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(54) **HIGH-STRENGTH STEEL SHEET FOR SOUR GAS EQUIPMENT, AND HIGH-STRENGTH STEEL PIPE USING SAME**

(57) Without any restriction on the maximum hardness of the surface layer, provided is a high strength steel plate for sour gas apparatuses having, excellent SSCC resistance in an environment equivalent to ISO-15156 Region 2 where pH is 3.5 or more and the H₂S partial pressure is 0.003 bar to 1 bar. The high strength steel plate for sour gas apparatuses having a chemical composition containing, in mass%, specified amounts of C,

Si, Mn, P, S, N, Al, and Ca, Ni of 0.10 % to 4.00 %, and at least one selected from the group consisting of Cr, Mo, W, and Nb in a specified amount, with the balance being Fe and inevitable impurities, in which a ratio HV_{min}/HV_{max} of the minimum value HV_{min} to the maximum value HV_{max} of Vickers hardness HV0.1 at 0.25 mm below a surface of the steel plate is 0.77 or more.

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Description

TECHNICAL FIELD

[0001] This disclosure relates to a high strength steel plate for sour gas apparatuses and a high strength steel pipe or tube using the same, which are suitable for use in sour gas apparatuses, such as line pipes used for transporting crude oil and natural gas and oil well pipes or tubes used for producing them.

BACKGROUND

[0002] Generally, for example, a line pipe is manufactured by forming a steel plate produced by a plate mill or hot rolling mill into a steel pipe or tube by, for example, UOE forming, press bend forming, and roll forming.

[0003] Here, line pipes used in the transportation environment of crude oil and natural gas containing hydrogen sulfide (sour environment) require sulfide stress corrosion cracking resistance (SSCC resistance) in addition to strength, toughness, weldability, and hydrogen-induced cracking resistance (HIC resistance). The sour environment is classified by ISO-15156 as Regions 1-3 based on pH and hydrogen sulfide partial pressure, and it is generally recognized that Region 3 with low pH and high H₂S partial pressure is the most severe environment. It is known that a steel plate with higher strength has more susceptibility to SSCC, and SSCC occurs mainly in the high-hardness region of the welded portion exposed to the Region 3 environment. Therefore, it has generally not been a problem in seamless steel pipes or tubes for oil wells and line pipes with relatively low hardness. In recent years, however, the environment where crude oil and natural gas are extracted has become increasingly severe, and it has been reported that SSCC can occur even in the base metal of line pipe in environments with high hydrogen sulfide partial pressure or low pH. Thus, the importance of controlling the hardness of the inner surface layer of steel pipe or tube to improve SSCC resistance in more severe corrosion environments has been pointed out. In environments where the hydrogen sulfide partial pressure is relatively low, localized corrosion called "fissure" may occur, and SSCC may occur starting from the localized corrosion, and it is widely recognized that SSCC may occur even in a relatively mild sour environment classified as Region 2 in ISO-15156 above, for example, where the H₂S partial pressure is about 0.003 bar to 1 bar. In detail, from the perspective of SSCC, the environment with low pH and high H₂S partial pressure (Region 3) is not generally the most severe, and when local corrosion is considered, SSCC risk is newly recognized in sour environments equivalent to Region 2 with H₂S partial pressures of 0.003 bar to 1 bar. Although there is strong demand for higher strength line pipe from the viewpoint of reducing construction cost, high strength line pipe steel plates for sour environments have not yet been put into practical use due to the above concerns about SSCC.

[0004] Normally, the thermo-mechanical control process (so-called TMCP) technique, which combines controlled rolling and controlled cooling, is applied in the production of high strength steel plates for line pipes. To increase the strength of steel plate using this TMCP technique, it is effective to increase the cooling rate during controlled cooling. However, when controlled cooling is performed at a high cooling rate, the surface layer of the steel plate is rapidly cooled, resulting in an increase in the hardness of the surface layer compared to the inside of the steel plate. Furthermore, it is known that when the steel plate is formed into a tube or pipe, the hardness of the surface layer is increased due to strain hardening, resulting in a decrease in SSCC resistance.

[0005] To solve the above problem, for example, WO2019/058422A1 (PTL 1) proposes a technique for suppressing the maximum hardness of a steel pipe within a range from the surface to a depth of 1.0 mm to 250 HV or less by carrying out a multi-stage cooling process after hot rolling. JP2020-012168A (PTL 2) also proposes that the maximum hardness of the surface layer of a steel plate be suppressed to 200 HV or less by performing a multi-stage cooling process after hot rolling, thereby improving SSCC resistance.

CITATION LIST

Patent Literature

[0006]

PTL 1: WO2019/058422A1

PTL 2: JP2020-012168A

SUMMARY

(Technical Problem)

[0007] Although the techniques described in PTLs 1 and 2 can improve SSCC resistance in environments equivalent to Region 3, which contains hydrogen sulfide with a partial pressure of 0.1 MPa (1 bar) or more, PTLs 1 and 2 do not consider SSCC caused by local corrosion, called fissure, in environments with low hydrogen sulfide partial pressures equivalent to Region 2. In detail, the techniques described in PTLs 1 and 2 are intended for sour environments with low pH and high H₂S partial pressure equivalent to Region 3 based on ISO-15156, and do not consider SSCC due to localized corrosion in sour environments equivalent to Region 2 where H₂S partial pressure is 0.003 bar to 1 bar. Furthermore, the techniques ensure SSCC resistance by limiting the maximum hardness of the surface layer of steel pipe or tube and steel plate and are therefore actually practical for application to the strength grade range of X60 to X70. For example, there is a major limitation for application to even higher strength grades such as X80, X90, and X100.

[0008] It could thus be helpful to provide, without imposing any restriction on the maximum hardness of the surface layer, a high strength steel plate for sour gas apparatuses with excellent SSCC resistance in an environment equivalent to ISO-15156 Region 2 where pH is 3.5 or more and the H₂S partial pressure is 0.003 bar to 1 bar and a high strength steel pipe or tube using the same.

(Solution to Problem)

[0009] In order to ensure SSCC resistance in an environment equivalent to Region 2, we first examined the SSCC mechanism in the Region 2 environment. As a result, we found that increasing corrosion resistance at the surface of the steel plate is important to ensure SSCC resistance of high strength steel pipe or tube in the Region 2 sour environment.

