(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 August 2013 (08.08.2013)

(10) International Publication Number
WO 2013/114519 A1

(51) International Patent Classification:
B21C 37/06 (2006.01) ***C22C 38/06*** (2006.01)
C21D 9/08 (2006.01) ***C22C 38/14*** (2006.01)
C21D 1/18 (2006.01) ***C22C 38/18*** (2006.01)
C22C 38/00 (2006.01) ***C22C 38/22*** (2006.01)
C22C 38/02 (2006.01) ***C22C 38/28*** (2006.01)
C22C 38/04 (2006.01)

(21) International Application Number:
PCT/JP2012/008456

(22) International Filing Date:
28 December 2012 (28.12.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2012-020614 2 February 2012 (02.02.2012) JP

(71) Applicant: **NIPPON STEEL & SUMITOMO METAL CORPORATION** [JP/JP]; 6-1, Marunouchi 2-chome, Chiyoda-ku, Tokyo, 1008071 (JP).

(72) Inventors: **NISHI, Yuuki**; c/o NIPPON STEEL & SUMITOMO METAL CORPORATION, 6-1, Marunouchi 2-chome, Chiyoda-ku, Tokyo, 1008071 (JP). **TAKAHASHI, Nobuaki**; c/o NIPPON STEEL & SUMITOMO METAL CORPORATION, 6-1, Marunouchi 2-chome, Chiyoda-ku, Tokyo, 1008071 (JP).

(74) Agents: **UEBA, Hidetoshi** et al.; Intelix International, Aqua Dojima West, 4-16, Dojimahama 1-chome, Kita-ku, Osaka-shi, Osaka, 5300004 (JP).

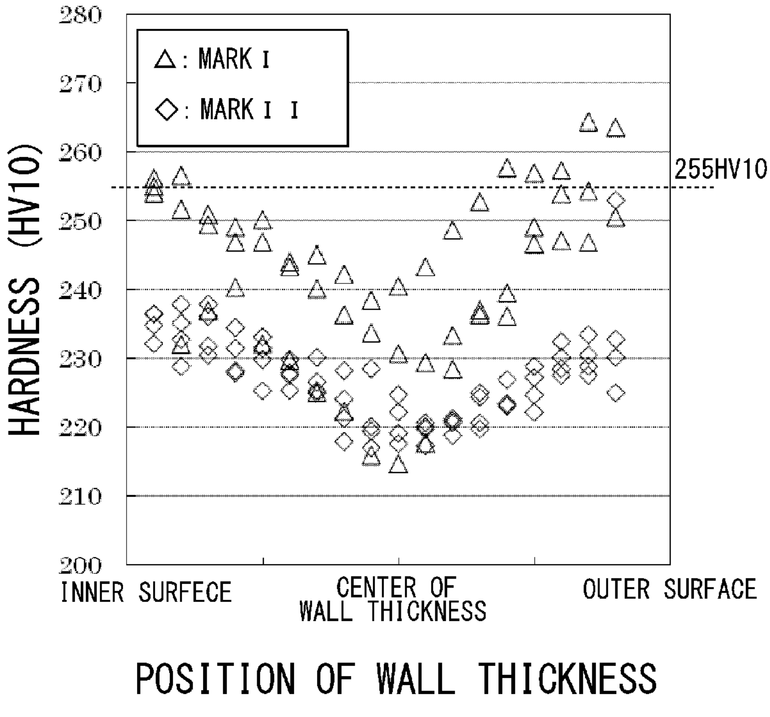
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

[Continued on next page]

(54) Title: UOE STEEL PIPE FOR LINE PIPE

FIG. 1



(57) Abstract: Provided is a UOE steel pipe for line pipe having excellent HIC resistance even when it has high strength. The UOE steel pipe for line pipe in this embodiment contains, by mass%, C: 0.01 to 0.1%, Si: 0.01 to 0.5%, Mn: 1.0 to 1.7%, P: at most 0.015%, S: at most 0.002%, Cr: 0.01 to 0.45%, Mo: 0.03 to 0.5%, Al: 0.005 to 0.05%, Ca: 0.0005 to 0.0050%, N: 0.001 to 0.005%, and Ti: 0.005 to 0.03%, the balance being Fe and impurities, and having a bainite single-phase structure. In this UOE steel pipe, the hardness of outer and inner surface layers of the UOE steel pipe is 200 to 255 in terms of HV10, the hardness of a center potion of wall thickness of the UOE steel pipe is 200 to 248 in terms of HV10, and the tensile strength is not less than 625 MPa.

