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(71) Applicant: **NIPPON STEEL CORPORATION**  
**Chiyoda-ku**  
**Tokyo 100-8071 (JP)**

(72) Inventors:  
• **NISHIBATA, Toshinobu**  
**Tokyo 100-8071 (JP)**  
• **ARAI, Yuji**  
**Tokyo 100-8071 (JP)**

(74) Representative: **Zimmermann & Partner**  
**Patentanwälte mbB**  
**Postfach 330 920**  
**80069 München (DE)**

(54) **STEEL MATERIAL FOR OIL WELL, AND OIL WELL PIPE**

(57) A steel was developed with a chemical composition consisting of (mass%) C (0.60-2.00%), Si (0.01-3.00%), Mn (16.0-30.0%), Al (0.07-6.00%), V (0.50-3.00%), N (0.500% or less), P (0.030% or less), S (0.030% or less), Cr (0-10.00%), Mo (0-3.00%), Cu (0-3.00%), Ni (0-20.00%), Ti (0-3.00%), Nb (0-3.00%), Zr (0-3.00%), Ta (0-6.00%), Hf (0-6.00%), W (0-6.00%), Ca (0-0.0050%), Mg (0-0.0050%), and B (0-0.0150%), with the balance being Fe and impurities. The value in

Formula (i) is between 0.55 and 1.54. In the steel microstructure, the total volume fraction of  $\alpha'$  martensite and ferrite is less than 0.1%, the volume fraction of  $\epsilon$  martensite, which has an HCP structure, is 10% or less, and the balance is austenite. The number density of carbonitride precipitates with an equivalent circular diameter of 5-100 nm is 100 particles/ $\mu\text{m}^2$  or more, the yield stress is 862 MPa or more, the SFE at 25°C is 30 mJ/m<sup>2</sup> or more, and the  $\gamma$  grain size is 100  $\mu\text{m}$  or smaller.

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**Description**

## TECHNICAL FIELD

5 **[0001]** The present invention relates to steel for oil wells and oil country tubular goods.

## BACKGROUND ART

10 **[0002]** In oil and gas wells (hereafter collectively referred to as "oil wells") for extracting crude oil, natural gas, and other resources, which contain hydrogen sulfide ( $H_2S$ ), sulfide stress cracking (hereafter referred to as "SSC") of steel in wet hydrogen sulfide environments poses a problem. Oil country tubular goods with excellent SSC resistance are therefore needed. Low-alloy oil country tubular goods with excellent SSC resistance and high strength are needed for use in casing applications.

15 **[0003]** SSC resistance decreases sharply with increasing strength of the steel material. Conventional steel with SSC resistance in an environment of NACE solution A (NACE TM0177-2005) containing 1-bar  $H_2S$ , which is the general evaluation condition, is up to 110-ksi grade (yield stress: 758 to less than 862 MPa). In many cases, steel of 125-ksi grade (yield stress: 862 to less than 965 MPa) and 140-ksi grade (yield stress: 965 to 1069 MPa), which has higher strength than that of steel of 110-ksi grade, have SSC resistance under only limited  $H_2S$  partial pressures (e.g., 0.1 bar or lower). It is thought that the demand for high-strength steel will continue to increase due to increases in oil-well depth.

20 Therefore, it is necessary to develop oil country tubular goods with high strength and excellent SSC resistance.

**[0004]** SSC is a kind of hydrogen embrittlement in which hydrogen generated on the surface of steel in a corrosive environment diffuses into the steel material. The steel consequently ruptures due to a synergetic effect with under applied stress. In steel that is highly susceptible to SSC, cracks are easily generated by a load stress that is lower than the yield stress.

25 **[0005]** Many studies have been conducted on the relationship between the steel microstructure and SSC resistance of low-alloy steels. Generally, to improve SSC resistance, a tempered martensitic structure is most effective and a fine-grained microstructure is desirable.

30 **[0006]** However, tempered martensite has a body-centered cubic (hereafter referred to as "BCC") structure. Tempered martensite and ferrite, which also has a BCC structure, are inherently susceptible to hydrogen embrittlement. Therefore, it is very difficult to completely prevent SSC for steel whose main microstructure is tempered martensite or ferrite. In particular, because SSC susceptibility increases with increasing material strength, obtaining low-alloy steel with high strength and excellent SSC resistance is difficult.

35 **[0007]** In contrast, steel with an austenitic structure, which has a face-centered cubic (hereafter referred to as "FCC") structure, has inherently low susceptibility to hydrogen embrittlement, and thus can be made to have excellent SSC resistance. For example, Patent Documents 1 to 4 describe high-strength steels that have a high Mn (an austenite-stabilizing element) content to give them excellent SSC resistance, and Patent Document 5 describes steel that has high toughness in addition to excellent SSC resistance.

## LIST OF PRIOR ART DOCUMENTS

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## PATENT DOCUMENTS

**[0008]**

45 Patent Document 1: WO 2015/012357  
 Patent Document 2: WO 2016/052271  
 Patent Document 3: WO 2016/052397  
 Patent Document 4: WO 2017/169811  
 Patent Document 5: JP2018-162507A

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## NON-PATENT DOCUMENTS

**[0009]** Non-Patent Document 1: A. Saeed-Akbari et al.: Metall. Mater. Trans. 40A (2009), 3076-3090.

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## SUMMARY OF INVENTION

## TECHNICAL PROBLEM

**[0010]** In Patent Documents 1 to 5, excellent SSC resistance and high strength are realized by increasing the content of austenite-stabilizing elements, such as C and Mn, and achieving precipitation hardening using elements such as Cr and V. However, for large oil-well depths, a different approach is required to obtain materials that can withstand harsh wet hydrogen sulfide environments.

**[0011]** The present invention solves the above problem. The proposed steel for oil wells has a yield stress of 125 ksi (862 MPa) or more and has SSC resistance that is higher than that of conventional steel. Oil country tubular goods made of this steel for oil wells are also described.

## SOLUTION TO PROBLEM

**[0012]** The proposed steel for oil wells and associated oil country tubular goods are described in the following.

**[0013]**

(1) The steel has the following chemical composition (mass%):

C: 0.60 to 2.00%,  
Si: 0.01 to 3.00%,  
Mn: 16.0 to 30.0%,  
Al: 0.07 to 6.00%,  
V: 0.50 to 3.00%,  
N: 0.500% or less,  
P: 0.030% or less,  
S: 0.030% or less,  
Cr: 0 to 10.00%,  
Mo: 0 to 3.00%,  
Cu: 0 to 3.00%,  
Ni: 0 to 20.00%,  
Ti: 0 to 3.00%,  
Nb: 0 to 3.00%,  
Zr: 0 to 3.00%,  
Ta: 0 to 6.00%,  
Hf: 0 to 6.00%,  
W: 0 to 6.00%,  
Ca: 0 to 0.0050%,  
Mg: 0 to 0.0050%,  
B: 0 to 0.0150%, and  
Fe and impurities: balance.