[0010] The Region 3 sour environment is an environment with a low pH and high H₂S partial pressure, and the Fe²⁺ ions eluted from the steel plate as a result of the corrosion reaction are quickly converted to FeS and deposited on a surface of the steel plate to form a dense and highly protective FeS film uniformly. As a result, local corrosion is unlikely to occur. However, SSCC is made apparent without necessarily requiring local corrosion, since the high driving force of hydrogen embrittlement is provided by the abundance of H₂S in the environment. In detail, SSCC in the Region 3 sour environment is a type of hydrogen embrittlement phenomenon that does not necessarily involve local corrosion. In general, it is known that high-hardness (high strength) steel plate has high susceptibility to hydrogen embrittlement. In detail, for SSCC suppression in Region 3, the "approach of constraining the maximum hardness of the surface layer of the steel pipe or tube and steel plate" described in PTLs 1 and 2 makes sense.

[0011] On the other hand, the Region 2 sour environment is an environment with a high pH and low H₂S partial pressure compared to the Region 3 environment, making it difficult for FeS to form, resulting in uneven protection of a surface of the steel plate. Furthermore, because pH is relatively high, driving force of hydrogen embrittlement is low. Therefore, SSCC becomes apparent only after the progression of preferential corrosion (local corrosion) at a less protective surface of the steel plate and the resulting pH drop in the local corrosion area. In view of the above, to improve SSCC resistance in Region 2, it is necessary to improve corrosion protection of the surface of the steel plate and suppress local corrosion. We repeated numerous experiments and studies on the chemical composition and producing conditions of steel plate. As a result, it was found that the inclusion of 0.1 mass% or more of Ni, as well as at least one of Cr, Mo, W, or Nb, has the effect of suppressing local corrosion. However, it was also found that the inclusion of Ni causes tight scale formation during the slab heating stage, resulting in hardness differences due to uneven cooling on a surface of the steel plate, which contributes to SSCC. In detail, when external stress is applied, this difference in hardness causes a large stress concentration, forming a minute plastic deformation zone, and the local corrosion suppressing effect of the alloying element Ni is not fully achieved. Therefore, it was found necessary to control the ratio HV_{\min}/HV_{\max} of the minimum value HV_{\min} to the maximum value HV_{\max} of Vickers hardness HV0.1 at 0.25 mm below a surface of the steel plate to 0.77 or more. As a result of further investigation to achieve this, it was found that by appropriately controlling the slab heating conditions and applying at least one pass of high reduction rolling with a pass rolling reduction of 4 % or more in the temperature range of 1000 °C to 1100 °C during the subsequent hot rolling, the dense structure of the scale formed on a surface of the steel plate is broken down and uneven cooling is suppressed, resulting in a reduction in hardness difference, and the SSCC resistance improvement effect of Ni can be effectively brought out, thereby improving the SSCC resistance of the steel plate.

[0012] Based on these discoveries, we provide:

[1] A high strength steel plate for sour gas apparatuses comprising a chemical composition containing (consisting of), in mass%,

C: 0.02 % or more and 0.20 % or less,

Si: 0.01 % or more and 0.70 % or less,

Mn: 0.10 % or more and 2.50 % or less,
P: 0.030 % or less,
S: 0.0050 % or less,
N: 0.0010 % or more and 0.0100 % or less,
Al: 0.010 % or more and 0.200 % or less,
Ca: 0.0005 % or more and 0.0050 % or less,
Ni: 0.10 % or more and 4.00 % or less, and

at least one selected from the group consisting of

Cr: 0.03 % or more and 1.00 % or less,
Mo: 0.03 % or more and 0.50 % or less,
W: 0.03 % or more and 0.50 % or less, and
Nb: 0.005 % or more and 0.100 % or less,

with the balance being Fe and inevitable impurities, wherein
a ratio HV_{min}/HV_{max} of the minimum value HV_{min} to the maximum value HV_{max} of Vickers hardness HV0.1 at 0.25 mm
below a surface of the steel plate is 0.77 or more.

[2] The high strength steel plate for sour gas apparatuses according to [1], wherein the chemical composition further
contains, in mass%, Cu: 0.01 % or more and 1.00 % or less.

[3] The high strength steel plate for sour gas apparatuses according to [1] or [2], wherein the chemical composition
further contains, in mass%, at least one selected from the group consisting of

V: 0.005 % or more and 0.1 % or less,
Ti: 0.005 % or more and 0.1 % or less,
Zr: 0.0005 % or more and 0.02 % or less,
Mg: 0.0005 % or more and 0.02 % or less, and
REM: 0.0005 % or more and 0.02 % or less.

[4] A high strength steel pipe or tube using the high strength steel plate for sour gas apparatuses according to [1] or [2].
[5] A high strength steel pipe or tube using the high strength steel plate for sour gas apparatuses according to [3].

(Advantageous Effect)

[0013] Without any restriction on the maximum hardness of the surface layer, the high strength steel plate for sour gas
apparatuses and the high strength steel pipe or tube using the same of this disclosure has excellent SSCC resistance in an
environment equivalent to ISO-15156 Region 2 where pH is 3.5 or more and the H_2S partial pressure is 0.003 bar to 1 bar.

DETAILED DESCRIPTION

[0014] The following is a specific description of the high strength steel plate for sour gas apparatuses of this disclosure.

[Chemical composition]

[0015] First, the chemical composition of the high strength steel plate of this disclosure and reasons for limitation will be
described. When components are expressed in " %" in the following description, this refers to "mass%" unless otherwise
noted

C: 0.02 % or more and 0.20 % or less

[0016] C effectively contributes to strength improvement, but sufficient strength cannot be secured when the content is
less than 0.02 %, so the C content should be 0.02 % or more, preferably 0.025 % or more. On the other hand, when the C
content exceeds 0.20 %, workability and weldability deteriorate significantly. Therefore, the C content should be 0.20 % or
less, preferably 0.15 % or less.