WO 2013/114519 A1

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

Description

Title of Invention: UOE STEEL PIPE FOR LINE PIPE

Technical Field

[0001] The present invention relates to a UOE steel pipe and, more particularly, to a UOE steel pipe for line pipe.

Background Art

[0002] Crude oil and natural gas produced in recent years contain wet hydrogen sulfide (H_2S). Pipelines which transmit the crude oil and natural gas obtained by drilling pose the problem of the occurrence of hydrogen-induced cracking (hereinafter referred to as HIC) caused by hydrogen sulfide. For this reason, UOE steel pipes used in pipelines are required to have excellent HIC resistance.

[0003] Furthermore, in recent pipelines an improvement in transmission efficiency is required. Although transmission efficiency is improved by increasing the operating pressure, it is necessary to increase the strength of UOE steel pipes constituting a pipeline in order to increase the operating pressure. Specifically, UOE steel pipes having high strength of not less than X80 grade of API Standard (tensile strength of not less than 625 MPa) are in demand.

[0004] JP5-271766 proposes a steel plate for pipeline having high strength and excellent HIC resistance. In this document, HIC is considered to be caused of center segregation and the contents of Mn, P and S which induce center segregation are reduced. Furthermore, Cr and Mo are contained in order to increase strength. This document describes that as a result of this, high strength and excellent HIC resistance are obtained.

[0005] However, JP5-271766 describes a proposal related to a steel plate, and not a UOE steel pipe, and is limited to an improvement in center segregation as a measure to improve HIC resistance. Therefore, even when center segregation is improved, HIC may sometimes occur due to other factors.

Disclosure of the Invention

[0006] The object of the present invention is to provide a UOE steel pipe for line pipe having excellent HIC resistance even when it has high strength.

[0007] The UOE steel pipe for line pipe in this embodiment contains, by mass%, C: 0.01 to 0.1%, Si: 0.01 to 0.5%, Mn: 1.0 to 1.7%, P: at most 0.015%, S: at most 0.002%, Cr: 0.01 to 0.45%, Mo: 0.03 to 0.5%, Al: 0.005 to 0.05%, Ca: 0.0005 to 0.0050%, N: 0.001 to 0.005%, and Ti: 0.005 to 0.03%, the balance being Fe and impurities, and has a bainite single-phase structure. In this UOE steel pipe, the hardness of outer and inner surface layers of the UOE steel pipe is 200 to 255 in terms of HV10, the hardness of a center portion of wall thickness of the UOE steel pipe is 200 to 248 in terms of HV10, and the tensile strength is not less than 625 MPa.

[0008] In this case, the UOE steel pipe for line pipe has excellent HIC resistance even when it has high strength.

[0009] The UOE steel pipe in this embodiment may further contain, in place of part of Fe, at least one selected from the group consisting of Cu: at most 0.5%, Ni: at most 0.5%, Nb: at most 0.05%, and V: at most 0.10%.

Brief Description of Drawings

[0010] [fig.1]Figure 1 is a diagram of hardness distribution in the cross section of a UOE pipe in a radial direction (a wall thickness direction).

[fig.2]Figure 2 is a cross sectional view of a UOE pipe.

[fig.3]Figure 3 is a diagram showing the relationship between a difference value delta of the hardness of the outer and inner surface layers of a steel plate for UOE steel pipe and the hardness of the outer and inner surface layers of a UOE steel pipe and t/D (wall thickness/outside diameter) of the UOE steel pipe.

Modes for Carrying Out the Invention

[0011] Embodiments of the present invention will be described in detail below with reference to the figures. Hereinafter, "%" of the contents of elements refers to mass%.

Outline of UOE steel pipe in the embodiments

[0012] The present inventors investigated and studied the HIC resistance of high-strength UOE steel pipes for line pipe. As a result, the inventors obtained the following findings.

[0013] (A) A steel plate in which center segregation is suppressed has excellent HIC resistance even when it has high strength. However, HIC may sometimes occur in the case where a UOE steel pipe is manufactured from such a steel plate by carrying out pipe-making processes such as C press forming, U press forming and O press forming.