**[0014]** The effective amount of C, defined in Formula (i) below, is between 0.55 and 1.54.

**[0015]** In the steel microstructure, the total volume fraction of  $\alpha'$  martensite and ferrite is less than 0.1%, the volume fraction of  $\epsilon$  martensite, which has an HCP structure, is 10% or less, and the balance is austenite.

**[0016]** The number density of carbonitrides with an equivalent circular diameter of 5 to 100 nm is 100 particles/ $\mu\text{m}^2$  or more, the yield stress is 862 MPa or more, the stacking fault energy (SFE) at 25°C is 30 mJ/m<sup>2</sup> or more, and the austenite grain size is 100  $\mu\text{m}$  or smaller.

$$C - 0.18V - 0.06(Cr + Mo) - 0.25Ti - 0.13(Nb + Zr) - 0.07(Ta + Hf + W) \quad \dots (i)$$

where each element symbol represents the content (mass%) of the corresponding element in the steel. If the element is not contained, 0 shall be substituted for the relevant element symbol.

**[0017]** (2) The steel described in (1), wherein:

the chemical composition contains one or more of the following elements (mass%):

Cr: 0.05 to 10.00% and

Mo: 0.10 to 3.00%.

**[0018]** (3) The steel described in (1) or (2), wherein:  
the chemical composition contains one or more of the following elements (mass%):

Cu: 0.10 to 3.00% and  
Ni: 0.10 to 20.00%.

**[0019]** (4) The steel described in any of (1) to (3), wherein:  
the chemical composition contains one or more of the following elements (mass%):

Ti: 0.005 to 3.00%,  
Nb: 0.005 to 3.00%,  
Zr: 0.005 to 3.00%,  
Ta: 0.005 to 6.00%,  
Hf: 0.005 to 6.00%, and  
W: 0.005 to 6.00%.

**[0020]** (5) The steel described in any of (1) to (4), wherein:  
the chemical composition contains one or more of the following elements (mass%):

Ca: 0.0003 to 0.0050% and  
Mg: 0.0003 to 0.0050%.

**[0021]** (6) The steel described in any of (1) to (5), wherein:  
the chemical composition contains (mass%):  
B: 0.0001 to 0.0150%.

**[0022]** (7) The steel described in (6), which satisfies Formula (ii) below:

$$\text{Mo}-200\text{B} \geq 0 \quad \dots \text{(ii)}$$

where each element symbol represents the content (mass%) of the corresponding element. If the element is not contained, 0 shall be substituted for the relevant element symbol.

**[0023]** (8) The steel described in any of (1) to (7), which satisfies Formula (iii) below:

$$0.40 < \text{Ti}/\text{Mo} < 0.60 \quad \dots \text{(iii)}$$

where each element symbol represents the content (mass%) of the corresponding element. If the element is not contained, 0 shall be substituted for the relevant element symbol.

**[0024]** (9) The steel described in any of (1) to (8), wherein the yield stress is 965 MPa or more.

**[0025]** (10) Oil country tubular goods made of the steel described in any of (1) to (9).

#### ADVANTAGEOUS EFFECTS OF INVENTION

**[0026]** With the present invention, it is possible to produce steel for oil wells that has a yield stress of 125 ksi (862 MPa) or more and has a SSC resistance that is higher than that of conventional steel, and oil country tubular goods that use this steel for oil wells.

#### DESCRIPTION OF EMBODIMENTS

**[0027]** To solve the problem described above, the present inventors conducted detailed investigations regarding the yield stress and SSC resistance of steel and obtained the following findings.

**[0028]** By increasing the content of C and Mn, austenite, which has excellent SSC resistance, can be stabilized. Furthermore, aging treatment with the addition of V improves the strength by precipitating fine carbonitrides as well as by refining the austenite grains.

**[0029]** The C and Mn content can serve as an index of austenite stability. However, even if austenite is stabilized, if

the austenitic structure easily changes from the FCC structure to a transformation phase (for example, the  $\epsilon$  phase with a hexagonal close-packed, hereafter referred to as "HCP", structure, or the  $\alpha$  phase with a BCC structure) due to applied stress in a corrosive environment, the hydrogen embrittlement susceptibility will increase, making it difficult to completely prevent SSC.

**[0030]** Therefore, to further improve SSC resistance, the present inventors focused on the SFE for austenite.

**[0031]** The SFE is the energy associated with plane defects, which are a type of lattice defect in the FCC structure. Increasing the SFE suppresses the occurrence of twin deformation, the localization of dislocations (planarization), the stress concentration at the periphery of austenite grain boundaries, and the precipitation of the transformation phase, even under applied stress in a corrosive environment.

**[0032]** The addition of Al increases the SFE, which suppresses the stress concentration at austenite grain boundaries and precipitation of the transformation phase. Furthermore, the addition of Al leads to the formation of a stable passivation layer that contains  $\text{Al}_2\text{O}_3$  on the surface, which suppresses hydrogen intrusion into the steel.

**[0033]** However, increasing the Al content in steel greatly reduces the hot ductility of austenite and significantly impairs manufacturability. It is thus generally considered desirable to reduce the Al content. Few studies have attempted to improve the SSC resistance by increasing the Al content.

**[0034]** The present inventors conducted research that confirmed that the addition of several percent Al to steel does not cause any particular production problems. The present inventors also found that increasing the Al content significantly improves the hydrogen embrittlement resistance compared to that for conventional steel.

**[0035]** The present invention is based on the above findings. The requirements of steel for one embodiment of the present invention are described in detail below.

## 1. Chemical Composition

**[0036]** The reasons for limiting the content of each element are as follows. Note that the symbol "%" with respect to content in the following description means mass percent.

C: 0.60 to 2.00%

**[0037]** Carbon (C) stabilizes austenite at low cost even if the content of elements referred to as austenite-forming elements such as Mn is reduced. It also increases the strength and can promote twin deformation, thereby improving work hardening and uniform elongation. C is thus a very important element in the present embodiment. The strength of the steel is improved by performing an aging treatment that causes carbonitrides to precipitate. C is consumed by this precipitation process. It is thus necessary to adjust the C content. Note that it is assumed that carbides are also included in the carbonitrides.

**[0038]** Excessive C content causes cementite to precipitate, reduces the grain boundary strength, and decreases the SSC resistance. It also lowers the fusion point of the material and decreases its hot workability. Therefore, the C content is varied between 0.60 and 2.00%. The lower limit of C content is preferably more than 0.70%, and more preferably is 0.80% or more. Furthermore, the upper limit of C content is preferably 1.60% or less, and more preferably is 1.30% or less.