Si: 0.01 % or more and 0.70 % or less

[0017] Si is added for deoxidation, but when the content is less than 0.01 %, the deoxidizing effect is not sufficient, so the

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Si content should be 0.01 % or more, preferably 0.05 % or more. On the other hand, when the Si content exceeds 0.70 %, toughness and weldability deteriorate. Therefore, the Si content should be 0.70 % or less, preferably 0.50 % or less.

Mn: 0.10 % or more and 2.50 % or less

[0018] Mn effectively contributes to the improvement of strength and toughness, but the effect is not fully realized when the content is less than 0.10 %. Therefore, the Mn content should be 0.10 % or more, preferably 0.30 % or more, and more preferably 0.50 % or more. On the other hand, when the Mn content exceeds 2.50 %, weldability deteriorates and hardness increases in the central segregation area, resulting in deterioration of HIC resistance. Therefore, the Mn content should be 2.50 % or less, preferably 2.00 % or less.

P: 0.030 % or less

[0019] P is an inevitable impurity element, which degrades weldability and increases the hardness of central segregation area, thereby degrading SSCC and HIC resistance. Since this effect becomes more pronounced when the P content exceeds 0.030 %, the P content should be 0.030 % or less, preferably 0.025 % or less, and more preferably 0.020 % or less. A lower P content is better, but from the perspective of refining cost, the P content is preferably 0.001 % or more.

S: 0.0050 % or less

[0020] S is an inevitable impurity element and should be kept low because it degrades HIC resistance by forming MnS inclusions in the steel. From this viewpoint, the S content should be 0.0050 % or less, preferably 0.0040 % or less, and more preferably 0.0030 % or less. A lower S content is better, but from the perspective of refining cost, the S content is preferably 0.0002 % or more.

N: 0.0010 % or more and 0.0100 % or less

[0021] N effectively contributes to the improvement of strength, but a content of less than 0.0010 % does not ensure sufficient strength. Therefore, the N content should be 0.0010 % or more, preferably 0.0015 % or more. On the other hand, when the N content exceeds 0.0100 %, the hardness of the central segregation area increases, which deteriorates HIC resistance. Toughness also degrades. Therefore, the N content should be 0.0100 % or less, preferably 0.0080 % or less.

Al: 0.010 % or more and 0.200 % or less

[0022] Al is added as a deoxidizer, but its effect is not fully realized when the Al content is less than 0.010 %. Therefore, the Al content should be 0.010 % or more, preferably 0.015 % or more. On the other hand, when the Al content exceeds 0.200 %, the cleanliness of the steel decreases and toughness deteriorates. Therefore, the Al content should be 0.200 % or less, preferably 0.150 % or less, and more preferably 0.100 % or less.

Ca: 0.0005 % or more and 0.0050 % or less

[0023] Ca is an effective element for improving HIC resistance through morphological control of sulfide inclusions, but its addition effect is not sufficient when the Ca content is less than 0.0005 %. Therefore, the Ca content should be 0.0005 % or more, preferably 0.0008 % or more. On the other hand, when the Ca content exceeds 0.0050 %, not only does the above effect become saturated, but the HIC resistance of the steel deteriorates due to a decrease in cleanliness. Therefore, the Ca content should be 0.0050 % or less, preferably 0.0045 % or less.

Ni: 0.10 % or more and 4.00 % or less

[0024] Ni is an important element in terms of improving SSCC resistance in the low H₂S partial pressure environment. In detail, as the steel plate dissolves due to corrosion, Ni reacts with H₂S in the sour environment to quickly form a NiS film on a surface of the steel plate. NiS has higher corrosion protection effect than the iron corrosion product FeS in sour environments, and the formation of a NiS protective film on a surface of the steel plate suppresses corrosion overall. In terms of local corrosion, as mentioned above, in the low H₂S partial pressure environment, the formation of protective FeS becomes non-uniform, resulting in local corrosion at weakly protective locations. However, due to the NiS protective action of the Ni content, even when corrosion starts at the weakly protective locations, the NiS film is formed again, thereby suppressing further corrosion growth and suppressing localized corrosion. In detail, SSCC resistance is improved by suppressing the formation of local corrosion, which is a precursor to SSCC in the low H₂S partial pressure environment. To

achieve this effect, the Ni content should be 0.10 % or more, preferably 0.20 % or more, and more preferably 0.30 % or more. When the Ni content is less than 0.10 %, the reformation of NiS film at the points where local corrosion has started becomes insufficient, and the improved corrosion resistance in the non-local corrosion area conversely promotes local corrosion, resulting in degradation of SSCC resistance. On the other hand, excessive Ni content deteriorates weldability and steel plate manufacturability, and is disadvantageous from a cost standpoint. Therefore, the Ni content should be 4.00 % or less, preferably 3.50 % or less, and more preferably 3.00 % or less. As mentioned above, Ni is an effective element from the viewpoint of improving SSCC resistance, but to fully utilize its effect, the coexistence of at least one of the alloying elements Cr, Mo, W, or Nb, as described below, and the suppression of expansion of surface layer hardness differences by optimizing producing conditions are necessary.

[0025] At least one selected from the group consisting of Cr: 0.03 % or more and 1.00 % or less, Mo: 0.03 % or more and 0.50 % or less, W: 0.03 % or more and 0.50 % or less, and Nb: 0.005 % or more and 0.100 % or less

[0026] Cr, Mo, W, and Nb are important elements for realizing the effect of Ni in improving SSCC resistance, and at least one of these elements must be included. These elements have the effect of promoting the reformation of the protective NiS film at the local corrosion initiation site. When Cr and Nb corrode in a sour environment, they form composite oxides FeCr_2O_4 and FeNbO_4 with iron as corrosion products, respectively. Further, Mo and W form FeWO_4 and FeMoO_4 , respectively. In detail, these elements inhibit the consumption of S^{2-} ions by Fe^{2+} ions generated by corrosion, i.e., FeS formation, thereby promoting the rapid formation of NiS at the local corrosion initiation site, and as a result, the effect of Ni in improving SSCC resistance is made apparent. To achieve the effect, when at least one selected from the group consisting of Cr, Mo, W, and Nb is added, each of the Cr, Mo, and W contents should be 0.03 % or more, and the Nb content should be 0.005 % or more. On the other hand, excessive contents of these elements deteriorate weldability and toughness, and are also disadvantageous from a cost standpoint. Therefore, the Cr content should be 1.00 % or less, preferably 0.80 % or less, and more preferably 0.70 % or less. Each of the Mo and W contents should be 0.50 % or less, preferably 0.45 % or less, and more preferably 0.40 % or less. The Nb content should be 0.100 % or less, preferably 0.080 % or less, and more preferably 0.070 % or less.

