which, when a total content of Mo, Nb, V, and Ti is defined as 100% by mass, a content of Mo is
 more than 50% by mass is 20 / μm^2 or more:

$$\text{Mn} \times \text{Sp} \leq 12.0 \quad (1)$$

$$0.05 \leq 7 \times \text{Ti} + 2 \times \text{Nb} + 3 \times \text{V} \leq 0.80 \quad (2)$$

where, in Formula (1), a content of Mn in percent by mass is substituted for "Mn", and a content of S in ppm is
 substituted for "Sp"; a content of a corresponding element in percent by mass is substituted for each symbol
 of an element in Formula (2); note that, when a corresponding element is not contained, "0" is substituted for
 the symbol of the relevant element.

2. The steel material according to claim 1, containing one or more elements selected from a group consisting of:

W: 0.01 to 0.50%,
 Co: 0.01 to 0.50%,
 Ni: 0.01 to 0.50%,
 rare earth metal: 0.001 to 0.020%,
 Cu: 0.01 to 0.50%, and
 B: 0.0001 to 0.0100%.

3. The steel material according to claim 1 or claim 2, wherein:
the steel material is an oil-well steel pipe.

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FIG. 1

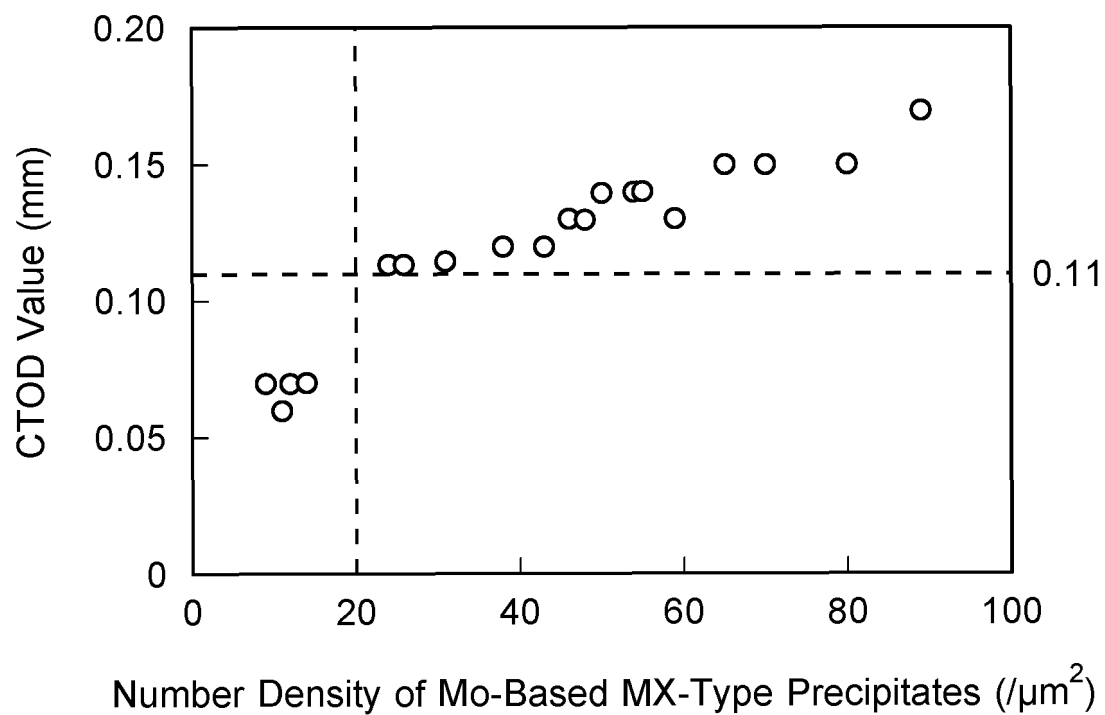


FIG. 2A

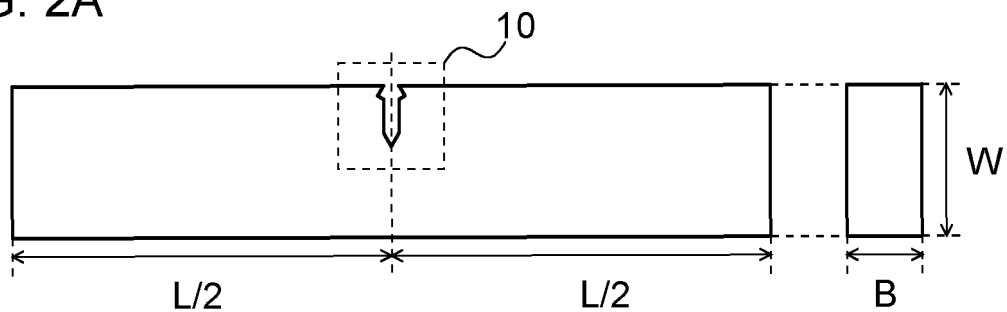
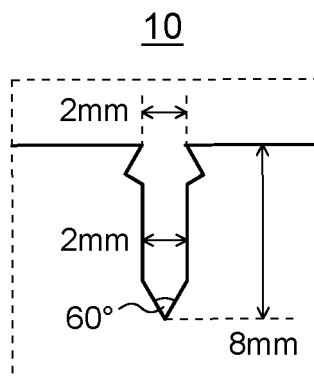


FIG. 2B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/014113

A. CLASSIFICATION OF SUBJECT MATTER

C21D 9/08(2006.01)i; **C22C 38/00**(2006.01)i; **C22C 38/54**(2006.01)i
 FI: C22C38/00 301F; C22C38/00 301Z; C22C38/54; C21D9/08 E

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)
 C21D9/08; 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 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-197507 A (DALMINE SPA) 18 October 2012 (2012-10-18) entire text	1-3
A	WO 2016/035316 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 10 March 2016 (2016-03-10) entire text	1-3
A	WO 2019/167945 A1 (NIPPON STEEL CORP.) 06 September 2019 (2019-09-06) entire text	1-3
A	JP 2011-94169 A (KOBE STEEL, LTD.) 12 May 2011 (2011-05-12) entire text	1-3

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

* Special categories of cited documents:

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

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

24 May 2023

Date of mailing of the international search report

06 June 2023

Name and mailing address of the ISA/JP

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/014113

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2012-197507 A	18 October 2012	US 2012/0199255 A1 entire text EP 2492361 A2 CN 102628145 A	
WO 2016/035316 A1	10 March 2016	US 2017/0292177 A1 entire text EP 3190200 A1 CN 106795602 A	
WO 2019/167945 A1	06 September 2019	US 2021/0371961 A1 entire text EP 3760754 A1	
JP 2011-94169 A	12 May 2011	(Family: none)	

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2006028612 A [0004] [0008]
- WO 2008123422 A [0004] [0008]
- JP 2017166060 A [0004] [0008]