Si: 0.01 to 3.00%

**[0039]** Silicon (Si) is necessary for the deoxidation of steel. If the Si content is less than 0.01%, deoxidation will be insufficient and many nonmetallic inclusions will remain, so that the desired SSC resistance will not be achieved. If the Si content is more than 3.00%, the grain boundary strength and the SSC resistance will decrease. Therefore, the Si content is varied in the range of 0.01 to 3.00%. The lower limit of Si content is preferably 0.10% or more, and more preferably is 0.20% or more. Furthermore, the upper limit of Si content is preferably 1.00% or less, and more preferably is 0.80% or less.

Mn: 16.0 to 30.0%

**[0040]** Manganese (Mn) stabilizes austenite at low cost. To obtain the stabilization effect of Mn in the present embodiment, the Mn content must be 16.0% or more. Mn dissolves preferentially in wet hydrogen sulfide environments, and thus it is difficult for stable corrosion products to form on the material surface. Consequently, the corrosion resistance may decrease with increasing Mn content. If the Mn content is more than 30.0%, the corrosion rate may exceed the standard corrosion rate for low-alloy oil country tubular goods. Therefore, the Mn content is varied in the range of 16.0 to 30.0%. The Mn content should preferably be between 17.0% (ideally 19.0%) and 25.0%.

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Al: 0.07 to 6.00%

**[0041]** Aluminum (Al) is necessary for the deoxidation of steel. It markedly increases the SFE for steel. In addition, as described above, because the presence of Al leads to the formation of a stable passivation layer that contains  $\text{Al}_2\text{O}_3$  on the surface and suppresses hydrogen intrusion into the steel, Al significantly improves the SSC resistance. To obtain these effects, the Al content must be 0.07% or more. If the Al content is more than 6.00%, the hot workability of the steel will markedly decrease and the ductility at room temperature will decrease. Therefore, the Al content is varied from 0.07 to 6.00%. The lower limit of Al content is preferably 0.50% or more, more preferably is more than 1.00%, and further preferably is 2.00% or more. Furthermore, the upper limit of Al content is preferably 5.00% or less, and more preferably is 4.00% or less. In the present embodiment, Al is in the form of acid-soluble Al (sol. Al).

V: 0.50 to 3.00%

**[0042]** Vanadium (V) can cause fine carbonitrides to precipitate in steel, which increases the strength. This can be achieved by performing a heat treatment at an appropriate temperature for an appropriate period of time. Excessive V content will saturate the aforementioned effect and consume a large amount of C, which stabilizes austenite. Therefore, the V content is varied from 0.50 to 3.00%. The lower limit of V content is preferably 0.60% or more, and more preferably is 0.70% or more. Furthermore, the upper limit of V content is preferably 2.00% or less, and more preferably is 1.80% or less.

N: 0.500% or less

**[0043]** Nitrogen (N) is usually considered to be an impurity in iron and steel and is removed by denitrification. Although N can be used to stabilize austenite, because austenite is stabilized by C and Mn in the present embodiment, N is not necessary for this task. Furthermore, excessive N increases the high-temperature strength and working stress, and decreases the hot workability. Therefore, the N content is required to be 0.500% or less. The N content should preferably be 0.100% or less (ideally 0.050% or less). Note that there is no need to perform denitrification from the viewpoint of refining cost. The N content should preferably be 0.001% or more.

P: 0.030% or less

**[0044]** Phosphorus (P) is unavoidably present in steel as an impurity. If the P content is more than 0.030%, P will segregate at grain boundaries, decreasing the SSC resistance. Therefore, the P content is set to 0.030% or less. Note that the P content should be minimized, preferably to 0.020% or less (ideally 0.012% or less). However, because obtaining a very low P content will increase the production cost, the P content should preferably be 0.001% or more (ideally 0.005% or more).

S: 0.030% or less

**[0045]** Sulfur (S) is unavoidably present in steel as an impurity. If the S content is more than 0.030%, S will segregate at grain boundaries, leading to the formation of sulfide-based inclusions, and thus reduce the SSC resistance. Therefore, the S content is set to 0.030% or less. Note that the S content should be minimized, preferably to 0.015% or less (ideally 0.010% or less). However, because obtaining a very low S content will increase the production cost, the S content should preferably be 0.001% or more (ideally 0.002% or more).

**[0046]** In addition to the elements described above, one or more other elements (i.e., Cr, Mo, Cu, Ni, Ti, Nb, Zr, Ta, Hf, W, B, Ca, and Mg) may be present in the proposed steel for oil wells according to the present embodiment.

Cr: 0 to 10.00%

**[0047]** The chromium (Cr) content can be as high as necessary because it improves the corrosion resistance of the steel. However, if the Cr content is excessive, Cr will decrease the SSC resistance and the stress corrosion cracking (SCC) resistance. Cr may also precipitate as carbonitrides during aging heat treatment and consume C in the base metal and thereby hinder the stabilization of austenite. In addition, when the Cr content is high, a higher solution heat treatment temperature is required, leading to economic disadvantages. Therefore, the Cr content is set to 10.00% or less. The Cr content is preferably 5.00% or less, and ideally 1.00% or less. Note that the Cr content should preferably be set to 0.05% or more (ideally 0.50% or more) to achieve the aforementioned effect.

Mo: 0 to 3.00%

**[0048]** The molybdenum (Mo) content can be as high as necessary because it stabilizes corrosion products in wet hydrogen sulfide environments and improves the corrosion resistance. However, if the Mo content is more than 3.00%, it may decrease the SSC resistance and the SCC resistance. Furthermore, Mo is very expensive. Therefore, the Mo content is set to 3.00% or less. Note that the Mo content should preferably be set to 0.10% or more (ideally 0.50% or more) to achieve the aforementioned effects.

Cu: 0 to 3.00%

**[0049]** Copper (Cu) stabilizes austenite and thus can be present in a small amount. However, when the influence of Cu on corrosion resistance is taken into consideration (Cu promotes local corrosion and is liable to form a stress-concentrated zone on the steel surface), excessive Cu content may decrease the SSC resistance and SCC resistance. For this reason, the Cu content is set to 3.00% or less. The Cu content should preferably be 1.00% or less. Note that the Cu content should preferably be set to 0.10% or more (ideally 0.20% or more) to stabilize austenite.

Ni: 0 to 20.00%

**[0050]** Nickel (Ni) stabilizes austenite and thus can be present in a small amount. However, when the influence on corrosion resistance is taken into consideration (Ni promotes local corrosion and is liable to form a stress-concentration zone on the steel surface), excessive Ni content may decrease the SSC resistance and SCC resistance. Furthermore, Ni is expensive. Therefore, the Ni content is set to 20.00% or less. The Ni content should preferably be 10.00% or less (ideally 5.00% or less). Note that the Ni content should preferably be set to 0.10% or more (ideally 0.50% or more) to stabilize austenite.