[0027] Although the basic components have been described above, the following optional elements may be contained.

Cu: 0.01 % or more and 1.00 % or less

[0028] Cu is an effective element for improving toughness, increasing strength, and improving SSCC and HIC resistance. To obtain these effects, the Cu content is preferably 0.01 % or more. However, the addition of Cu in excess of 1.00 % inhibits the formation of NiS and degrades SSCC resistance. Therefore, when Cu is added, the Cu content should be 1.00 % or less, preferably 0.80 % or less, and more preferably 0.60 % or less.

[0029] At least one selected from the group consisting of V: 0.005 % or more and 0.1 % or less, Ti: 0.005 % or more and 0.1 % or less, Zr: 0.0005 % or more and 0.02 % or less, Mg: 0.0005 % or more and 0.02 % or less, and REM: 0.0005 % or more and 0.02 % or less

[0030] Both V and Ti are elements that can be optionally added to increase the strength and toughness of the steel plate. For each element, when the content is less than 0.005 %, the effect is not fully realized. Therefore, when these elements are added, the content of each element is preferably 0.005 % or more. On the other hand, when the content of each element exceeds 0.1 %, the toughness of the welded portion deteriorates. Therefore, when these elements are added, the content of each element is preferably 0.1 % or less.

[0031] Zr, Mg, and REM are elements that can be optionally added to increase toughness through crystal grain refinement and to increase cracking resistance through control of inclusion properties. For each element, when the content is less than 0.0005 %, the effect is not fully realized. Therefore, when these elements are added, the content of each element is preferably 0.0005 % or more. On the other hand, when the content of each element exceeds 0.02 %, the effect becomes saturated, so it is preferable to set the content of each element to 0.02 % or less if added.

[0032] The balance other than the aforementioned elements is Fe and inevitable impurities. However, other trace elements may be contained as long as they do not impair the effects of this disclosure. For example, O is an inevitable element in steel, but is acceptable in this disclosure when its content is 0.0050 % or less, preferably 0.0040 % or less.

[Hardness]

[0033] In the high strength steel plate for sour gas apparatuses of this disclosure, it is extremely important to control the hardness of the surface layer as follows.

[0034] The ratio $\text{HV}_{\min}/\text{HV}_{\max}$ of minimum value HV_{\min} to maximum value HV_{\max} of Vickers hardness HV0.1 at 0.25 mm below surface of steel plate, being 0.77 or more

[0035] As mentioned above, while Ni is a necessary element in this disclosure to ensure the SSCC resistance of steel plate, Ni increases the adhesion of oxide scale on a surface of the steel plate during the production process, causing uneven cooling on the surface of the steel plate and a large difference between the maximum and minimum hardness

values in a surface layer of the steel plate. When there is a large difference between the maximum and minimum hardness values in the surface layer of the steel plate, stress concentration occurs in the presence of external stress, resulting in local plastic deformation. Since the non-plastic deformation area has high protective properties due to the protective NiS, the area where the protective NiS formed on a surface of the steel plate is mechanically destroyed by plastic deformation acts as an active dissolution site and becomes a strong driving force for SSCC from local corrosion. Thus, even when the chemical composition satisfies the above, SSCC resistance cannot be ensured. SSCC due to this hardness difference is made apparent when the ratio of the minimum to the maximum hardness is less than 0.77. Therefore, the ratio HV_{\min}/HV_{\max} of the minimum value HV_{\min} to the maximum value HV_{\max} of Vickers hardness HV0.1 in a surface layer of the steel plate, specifically at 0.25 mm below a surface of the steel plate is set to 0.77 or more. HV_{\min}/HV_{\max} is preferably 0.80 or more and more preferably 0.82 or more. No upper limit is placed on HV_{\min}/HV_{\max} and HV_{\min}/HV_{\max} may be 1.00.

[0036] To achieve a ratio of the minimum to the maximum Vickers hardness HV0.1 in a surface layer of the steel plate of 0.77 or more as described above, it is important to properly control the producing conditions described below, especially to properly control the slab heating retention temperature and to apply high reduction rolling at high temperature during the hot rolling process.

[0037] HV_{\min} and HV_{\max} are measured as follows. That is, when the width of the steel plate is W (mm), the steel plate is cut parallel to the rolling direction and perpendicular to a surface of the steel plate at the center position in the width direction of the steel plate (perpendicular to the rolling direction and perpendicular to the thickness direction of the steel plate). Then, at a depth of 0.25 mm from a surface of the steel plate of the cross section of the cut steel plate (cross section along the rolling direction (L-cross section)), Vickers hardness is measured at 20 points in the rolling direction of the steel plate under the conditions of test force: 0.1 kgf (0.9807 N) and pitch: 1 mm, in accordance with JIS Z 2244 (2009). Among them, the minimum value is HV_{\min} and the maximum value is HV_{\max} .

[0038] Apart from the hardness ratio, when the hardness of the steel plate is excessively low, it will be difficult to provide sufficient strength as a high strength steel plate. On the other hand, when the hardness is excessively high, the steel plate has poor workability, making it difficult to use properly as structural parts. Therefore, HV_{\min} is preferably 190 or more. HV_{\max} is preferably 360 or less.

[Microstructure]

[0039] To obtain the strength required for the high strength steel plate of this disclosure, the microstructure of the steel plate is not particularly limited, but to obtain a good strength-toughness balance as a structural steel plate, it is preferable that the microstructure be mainly composed of bainite with a bainite fraction of 60 % or more.

[Strength]

[0040] The high strength steel plate of this disclosure shall be a steel plate for steel pipe or tube having a strength of API 5L grade X60 or more and a tensile strength of 520 MPa or more.

[Thickness]

[0041] The suitable thickness of the steel plate is 3 mm or more and 60 mm or less.

[Production method]

[0042] In a suitable producing method for the steel plate of this disclosure, a steel slab or billet having the above chemical composition is heated and then hot rolled to make a steel plate, and then the steel plate is subjected to controlled cooling under predetermined conditions.

[0043] First, molten steel having the chemical composition described above is prepared by steelmaking in a publicly known furnace such as a converter or an electric furnace, and made into a slab or billet, by a publicly known method such as continuous casting or ingot casting. Vacuum degassing refining or the like may be performed upon steelmaking. The chemical composition of the molten steel may be adjusted through a publicly known steel refining method.

[0044] The above slab or billet is then hot rolled to a desired size and shape to make a steel plate. In this process, from the viewpoint of ensuring SSCC resistance, it is extremely important to heat the slab or billet to a temperature range of 1050 °C to 1250 °C and hold it for at least 20 minutes before hot rolling.

[0045] In detail, in the steel plate of this disclosure that contains Ni, Ni-enriched subscale gradually develops on the surface of the slab or billet in the temperature range of 950 °C or higher during the heating process, forming an oxide scale with high adhesion with the steel plate. During the cooling process after hot rolling, the oxide scale causes uneven cooling on a surface of the steel plate, resulting in hardness differences and degrading the SSCC resistance of steel plate. However, while the steel plate is heated in the temperature range of 1050 °C to 1250 °C, the scale-out rate (outward scale

growth rate) of the steel plate is relatively fast, so that subscale growth is not pronounced and the formation of adhesive scales can be stalled. When heating is performed above 1250 °C, the driving force of internal oxidation is very strong, causing the subscale to grow significantly and the formation of adhesive scales to proceed. From the viewpoint of suppressing the formation of such adhesive scales, it is important to set the heating temperature at 1050 °C or higher, preferably 1070 °C or higher, and more preferably 1100 °C or higher. It is also important to set the heating temperature at 1250 °C or lower, preferably 1230 °C or lower and the holding time to 20 minutes or more, preferably 30 minutes or more.

[0046] No upper limit is placed on the holding time, but from the viewpoint of productivity, etc., the holding time is preferably 1000 minutes or less.

[0047] From the viewpoint of ensuring SSCC resistance, it is extremely important to apply at least one pass of high reduction rolling with a pass rolling reduction of 4 % or more in the temperature range of 1000 °C to 1100 °C during the hot rolling of slab or billet.

[0048] In detail, in the steel plate of this disclosure that contains Ni as described above, the formation of adhesive scales can be suppressed to some extent by controlling the heating conditions during the heating process, but the formation itself is unavoidable and simply controlling the heating conditions is insufficient to ensure SSCC resistance. In order to suppress the hardness difference expansion due to the adhesive scales, it is important to sufficiently crush the adhesive scales formed on the surface of the slab or billet by applying at least one pass of high reduction rolling with a pass rolling reduction of 4 % or more, preferably 5 % or more in the temperature range of 1000 °C to 1100 °C during the hot rolling process. Reduction rolling in the temperature range above 1100 °C is not effective enough because even if the scales are crushed once by reduction rolling, oxidation quickly progresses again, and adhesive scales are regenerated. In addition, when reduction rolling in the temperature range below 1000 °C, scale crushing by reduction rolling does not occur sufficiently because the scale becomes harder due to the temperature drop. Even in the temperature range of 1000 °C to 1100 °C, a path rolling reduction of less than 4 % is insufficient for scale crushing.

[0049] Although no upper limit is placed on the pass rolling reduction, the pass rolling reduction is preferably 40 % or less, since excessive high reduction rolling is undesirable for rolling line maintenance.

[0050] In order to obtain high toughness as well as strength of API 5L grade X60 or more, which is the target of the steel plate of this disclosure, it is preferable to control the rolling finish temperature in the hot rolling process and to control the cooling rate and cooling stop temperature in the controlled cooling. These temperatures mean "average steel plate temperature". Although the average steel plate temperature cannot be physically measured directly, it can be calculated in real time from the results obtained by, for example, using a process computer to calculate the temperature distribution within the cross section along the thickness direction by differential calculation based on the surface temperature at the start of cooling measured with a radiation thermometer and the surface temperature at the target time when cooling is to be stopped. The average value of the temperature in the thickness direction in the temperature distribution is defined as the "average steel plate temperature".

[[Rolling finish temperature]]

[0051] The rolling finish temperature is preferably at or above the Ar_3 transformation temperature in terms of the average steel plate temperature. Here, the Ar_3 transformation temperature means the temperature at which ferrite transformation starts during cooling, and can be determined, for example, from the composition of the steel by the following formula:

$$Ar_3(^{\circ}C) = 910 - 310[\%C] - 80[\%Mn] - 20[\%Cu] - 15[\%Cr] - 55[\%Ni] - 80[\%Mo]$$

where, [%X] represents the content (in mass%) of X element in the steel.

[[Cooling rate of controlled cooling]]

[0052] Cooling after the end of hot rolling is preferably accelerated cooling with a cooling rate of 10 °C/s to 120 °C/s within a temperature range of 750 °C to 600 °C of average steel plate temperature.

[[Cooling stop temperature]]

[0053] The cooling stop temperature is preferably 200 °C or higher in terms of average steel plate temperature. The cooling stop temperature is preferably 600 °C or lower in terms of average steel plate temperature. If the cooling stop temperature exceeds 600 °C, transformation to bainitic microstructure with excellent strength and toughness balance becomes incomplete. When the cooling stop temperature is lower than 200 °C, the microstructure may become excessively hardened and toughness may not be ensured.

[0054] After controlled cooling, the steel plate may be reheated up to 700 °C to homogenize the microstructure.

[High strength steel pipe or tube]

[0055] By forming the high strength steel plate of this disclosure into a tubular shape by press bend forming, roll forming, UOE forming, or the like, and subjecting the butted portions of the tubular product to welding, a high strength steel pipe or tube for sour gas apparatuses suitable for application to pipes for transporting and producing crude oil and natural gas (such as a UOE steel pipe or tube, electric resistance welded steel pipe or tube, or spiral steel pipe or tube) can be produced.