**[0051]**

Ti: 0 to 3.00%

Nb: 0 to 3.00%

Zr: 0 to 3.00%

**[0052]** Titanium (Ti), niobium (Nb), and zirconium (Zr) strengthen steel by combining with C or N to form fine carbonitrides; the content of these elements can thus be as high as necessary. However, this strengthening effect is limited compared to that of V. Furthermore, if these elements are present in high concentrations, the effect will be saturated, the toughness may decrease, and austenite may destabilize. Therefore, the content of each of these elements is set to 3.00% or less (preferably 2.00% or less). Note that the content of one or more of these elements should preferably be 0.005% or more (ideally 0.05% or more) to achieve the aforementioned effect.

**[0053]**

Ta: 0 to 6.00%

Hf: 0 to 6.00%

W: 0 to 6.00%

**[0054]** Tantalum (Ta), hafnium (Hf), and tungsten (W) strengthen steel by combining with C or N to form minute carbonitrides; their content can thus be as high as necessary. However, this strengthening effect is limited compared to that of V. Further, if these elements are present at high concentrations, the effect will be saturated, the toughness may decrease, and austenite may destabilize. Therefore, the content of each of these elements is set to 6.00% or less (preferably 3.00% or less). Note that one or more of these elements should preferably be 0.005% or more (ideally 0.05% or more) to achieve the aforementioned effect.

**[0055]**

Ca: 0 to 0.0050%

Mg: 0 to 0.0050%

**[0056]** Calcium (Ca) and magnesium (Mg) concentrations can be as high as necessary because they improve the toughness and corrosion resistance by controlling the morphology of inclusions and they enhance casting properties by suppressing nozzle clogging. However, if these elements are present at high concentrations, the effects will be saturated, inclusions are liable to become clustered, and the toughness and corrosion resistance will decrease. Therefore, the content of each element is set to 0.0050% or less (preferably 0.0030% or less). Furthermore, when both Ca and Mg are

present, the total content of these elements should preferably be 0.0050% or less. To obtain the aforementioned effects, the total content of one or more of these elements should preferably be 0.0003% or more (ideally 0.0005% or more).

B: 0 to 0.0150%

**[0057]** Boron (B) mainly strengthens grain boundaries and thus its content can be as high as necessary. However, if the B content is high, low-melting-point compounds may form and hot workability may decrease. There are cases where hot workability decreases markedly when the B content is more than 0.0150%. Therefore, the B content is set to 0.0150% or less. Note that the B content should preferably be set to 0.0001% or more to achieve the aforementioned effect.

**[0058]** The proposed steel for oil wells according to the present embodiment has a chemical composition that consists of the elements described above (the balance is Fe and impurities). Here, the term impurities refers to components which, during industrial production of the steel, are mixed in from raw materials such as ore, scrap, or other materials introduced during the production process, at a concentration that does not adversely affect the present embodiment.

Effective amount of C: 0.55 or more and less than 1.54

**[0059]** In the present embodiment, to stabilize austenite, the C content is between 0.55 and 1.54. However, because the steel is strengthened mainly by precipitated carbonitrides of V, some C will be consumed, and thus there is a risk that the austenite stability will decrease. C is the most consumed when all V is precipitated as the carbonitrides. In addition, if Cr, Mo, Ti, Nb, Zr, Ta, Hf, or W is present in the steel, C will be consumed by precipitation of carbonitrides of these elements.

**[0060]** Therefore, to achieve stabilization of austenite, it is necessary to adjust the content of C, V, Cr, Mo, Ti, Nb, Zr, Ta, Hf, and W so that the effective C content given in Formula (i) is 0.55 or more. If the effective C content is 1.54 or more, the microstructure will become inhomogeneous and the hot workability will decrease, accompanying the formation of compounds such as cementite. It is thus necessary to adjust the content of C, V, Cr, Mo, Ti, Nb, Zr, Ta, Hf, and W so that the effective C content is less than 1.54. The lower limit of effective amount of C is preferably 0.65 or more, and more preferably is 0.70 or more. Furthermore, the upper limit of effective amount of C is preferably 1.40 or less, more preferably is 1.30 or less, and further preferably is 1.20 or less.

$$C - 0.18V - 0.06(Cr + Mo) - 0.25Ti - 0.13(Nb + Zr) - 0.07(Ta + Hf + W) \quad \dots (i)$$

where each element symbol represents the content (mass%) of the corresponding element in the steel. If the element is not contained, 0 shall be substituted for the relevant element symbol.

**[0061]** As described above, B strengthens grain boundaries. In addition, although the detailed mechanism is not clear, grain boundaries are further strengthened and the SSC resistance is greatly improved when B is used in combination with Mo. To obtain this effect, it is preferable to add Mo and B in combination to satisfy Formula (ii). The value of Mo-200B in Formula (ii) should preferably be 0.10 or more (ideally 0.20 or more). The upper limit value of Mo-200B in Formula (ii) for the steel is 2.98.

$$Mo - 200B \geq 0 \quad \dots (ii)$$

where each symbol represents the content (mass%) of the corresponding element contained in the steel material. If the element is not contained, 0 shall be substituted for the relevant element symbol.

**[0062]** Although the detailed mechanism is not clear, when Mo is used in combination with Ti, the amount of carbonitrides that effectively strengthen the steel increases, and localization (planarization) of dislocations is suppressed. Therefore, the SSC resistance is also significantly improved. To obtain this effect, the Ti and Mo content should satisfy Formula (iii). The lower limit value of Ti/Mo in Formula (iii) is more preferably 0.45 or more, and further preferably is 0.48 or more. Furthermore, the upper limit value of Ti/Mo in Formula (iii) is more preferably 0.55 or less.

$$0.40 < Ti/Mo < 0.60 \quad \dots (iii)$$

where each symbol represents the content (mass%) of the corresponding element in the steel. If the element is not contained, 0 shall be substituted for the relevant element symbol.



## 2. Steel Microstructure

**[0063]** The steel in the present embodiment has a microstructure in which the total volume fraction of  $\alpha'$  martensite and ferrite is less than 0.1%, the volume fraction of  $\varepsilon$  martensite is 10% or less, and the balance is austenite. If  $\alpha'$  martensite, ferrite, and other phases, which have a BCC structure, are intermixed in the steel microstructure, SSC resistance will be reduced. However, as the matrix of the steel material,  $\alpha'$  martensite and ferrite are permitted to be present as long as the total volume fraction of  $\alpha'$  martensite and ferrite is less than 0.1%.

**[0064]** Furthermore, it is also permissible for  $\varepsilon$  martensite to be intermixed in the steel microstructure. Therefore, the volume fraction of  $\varepsilon$  martensite is set to 10% or less (ideally 2% or less).

**[0065]** Because  $\alpha'$  martensite, ferrite,  $\varepsilon$  martensite, and other phases are present in the steel microstructure as fine crystals, measurement of their volume fractions using methods such as X-ray diffraction and microscopic observation is difficult. The total volume fraction of microstructures with BCC and HCP structures can be measured using a ferrite meter and electron backscattering diffraction pattern analysis.

**[0066]** The strength of steel with the microstructure described above is generally lower than that of steel that is mainly composed of ferrite. Therefore, in the present embodiment, the steel is strengthened by causing carbonitrides to precipitate, thus suppressing dislocation movement. However, if the equivalent circular diameter of the carbonitride precipitates is less than 5 nm, little strengthening will occur. Also, if the precipitates are too coarse (equivalent circular diameter of more than 100 nm) and the content of each element is within the range of the present embodiment, the number of precipitates will greatly decrease, and the strengthening effect will also be small. Therefore, the precipitate size should be 5 to 100 nm (ideally 15 to 50 nm).

**[0067]** To obtain a yield stress of 862 MPa or more, carbonitride precipitates with a size of 5 to 100 nm need to be present at a number density of 100 particles/ $\mu\text{m}^2$  or more. If the number density is more than 500 particles/ $\mu\text{m}^2$ , the strengthening effect will be saturated. Prolonged aging treatment after this saturation point would unnecessarily increase the production cost. Therefore, the upper limit is 500 particles/ $\mu\text{m}^2$  (ideally 400 particles/ $\mu\text{m}^2$ ).

**[0068]** The number density of carbonitride precipitates is measured using the following method. A thin film with a thickness of 100 nm is prepared from the center of the wall thickness or that of the plate thickness of the steel. This thin film is observed using transmission electron microscopy (TEM) and the number of carbonitride precipitates with an equivalent circular diameter of 5 to 100 nm in the visual field ( $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) is counted. The number density measurement should be carried out using various visual fields and the average value should be used.

**[0069]** Note that the carbonitride precipitates include V carbonitride precipitates and that when the steel contains Cr, Mo, Ti, Nb, Zr, Ta, Hf, or W, carbonitrides of these elements may be included. There may also be other complex carbonitrides present.

**[0070]** As described above, increasing the C and Mn content increases the stability of austenite. However, if the FCC structure easily changes to a transformation phase due to applied stress in a corrosive environment, the hydrogen embrittlement susceptibility will increase and it will be difficult to improve the SSC resistance.

**[0071]** Even when stress is applied in a corrosive environment, appropriate adjustment of the components of the steel material according to the present embodiment to control the SFE at 25°C to be 30 mJ/m<sup>2</sup> or more makes it easy to prevent structures other than austenitic structures (e.g.,  $\alpha'$  martensite, ferrite, and  $\varepsilon$  martensite) from becoming mixed into the steel microstructure. At the same time, localization (planarization) of dislocations is also prevented, localized stress concentration is avoided, and hydrogen accumulation is greatly suppressed. Therefore, the SSC resistance significantly improves. The SFE should preferably be 40 mJ/m<sup>2</sup> or more (ideally 50 mJ/m<sup>2</sup> or more). The upper limit should be 100 mJ/m<sup>2</sup>. Note that the SFE is calculated in conformity with Non-Patent Document 1.

**[0072]** Generally, the SSC resistance is improved by making the steel have a fine-grained microstructure. The effect is particularly large for steel with a microstructure mainly composed of ferrite. In the present embodiment, the microstructure is mainly composed of austenite. Even though the aforementioned effect is less than that for steel mainly composed of ferrite, the SSC resistance is greatly improved when the grain size is 100  $\mu\text{m}$  or smaller. The grain size of the austenite should preferably be 80  $\mu\text{m}$  or smaller (ideally 60  $\mu\text{m}$  or smaller). If it is smaller than 1  $\mu\text{m}$ , grain boundary sliding will occur and the strength will markedly decrease. Therefore, the lower grain size limit is 1  $\mu\text{m}$ .

**[0073]** Here, a method for measuring the grain size of austenite is described. First, the steel sample is cut to reveal a cross section that is parallel to the rolling and thickness directions. From this cross section, a sample is taken in a manner such that a position at a depth of  $1/4\ t$ , where  $t$  is the wall or plate thickness, from the surface becomes the observation surface. After the observation surface is etched with a nital etching reagent, observation is performed using optical microscopy at a magnification of 100 to 1000 $\times$ . The grain size of austenite is then determined using the intercept method defined in JIS G 0551 (2013).

## 3. Mechanical Properties

**[0074]** Although the SSC resistance sharply decreases as the strength of steel increases, the steel in the present

embodiment can achieve both a high yield stress of 862 MPa or more and excellent SSC resistance that exceeds that of prior art. Further, in the proposed steel for oil wells according to the present invention, the SSC resistance is stable even at a yield stress of 965 MPa or more. The upper limit of the yield stress is 1275 MPa (preferably 1241 MPa and ideally 1206 MPa).

**[0075]** Note that excellent SSC resistance means that with a yield stress of 95% applied using a constant-load tensile testing machine, the steel does not rupture when immersed in Solution A defined in NACE TM0177-2005 (aqueous solution of 5% NaCl + 0.5% CH<sub>3</sub>COOH saturated with 1-bar H<sub>2</sub>S) and held at 24°C for 336 h. A method in which stress is applied to one surface by a four-point bending method is also available for applying stress. However, with this method, stress relaxation can occur during the test, making the evaluation less accurate. This method is thus not adopted in the present embodiment.

#### 4. Production Method

**[0076]** The steel in the present embodiment can be produced using the following method. Other methods can also be used.

##### <Melting and Casting>

**[0077]** General austenitic steel materials can be produced using melting and casting (ingot or continuous casting). To produce seamless pipes, the steel may be cast into the shape of a round billet for pipe-making by round continuous casting.

##### <Hot Working (forging, piercing, rolling)>

**[0078]** After casting, hot working (e.g., forging, piercing, and rolling) is performed. Note that in the case where a round billet is cast to produce seamless pipes using round continuous casting, processes such as forging and blooming for forming a round billet are unnecessary. In the case where the steel is a seamless pipe, after the piercing process, rolling is performed using a mandrel mill or a plug mill. In the case where the steel is a plate, the process includes performing finishing rolling after a slab has been rough-rolled. The desirable conditions for hot working (e.g., piercing and rolling) are described below.