[0056] For example, the UOE steel pipe or tube is produced by performing groove machining on ends of the steel plate, forming the steel plate into a steel pipe or tube shape by C press, U-ing press, or O-ing press, then subjecting the butted portions to seam welding by internal and external welding, and then undergoing a pipe or tube expansion process if necessary. Any welding method that provides sufficient joint strength and joint toughness is acceptable, but submerged arc welding is preferred for excellent weld quality and producing efficiency. The pipe or tube expansion process can also be performed on a steel pipe or tube that has been formed into a tubular shape by press bend forming and then subjected to seam welding at the butted portions.

EXAMPLES

[0057] Steels having the chemical compositions listed in Table 1 (with the balance being Fe and inevitable impurities) were made into slabs by continuous casting, and the slabs were heated and held at the temperatures and times listed in Table 2, and then hot rolled under the conditions including the maximum rolling reductions per pass in the range of 1000 °C to 1100 °C listed Table 2 and the rolling finish temperature of 900 °C to obtain steel plates with a thickness of 20 mm. The steel plates were then subjected to accelerated cooling to a cooling stop temperature of 300 °C by water cooling at a cooling rate of 35 °C/s. After accelerated cooling, the steel plates were raised to 400 °C and then cooled to room temperature by air cooling.

[0058] HV_{min} and HV_{max} were then determined for each of the obtained steel plates by the method described above and were listed in Table 2.

[Evaluation of SSCC resistance]

[0059] A SSCC test piece with a size of 5 × 15 × 115 mm was taken from a position of 0.25 mm below a surface of the steel plate. The surface of the test piece was polished with an emery paper No. 240. The SSCC test piece was applied with a stress of 90 % of the actual yield stress (0.5 % YS) of the corresponding steel plate and subjected to the 4-point bending SSCC test using a NACE standard TM0177 Solution A solution with an initial pH of 3.5 and hydrogen sulfide partial pressure of 0.01 bar in accordance with the EFC 16 standard. After immersion for 720 hours, a cross section of the test piece was cut out and the maximum crack depth (distance from the test piece surface to the crack tip) of the cracks present in the cross section was measured to evaluate SSCC resistance using the criteria below. The results are provided in Table 2.

◎ (Acceptable, remarkably good): the maximum crack depth is less than 100 μm.

○ (Acceptable): the maximum crack depth is 100 μm or more and 500 μm or less

× (Failed): the maximum crack depth is 500 μm or more.

[Table 1]

Steel sample ID	Chemical Composition (mass%)																	Remarks		
	C	Si	Mn	P	S	N	Al	Ca	Ni	Cr	Mo	W	Nb	Cu	V	Ti	Zr		Mg	REM
1	0.07	0.33	1.34	0.010	0.0009	0.0032	0.022	0.0023	0.81	0.52	-	-	-	-	-	-	-	-	-	Conforming steel
2	0.09	0.29	1.41	0.013	0.0015	0.0031	0.021	0.0015	0.11	-	0.47	-	-	-	-	-	-	-	-	Conforming steel
3	0.06	0.07	1.51	0.006	0.0013	0.0027	0.029	0.0030	0.34	-	-	0.15	-	-	-	-	-	-	-	Conforming steel
4	0.03	0.12	0.99	0.010	0.0012	0.0050	0.028	0.0011	3.89	0.08	-	-	-	0.03	-	-	-	-	-	Conforming steel
5	0.07	0.13	1.25	0.008	0.0009	0.0026	0.012	0.0020	2.52	0.18	-	-	0.085	-	-	-	-	-	-	Conforming steel
6	0.06	0.32	1.32	0.029	0.0008	0.0019	0.022	0.0049	1.20	0.23	-	-	-	-	0.025	-	-	-	-	Conforming steel
7	0.08	0.24	1.43	0.004	0.0035	0.0041	0.102	0.0005	0.60	0.96	-	-	-	-	-	0.013	-	-	-	Conforming steel
8	0.03	0.52	1.99	0.011	0.0011	0.0025	0.045	0.0024	0.47	-	0.08	-	-	0.12	-	-	-	-	-	Conforming steel
9	0.08	0.35	2.44	0.009	0.0009	0.0032	0.030	0.0029	0.26	-	0.15	-	-	-	-	-	-	0.012	-	Conforming steel
10	0.18	0.16	1.75	0.015	0.0010	0.0031	0.019	0.0031	0.25	-	0.26	-	-	-	-	-	-	-	0.016	Conforming steel
11	0.05	0.05	1.51	0.009	0.0009	0.0032	0.028	0.0025	0.37	-	-	0.07	-	0.46	-	-	-	-	-	Conforming steel
12	0.07	0.42	1.65	0.010	0.0042	0.0034	0.030	0.0032	1.32	-	-	0.46	-	-	-	-	0.015	-	-	Conforming steel
13	0.14	0.14	1.94	0.011	0.0010	0.0028	0.011	0.0026	0.59	-	-	0.29	-	-	-	-	-	-	-	Conforming steel
14	0.06	0.17	1.35	0.013	0.0012	0.0032	0.021	0.0014	0.75	-	-	-	0.062	-	-	-	-	-	-	Conforming steel
15	0.04	0.25	1.05	0.006	0.0009	0.0031	0.029	0.0027	1.89	-	-	-	0.033	-	-	0.013	-	-	-	Conforming steel
16	0.09	0.15	1.20	0.010	0.0028	0.0037	0.021	0.0034	0.91	0.65	-	-	-	0.19	0.032	-	-	-	-	Conforming steel
17	0.06	0.16	1.89	0.007	0.0006	0.0029	0.022	0.0026	0.15	-	0.23	-	0.040	0.26	-	0.011	-	-	-	Conforming steel
18	0.08	0.28	1.12	0.007	0.0011	0.0032	0.025	0.0018	0.81	0.28	-	0.35	-	0.22	0.028	0.009	-	-	-	Conforming steel
19	0.05	0.22	1.19	0.006	0.0010	0.0035	0.028	0.0019	2.15	0.15	0.12	-	-	0.37	-	-	-	-	-	Conforming steel
20	0.04	0.30	1.75	0.005	0.0014	0.0029	0.029	0.0022	0.45	-	0.35	0.32	0.006	-	-	-	-	0.010	-	Conforming steel

Table 1 (cont'd)