**[0079]** For producing a seamless pipe, the billet may be heated to an extent such that hot piercing can be performed on a piercing-rolling mill. The desirable heating temperature range is 1000 to 1250°C. The heating time should preferably be set to 0.5 to 10 h. Although there are no particular constraints with respect to piercing-rolling and rolling using another rolling mill (e.g., a mandrel mill or a plug mill), from the viewpoint of hot workability, specifically to prevent surface defects, it is desirable to set the finishing temperature to 900°C or more. Although there is also no particular constraint on the upper limit of the finishing temperature, a finishing temperature of 1100°C or lower is desirable.

**[0080]** For producing a steel plate, the heating temperature of the slab can be set within a temperature range in which hot rolling can be performed (e.g., 1000 to 1250°C). The heating time should preferably be set to 0.5 to 10 h. Although the pass schedule of hot rolling can be arbitrarily set, considering hot workability (reducing the occurrence of surface defects, edge cracks, etc.) in the product, it is desirable to set the finishing temperature to 900°C or more. The maximum finishing temperature should be 1100°C (as in the case of the seamless pipe).

##### <Solution Heat Treatment>

**[0081]** After the steel has been subjected to hot working, it is heated to a temperature that is sufficient to completely dissolve carbonitrides and other precipitates and then rapidly cooled. In this case, after being held at 1000 to 1200°C for 10 min or more, the steel is rapidly cooled. If the solution heat treatment temperature is lower than 1000°C, carbonitrides will not be completely dissolved and precipitation strengthening will be insufficient, making it difficult to obtain a yield stress of 852 MPa or more. If the solution heat treatment temperature is more than 1200°C, phases such as ferrite, which easily cause SSC, may be precipitated. Furthermore, if the holding time is less than 10 min, the effect of the solution heat treatment will be insufficient, and the target strength (i.e., a yield stress of 862 MPa or more) may not be obtained.

**[0082]** The upper limit of the holding time depends on the size and shape of the steel sample and cannot be determined unconditionally. Although it is necessary to have a holding time sufficient to allow the entire steel sample to be soaked, to decrease production cost, an excessive holding time is undesirable. It is usually appropriate to set the holding time to within 1 h. To prevent precipitation of carbonitrides and other intermetallic compounds during cooling, it is desirable to cool the steel at a rate that is equal to or higher than the cooling rate for oil cooling.

**[0083]** Note that the minimum holding time is that for the case where the steel material is reheated at 1000 to 1200°C after it had cooled once to less than 1000°C after hot working. However, in the case where the end temperature of hot

working (finishing temperature) is 1000 to 1200°C, if supplementary heating is performed at that temperature for around 5 min or more, the same effect as that of a solution heat treatment performed under the aforementioned conditions is obtained. Rapid cooling can be performed in this state without reheating the steel material. Therefore, the lower limit of the holding time in the present embodiment includes the case where the end temperature of hot working (finishing temperature) is 1000 to 1200°C and supplementary heating is performed at that temperature for around 5 min or more.

#### <Aging Treatment>

**[0084]** After the steel has undergone the solution heat treatment, it is subjected to an aging treatment to precipitate fine carbonitrides to enhance the strength. The effect of the aging treatment (age hardening) depends on the temperature and the holding time at the set temperature. A shorter (longer) holding time is required for a higher (lower) temperature. Therefore, an appropriately temperature and holding time should be selected so that the predetermined target strength is obtained. Regarding the heat treatment conditions, preferably the steel material should be heated to a temperature of 600 to 800°C and held at that temperature for 30 min or more.

**[0085]** If the heating temperature for the aging treatment is lower than 600°C, precipitation of carbonitrides will be insufficient and it will be difficult to obtain a yield stress of 862 MPa or more. If the heating temperature is higher than 800°C, carbonitrides will easily dissolve and it will be difficult for carbonitrides to precipitate, making it difficult to obtain the aforementioned yield stress.

**[0086]** In the case where the holding time for the aging treatment is less than 30 min, the precipitation of carbonitrides will be insufficient and it will be difficult to obtain the aforementioned yield stress. Although there is no particular constraint regarding the upper limit of the holding time, it is usually appropriate to set the upper limit to within 72 h. Holding the steel at the heating temperature after precipitation hardening has saturated wastes energy and thus increases the production cost. After the aging treatment ends, the steel should be allowed to cool.

#### 5. Applications

**[0087]** The proposed steel for oil wells according to the present embodiment can be used to make oil country tubular goods for use in wet hydrogen sulfide environments.

**[0088]** Below, the present invention is clarified using examples. Note that the present invention is not limited to these examples.

#### EXAMPLES

**[0089]** Thirty-two kinds of steel (chemical compositions given in Table 1) were melted in a 30-kg vacuum furnace and cast into ingots. Each of the ingots was heated at 1180°C for 3 h, and then forged and cut by electrical discharge machining. Thereafter, the cut ingot was held at 1150°C for 1 h, and then hot-rolled into a plate with a thickness of 20 mm. The end temperature of the hot working process was 1000 to 1200°C. In addition, the plate was subjected to solution heat treatment (water cooling was performed after the heat treatment) at 1100°C for 1 h. An aging treatment was then performed at a heating temperature of 650°C and a holding time of 16 h to produce a test material. For Test No. 29, an aging treatment with a holding time of 100 h was carried out.

[Table 1]

[0090]

Table 1

Test No.	Chemical composition (by mass%, balance: Fe and impurities)								Formula (i)	Value of Mo-200B in Formula (ii)	Value of Ti/Mo in Formula (iii)	SFE (mJ/m <sup>2</sup> )
	C	Si	Mn	Al	V	N	P	S	Other			
1	0.78	0.23	19.6	1.00	1.21	0.030	0.015	0.005	-	0.56	0	36
2	1.60	0.33	20.2	0.11	1.22	0.011	0.011	0.006	-	1.38	0	49
3	1.10	0.16	26.3	2.10	2.60	0.012	0.012	0.005	-	0.63	0	63
4	0.90	0.55	16.4	4.10	1.30	0.010	0.011	0.005	-	0.67	0	57
5	0.81	2.10	21.1	3.00	1.18	0.300	0.009	0.006	-	0.60	0	52
6	0.77	0.05	20.1	2.56	1.10	0.030	0.015	0.006	-	0.57	0	45
7	1.20	0.26	20.6	1.10	1.10	0.010	0.012	0.004	Cr: 5.10, Ni: 0.01	0.70	0	47
8	1.10	0.28	19.1	2.10	1.33	0.010	0.011	0.005	Mo: 1.20	0.79	1.20	50
9	0.85	0.44	21.2	1.40	1.28	0.010	0.012	0.005	Cr: 0.11, Mo: 0.55	0.58	0.55	41
10	1.05	0.23	20.9	1.50	1.22	0.011	0.015	0.004	Cu: 1.50	0.83	0	47
11	0.88	0.36	22.5	1.08	1.16	0.011	0.013	0.004	Ni: 2.10	0.67	0	42
12	1.43	0.26	19.6	2.40	1.37	0.011	0.012	0.005	Cu: 1.10, Ni: 1.00	1.18	0	60
13	1.72	2.91	25.1	2.74	2.30	0.021	0.015	0.004	Ti: 1.21	1.00	0	73
14	1.39	2.50	24.6	5.85	2.00	0.011	0.015	0.004	Nb: 1.20	0.87	0	84
15	0.98	0.34	27.7	2.79	1.40	0.040	0.011	0.006	Zr: 1.22	0.57	0	64
16	1.10	1.36	27.1	1.67	1.10	0.020	0.013	0.005	Ta: 2.10	0.76	0	60
17	0.95	1.93	18.9	0.44	1.40	0.220	0.011	0.004	Hf: 1.80	0.57	0	30
18	1.10	2.50	24.6	5.53	1.70	0.010	0.014	0.004	W: 2.00	0.65	0	79
19	1.79	1.95	17.3	1.61	2.40	0.048	0.011	0.004	Ca: 0.0015	1.36	0	61
20	1.01	1.84	18.5	4.49	2.10	0.026	0.014	0.006	Mg: 0.0020	0.63	0	61

(continued)

Test No.	Chemical composition (by mass%, balance: Fe and impurities)								Formula (i)	Value of Mo-200B in Formula (ii)	Value of Ti/Mo in Formula (iii)	SFE (mJ/m <sup>2</sup> )
	C	Si	Mn	Al	V	N	P	S	Other			
21	1.62	2.98	17.9	3.17	1.10	0.004	0.013	0.006	B: 0.0026	1.42	-	73
22	1.15	1.56	24.3	0.86	1.70	0.012	0.014	0.005	Mo: 1.00, B: 0.0018	0.78	0	51
23	1.11	0.02	28.8	4.40	1.80	0.046	0.013	0.005	Mo: 0.61, Ti: 0.33	0.67	0.54	82
24	0.56	0.64	20.7	1.14	0.99	0.010	0.009	0.003	-	0.38	-	30
25	2.51	0.24	20.3	3.22	2.45	0.011	0.011	0.004	Ti: 1.40	1.72	-	81
26	0.85	0.96	14.3	0.70	1.50	0.012	0.011	0.004	-	0.58	-	29
27	0.94	0.22	18.1	0.02	2.14	0.041	0.011	0.005	Ca: 0.0010	0.55	-	29
28	0.99	0.22	20.7	3.16	0.45	0.010	0.013	0.005	-	0.91	-	57
29	1.32	0.27	21.9	0.90	1.10	0.053	0.014	0.006	Cr: 2.30	0.98	-	54
30	0.91	0.26	18.9	1.11	1.35	0.210	0.012	0.003	Hf: 1.19	0.58	-	36
31	0.95	0.55	20.5	1.20	1.56	0.020	0.011	0.003	Mo: 0.90, B: 0.0021	0.62	0	43
32	0.91	0.28	16.1	0.07	1.01	0.350	0.009	0.003	Cr: 2.80, Ni: 6.31	0.56	-	27
(i) C-0.18V-0.06(Cr+Mo)-0.25Ti-0.13(Nb+Zr)-0.07(Ta+Hf+W) (ii) Mo-200B $\geq$ 0 (iii) 0.40<Ti/Mo<0.60												

**[0091]** The SFE was calculated in the manner described above. The austenite grain size was determined using the intercept method. In addition, for each of the test materials, the presence or absence of  $\varepsilon$  martensite was determined by X-ray diffraction measurements, and the volume ratio of  $\alpha'$  martensite and ferrite was measured using a ferrite meter. This volume ratio was determined to 0.1% or more for Test Nos. 24, 26, and 27, and the presence of  $\varepsilon$  martensite was confirmed. Neither  $\varepsilon$  martensite,  $\alpha'$  martensite, nor ferrite was detected for Test Nos. 1 to 23, 25, and 28 to 32.

**[0092]** A thin film with a thickness of 100 nm was prepared from the center of the plate thickness of each test material. Each thin film was observed using transmission electron microscopy (TEM). The number of carbonitride precipitates with an equivalent circular diameter of 5 to 100 nm within a visual field of  $1\ \mu\text{m} \times 1\ \mu\text{m}$  was measured. In addition, a round bar tensile test specimen with a parallel portion that had an external diameter of 6 mm and a length of 40 mm was taken from the aforementioned central portion of the plate thickness for each test material, and a tensile test was performed at room temperature (25°C). The yield stress YS (0.2% proof stress) (MPa) was determined. Note that the axial direction of the round bar tensile test specimen was parallel to the rolling direction of the test material. Evaluation of the SSC resistance was then performed in the manner described above. If the round bar tensile test specimen did not rupture, it was evaluated as acceptable (marked with  $\bigcirc$  symbol in Table 2); if the round bar tensile test specimen ruptured, it was evaluated as unacceptable (marked with  $\times$  symbol in Table 2). A summary of these results is shown in Table 2.

[Table 2]

**[0093]**

Table 2

Test No.	Number density of carbonitride precipitates (particles/ $\mu\text{m}^2$ )	Austenite grain size ( $\mu\text{m}$ )	Yield stress (MPa)	SSC resistance (95%AYS)	
1	119	51	908	$\bigcirc$	Inventive example
2	115	56	997	$\bigcirc$	
3	235	25	1189	$\bigcirc$	
4	121	48	1013	$\bigcirc$	
5	110	45	989	$\bigcirc$	
6	106	44	908	$\bigcirc$	
7	104	48	971	$\bigcirc$	
8	178	44	1019	$\bigcirc$	
9	139	43	1000	$\bigcirc$	
10	111	45	997	$\bigcirc$	
11	106	52	957	$\bigcirc$	
12	125	41	1027	$\bigcirc$	
13	329	29	1158	$\bigcirc$	
14	285	28	1123	$\bigcirc$	
15	186	41	1032	$\bigcirc$	
16	155	45	971	$\bigcirc$	
17	181	40	1032	$\bigcirc$	
18	217	38	1081	$\bigcirc$	
19	219	30	1169	$\bigcirc$	
20	199	30	1135	$\bigcirc$	
21	101	50	971	$\bigcirc$	
22	198	27	1081	$\bigcirc$	
23	221	26	1096	$\bigcirc$	

(continued)

Test No.	Number density of carbonitride precipitates (particles/ $\mu\text{m}^2$ )	Austenite grain size ( $\mu\text{m}$ )	Yield stress (MPa)	SSC resistance (95%AYS)	
24	101	52	698	○	Comparative example
25	371	25	1174	×	
26	127	39	1047	×	
27	145	40	1140	×	
28	45	52	744	○	
29	39	193	588	○	
30	151	54	1023	○	Inventive example
31	182	29	1060	○	
32	100	45	967	×	Comp. ex.