Steel sample ID	Chemical Composition (mass%)																		Remarks	
	C	Si	Mn	P	S	N	Al	Ca	Ni	Cr	Mo	W	Nb	Cu	V	Ti	Zr	Mg		REM
21	0.05	0.10	1.71	0.006	0.0005	0.0040	0.029	0.0016	0.29	0.42	0.03	0.03	0.031	-	-	-	-	-	-	Conforming steel
22	0.04	0.09	1.45	0.002	0.0007	0.0011	0.025	0.0021	0.75	0.35	0.22	-	0.038	0.02	-	0.010	-	-	-	Conforming steel
23	0.05	0.07	1.70	0.003	0.0004	0.0021	0.029	0.0023	0.21	0.23	0.37	-	0.045	-	-	0.013	-	-	-	Conforming steel
24	0.05	0.14	1.31	0.004	0.0005	0.0025	0.030	0.0024	0.15	0.11	0.13	0.13	0.044	0.03	-	0.012	-	-	-	Conforming steel
25	0.06	0.08	1.69	0.013	0.0009	0.0033	0.045	0.0031	-	-	-	-	-	-	-	-	-	-	-	Comparative steel
26	0.07	0.12	1.93	0.016	0.0015	0.0036	0.028	0.0024	-	-	-	-	0.028	-	-	0.010	-	-	-	Comparative steel
27	0.08	0.30	1.45	0.017	0.0013	0.0032	0.032	0.0014	0.52	-	-	-	-	-	-	-	-	-	-	Comparative steel
28	0.03	0.38	1.55	0.019	0.0012	0.0031	0.031	0.0027	<u>0.05</u>	0.45	-	-	-	-	0.022	-	-	-	-	Comparative steel
29	0.07	0.32	1.96	0.010	0.0011	0.0027	0.032	0.0022	<u>0.06</u>	-	0.22	-	-	-	-	0.014	-	-	-	Comparative steel
30	0.08	0.33	1.88	0.007	0.0022	0.0042	0.032	0.0023	-	0.35	0.24	-	-	-	-	-	-	-	-	Comparative steel
31	0.15	0.24	1.72	0.008	0.0008	0.0036	0.029	0.0013	-	0.28	-	0.10	-	-	-	-	0.011	-	-	Comparative steel
32	0.09	0.15	1.25	0.010	0.0008	0.0041	0.028	0.0043	0.39	-	-	<u>0.02</u>	-	0.32	-	-	-	0.020	-	Comparative steel
33	0.07	0.29	1.47	0.009	0.0009	0.0025	0.022	0.0029	0.21	<u>0.01</u>	<u>0.01</u>	-	-	-	-	-	-	-	-	Comparative steel
34	0.09	0.19	1.45	0.011	0.0010	0.0032	0.031	0.0024	2.80	-	-	-	-	0.18	-	-	-	-	-	Comparative steel
35	0.08	0.34	1.45	0.009	0.0007	0.0028	0.029	0.0018	-	0.34	0.19	0.09	-	-	-	-	-	-	0.011	Comparative steel
36	0.09	0.32	1.28	0.014	0.0007	0.0037	0.031	0.0017	-	-	0.38	-	-	0.22	-	-	-	-	-	Comparative steel
37	0.06	0.23	1.95	0.004	0.0010	0.0016	0.034	0.0019	0.29	0.25	-	-	0.032	0.16	0.022	0.012	-	-	-	Conforming steel
38	0.04	0.08	1.81	0.002	0.0007	0.0019	0.025	0.0029	0.12	0.34	-	0.25	0.044	0.29	-	-	-	-	-	Conforming steel
39	0.05	0.12	1.72	0.001	0.0007	0.0011	0.030	0.0022	0.20	0.17	0.38	-	0.028	0.22	-	0.013	-	-	-	Conforming steel

*Underlined if outside the scope of the disclosure.

[Table 2]

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[0060]

Table 2

No.	Steel sample ID	Producing Conditions			Surface Layer Hardness, HV0.1			SSCC resistance		Remarks
		Heating retention temperature (°C)	Heating retention time (mm)	Maximum rolling reduction per pass at 1000°C - 1100°C (%)	Hvmin	Hvmax	Hvmin/Hvmax	Crack depth (μm)	Evaluation	
1	1	1100	50	10	269	320	0.84	50	⊙	Example
2	2	1050	50	15	262	305	0.86	320	○	
3	3	1100	20	5	231	298	0.78	300	○	
4	4	1150	60	10	265	323	0.82	80	⊙	
5	5	1200	60	8	269	318	0.85	60	⊙	
6	6	1150	120	15	273	310	0.88	70	⊙	
7	7	1250	120	4	283	355	0.80	180	○	
8	8	1150	600	12	243	304	0.80	220	○	
9	9	1150	60	6	293	349	0.84	410	○	
10	10	1150	60	7	293	348	0.84	350	○	
11	11	1200	120	6	231	288	0.80	330	○	
12	12	1150	30	8	269	329	0.82	80	⊙	
13	13	1100	20	10	261	315	0.83	200	○	
14	14	1050	50	12	263	305	0.86	220	○	
15	15	1150	60	10	280	315	0.89	80	⊙	
16	16	1150	50	11	282	339	0.83	50	⊙	
17	17	1150	120	9	270	320	0.84	290	○	
18	18	1200	60	5	252	299	0.84	70	⊙	
19	19	1100	60	6	296	357	0.83	60	⊙	
20	20	1100	50	20	278	318	0.87	190	○	
21	21	1100	30	8	260	316	0.82	210	○	
22	22	1150	60	10	274	310	0.88	50	⊙	

(continued)

No.	Steel sample ID	Producing Conditions			Surface Layer Hardness, HV0.1			SSCC resistance		Remarks
		Heating retention temperature (°C)	Heating retention time (mm)	Maximum rolling reduction per pass at 1000°C - 1100°C (%)	Hvmin	Hvmax	Hvmin/Hvmax	Crack depth (µm)	Evaluation	
23	23	1150	30	8	285	311	0.92	40	⊙	Comparative example
24	24	1200	60	8	240	264	0.91	50	⊙	
25	<u>25</u>	1100	60	10	235	290	0.81	1510	×	
26	<u>26</u>	1150	30	5	251	295	0.85	1090	×	
27	<u>27</u>	1150	20	9	245	291	0.84	1200	×	
28	<u>28</u>	1200	50	12	258	313	0.82	740	×	
29	<u>29</u>	1100	80	10	270	315	0.86	800	×	
30	<u>30</u>	1150	120	8	282	331	0.85	1230	×	
31	<u>31</u>	1150	50	15	268	323	0.83	1420	×	
32	<u>32</u>	1200	60	12	241	296	0.81	920	×	
33	<u>33</u>	1150	120	8	234	281	0.83	890	×	
34	<u>34</u>	1200	60	6	293	358	0.82	1050	×	
35	<u>35</u>	1150	60	5	301	350	0.86	1390	×	
36	<u>36</u>	1100	60	8	249	300	0.83	1300	×	
37	6	1300	60	12	240	315	<u>0.76</u>	620	×	
38	6	1030	50	6	238	314	<u>0.76</u>	650	×	
39	6	1100	50	3	240	319	<u>0.75</u>	530	×	
40	10	1100	10	10	263	345	<u>0.76</u>	690	×	
41	10	1280	30	3	221	289	<u>0.76</u>	710	×	
42	10	1040	60	3	255	336	<u>0.76</u>	660	×	

(continued)

No.	Steel sample ID	Producing Conditions			Surface Layer Hardness, HV0.1			SSCC resistance		Remarks
		Heating retention temperature (°C)	Heating retention time (mm)	Maximum rolling reduction per pass at 1000°C - 1100°C (%)	Hvmin	Hvmax	Hvmin/Hvmax	Crack depth (μm)	Evaluation	
43	37	1150	60	10	260	311	0.84	310	○	Example
44	38	1150	60	9	272	318	0.86	70	◎	
45	39	1150	60	10	275	323	0.85	60	◎	
*Underlined if outside the scope of the disclosure.										

[0061] As listed in Table 2, all our examples had excellent SSCC resistance. On the other hand, none of the comparative examples indicated sufficient SSCC resistance.

INDUSTRIAL APPLICABILITY

[0062] Without any restriction on the maximum hardness of the surface layer, the high strength steel plate for sour gas apparatuses of this disclosure has excellent SSCC resistance in an environment equivalent to ISO-15156 Region 2 where pH is 3.5 or more and the H₂S partial pressure is 0.003 bar to 1 bar. Therefore, the steel pipe or tube using this steel plate is suitable for use in sour gas apparatuses, such as line pipes for transporting crude oil and natural gas and oil well pipes or tubes for production of them.

Claims

1. A high strength steel plate for sour gas apparatuses comprising a chemical composition containing, in mass%,

C: 0.02 % or more and 0.20 % or less,
 Si: 0.01 % or more and 0.70 % or less,
 Mn: 0.10 % or more and 2.50 % or less,
 P: 0.030 % or less,
 S: 0.0050 % or less,
 N: 0.0010 % or more and 0.0100 % or less,
 Al: 0.010 % or more and 0.200 % or less,
 Ca: 0.0005 % or more and 0.0050 % or less,
 Ni: 0.10 % or more and 4.00 % or less, and

at least one selected from the group consisting of

Cr: 0.03 % or more and 1.00 % or less,
 Mo: 0.03 % or more and 0.50 % or less,
 W: 0.03 % or more and 0.50 % or less, and
 Nb: 0.005 % or more and 0.100 % or less,

with the balance being Fe and inevitable impurities, wherein

a ratio HV_{min}/HV_{max} of the minimum value HV_{min} to the maximum value HV_{max} of Vickers hardness HV0.1 at 0.25 mm below a surface of the steel plate is 0.77 or more.

2. The high strength steel plate for sour gas apparatuses according to claim 1, wherein the chemical composition further contains, in mass%, Cu: 0.01 % or more and 1.00 % or less.

3. The high strength steel plate for sour gas apparatuses according to claim 1 or 2, wherein the chemical composition further contains, in mass%, at least one selected from the group consisting of

V: 0.005 % or more and 0.1 % or less,
 Ti: 0.005 % or more and 0.1 % or less,
 Zr: 0.0005 % or more and 0.02 % or less,
 Mg: 0.0005 % or more and 0.02 % or less, and
 REM: 0.0005 % or more and 0.02 % or less.

4. A high strength steel pipe or tube using the high strength steel plate for sour gas apparatuses according to claim 1 or 2.

5. A high strength steel pipe or tube using the high strength steel plate for sour gas apparatuses according to claim 3.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/006882

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; *C21D 8/02*(2006.01)i; *C22C 38/58*(2006.01)i
 FI: C22C38/00 301F; C22C38/00 301Z; C22C38/58; C21D8/02 C

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)

C22C38/00-C22C38/60; C21D8/02

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 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	WO 2021/193383 A1 (JFE STEEL CORP.) 30 September 2021 (2021-09-30) claims, paragraphs [0001]-[0014], [0065]	1-5
A	WO 2020/067209 A1 (JFE STEEL CORP.) 02 April 2020 (2020-04-02) claims, paragraphs [0001]-[0014], [0037]	1-5
A	JP 2016-79492 A (JFE STEEL CORP.) 16 May 2016 (2016-05-16) claims, paragraph [0071]	1-5
A	WO 2016/104527 A1 (KOBE STEEL, LTD.) 30 June 2016 (2016-06-30) claims, paragraph [0097]	1-5

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

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Date of the actual completion of the international search

27 April 2023

Date of mailing of the international search report

16 May 2023

Name and mailing address of the ISA/JP

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Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/006882

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2021/193383 A1	30 September 2021	EP 4129510 A1 claims, paragraphs [0001]- [0014], [0062] CN 115298340 A	
WO 2020/067209 A1	02 April 2020	EP 3859027 A1 claims, paragraphs [0001]- [0014], [0032] CN 112752857 A	
JP 2016-79492 A	16 May 2016	(Family: none)	
WO 2016/104527 A1	30 June 2016	EP 3239320 A1 claims, paragraph [0099] CN 107109565 A JP 2016-125138 A	

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

REFERENCES CITED IN THE DESCRIPTION

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- JP 2020012168 A [0005] [0006]