**[0094]** From Table 2, it can be seen that for Test Nos. 1 to 23, 30, and 31, which are example embodiments of the present invention, the number density of carbonitride precipitates was 100 particles/ $\mu\text{m}^2$  or more, SFE was 30 mJ/m<sup>2</sup> or more, grain size was 100  $\mu\text{m}$  or smaller, and Formula (i) was satisfied. Therefore, all these steel samples had excellent SSC resistance and had a yield stress of 862 MPa or more. Note that for Test Nos. 22 and 23, the round bar tensile test specimens did not rupture even when a yield stress of 100% was applied when evaluating the SSC resistance.

**[0095]** For Test No. 24, a comparative example, although the SSC resistance was acceptable, the strength was low because the C content was low. For Test No. 25, the SSC resistance was poor because the C content was too high. For Test No. 26, the Mn content was low and the SFE was low, and consequently the SSC resistance was poor. For Test No. 27, the Al content was low and the SFE was low, and consequently the SSC resistance was poor. For Test No. 28, although the SSC resistance was acceptable, the V content was low and the yield stress was insufficient. For Test No. 29, although the SSC resistance was acceptable, the number density of carbonitride precipitates was low and the austenite grain size was large, and consequently the strength was low. For Test No. 32, the SFE was low, and consequently the SSC resistance was poor.

#### INDUSTRIAL APPLICABILITY

**[0096]** The proposed steel has excellent SSC resistance because it has an austenitic structure. It has a high yield stress of 862 MPa or more, which is obtained by precipitation strengthening. Therefore, the proposed steel for oil wells according to the present invention can be used to make oil country tubular goods for use in wet hydrogen sulfide environments.

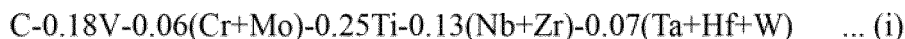
#### Claims

1. A steel with a chemical composition consisting of (mass%),

C: 0.60 to 2.00%,  
 Si: 0.01 to 3.00%,  
 Mn: 16.0 to 30.0%,  
 Al: 0.07 to 6.00%,  
 V: 0.50 to 3.00%,  
 N: 0.500% or less,  
 P: 0.030% or less,  
 S: 0.030% or less,  
 Cr: 0 to 10.00%,  
 Mo: 0 to 3.00%,  
 Cu: 0 to 3.00%,  
 Ni: 0 to 20.00%,  
 Ti: 0 to 3.00%,

Nb: 0 to 3.00%,  
 Zr: 0 to 3.00%,  
 Ta: 0 to 6.00%,  
 Hf: 0 to 6.00%,  
 W: 0 to 6.00%,  
 Ca: 0 to 0.0050%,  
 Mg: 0 to 0.0050%,  
 B: 0 to 0.0150%, and  
 Fe and impurities: balance, wherein  
 an effective amount of C defined by Formula (i) is 0.55 or more and less than 1.54;  
 in the steel microstructure:

a total volume fraction of  $\alpha'$  martensite and ferrite is less than 0.1%,  
 a volume fraction of  $\epsilon$  martensite, which has an HCP structure, is 10% or less, and  
 the balance is austenite;  
 a number density of carbonitride precipitates with an equivalent circular diameter of 5 to 100 nm is 100  
 particles/ $\mu\text{m}^2$  or more;  
 a yield stress is 862 MPa or more;  
 a SFE at 25°C is 30 mJ/m<sup>2</sup> or more, and  
 an austenite grain size is 100  $\mu\text{m}$  or smaller:



where, each symbol represents the content (mass%) of the element, with 0 being substituted for the relevant  
 element symbol when the element is not contained.

2. The steel material according to claim 1, wherein the chemical composition contains one or more of the following  
 elements (mass%):

Cr: 0.05 to 10.00% and  
 Mo: 0.10 to 3.00%.

3. The steel material according to claim 1 or claim 2, wherein the chemical composition contains one or more of the  
 following elements (mass%):

Cu: 0.10 to 3.00% and  
 Ni: 0.10 to 20.00%.

4. The steel material according to any of claims 1 to 3, wherein the chemical composition contains one or more of the  
 following elements (mass%):

Ti: 0.005 to 3.00%,  
 Nb: 0.005 to 3.00%,  
 Zr: 0.005 to 3.00%,  
 Ta: 0.005 to 6.00%,  
 Hf: 0.005 to 6.00%, and  
 W: 0.005 to 6.00%.

5. The steel material according to any of claims 1 to 4, wherein the chemical composition contains one or more of the  
 following elements (mass%):

Ca: 0.0003 to 0.0050% and  
 Mg: 0.0003 to 0.0050%.

6. The steel material according to any of claims 1 to 5, wherein the chemical composition contains (mass%):  
 B: 0.0001 to 0.0150%.



7. The steel material according to claim 6, which satisfies Formula (ii) below:

$$\text{Mo}-200\text{B} \geq 0 \quad \dots \text{(ii)}$$

where, each symbol represents the content (mass%) of the corresponding element, with 0 being substituted for the relevant element symbol when the element is not contained.

8. The steel material according to any of claims 1 to 7, which satisfies Formula (iii) below:

$$0.40 < \text{Ti}/\text{Mo} < 0.60 \quad \dots \text{(iii)}$$

where, each symbol represents the content (mass%) of the corresponding element, with 0 being substituted for the relevant element symbol when the element is not contained.

9. The steel material according to any of claims 1 to 8, wherein the yield stress is 965 MPa or more.

10. Oil country tubular goods made of a steel material according to any of claims 1 to 9.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/047181

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C21D8/02 (2006.01) i, C21D8/10 (2006.01) i, C21D9/08 (2006.01) i,  
C22C38/00 (2006.01) i, C22C38/58 (2006.01) i

FI: C22C38/00302A, C22C38/58, C21D8/02D, C21D8/10D, C21D9/08E

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C21D8/00-8/10, 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 1971-2021

Registered utility model specifications of Japan 1996-2021

Published registered utility model applications of Japan 1994-2021

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

CAplus/REGISTRY (STN)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2019-519680 A (ARCELORMITTAL) 11 July 2019 (2019-07-11), claims, paragraphs [0035], [0064]- [0075]	1-6, 9 7-8, 10
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Further documents are listed in the continuation of Box C.



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02 March 2021Name and mailing address of the ISA/  
Japan Patent Office  
3-4-3, Kasumigaseki, Chiyoda-ku,  
Tokyo 100-8915, Japan

Authorized officer

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/047181

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