[0014] (B) The cause of the occurrence of the above-described HIC is an increase in the hardness of a steel plate in the pipe-making processes. Figure 1 is a diagram of the hardness distribution in the cross section of a UOE steel pipe in a radial direction (a wall thickness direction). Figure 1 was obtained by the following method. Two steel plates having almost constant hardness in the through-thickness direction and having hardnesses different from each other were prepared. The chemical compositions of these steel plates are in the range of the chemical composition of this embodiment, which will be described later, and the tensile strength was not less than 625 MPa. Each steel plate was subjected to C press forming, U press forming, and O press forming and two UOE steel pipes were produced (mark I, mark II). In the cross section (the section orthogonal to the axis direction of the UOE steel pipe) of each of the produced UOE steel pipes, the top of the section was assumed to be the origin (0 degree). At positions at clockwise 90 degrees (the 90-degree position) and at 180 degrees (the 180-degree position), the Vickers hardness test in accordance with JIS Z2244 (2009) was carried out with a 0.5 mm pitch radially (in the wall thickness direction) from the outer surface to the inner surface. The test force was 10 kgf = 98.07 N. Figure 1 was completed on the basis of the obtained hardness (HV10).

[0015] The triangle shape mark in the figure 1 indicates the test result of the UOE steel pipe of mark I, and the diamond shape mark indicates the test result of the UOE steel pipe of mark II. Referring to Figure 1, in either of the UOE steel pipes, the hardness of the center portion of the wall thickness in the radial direction (wall thickness direction) of the steel pipes was almost the same as the hardness of the steel plates before pipe-making. However, the hardness increased from the center portion of the wall thickness toward the inner surface and the outer surface. In the steel pipe of mark I, maximum values of hardness of the inner surface layer including the inner surface and of the outer surface layer including the outer surface exceeded 255 HV10.

[0016] The HIC test, which will be described later, was carried out for the UOE steel pipes of mark I and mark II. As a result, HIC occurred in mark I, whereas HIC did not occur in mark II. The following facts are derived from Figure 1 and the results of the HIC test.

[0017] (C) First, the occurrence of HIC is related to the hydrogen concentration (C0) in steel and the hydrogen concentration (Cth) which is allowed until the occurrence of HIC in steel. The hydrogen concentrations Cth allowed in the outer and inner surface layers are low compared to those of portions other than the outer and inner surface layers and the center portion of the wall thickness. This is because the outer and inner surface layers include floating inclusions (for example, oxide-based inclusions, such as Al_2O_3 and CaO) generated during continuous casting and because these floating inclusions lower the allowable hydrogen concentration Cth (hereinafter referred to as the allowable hydrogen concentration).

[0018] (D) On the other hand, the allowable hydrogen concentration Cth in the center portion of the wall thickness is lower than the allowable hydrogen concentration Cth of the outer and inner surface layers. This is because in the center portion of the wall thickness, more carbonitrides are generated and grow due to center segregation and because these carbonitrides increase HIC sensitivity more than oxide-based inclusions do. Furthermore, because in the center portion of the wall thickness hydrogen is apt to condense due to center segregation, the hydrogen concentration C0 in the center portion of the wall thickness is higher than in portions other than the center portion of the wall thickness. That is, from the standpoint of the hydrogen concentrations C0 and Cth, the HIC sensitivity is highest in the center portion of the wall thickness and is second highest in the portions of the outer and inner surface layers.

[0019] (E) Incidentally, in a UOE steel pipe, the hardness of the outer and inner surface layers increases due to steelmaking processes even when there is no hardness variation in the through-thickness direction of a steel plate which is the base material. During pipe-making, tensile stress is applied to the outer surface layer (the surface layer including the outer surface) and compressive stress is applied to the inner surface layer (the surface layer including the inner surface). On the other hand, strain is not much applied to the center portion of the wall thickness compared to the outer and inner surface layers. For this reason, the hardness of the outer and inner surface layers increases remarkably compared to the hardness in the center portion of the wall thickness. This increase in hardness increases HIC sensitivity.

[0020] (F) From the foregoing, for the occurrence of HIC in UOE steel pipes, it is necessary to consider not only the crack sensitivity related to the hydrogen concentration in steel and the allowable hydrogen concentration, but also the synergistic effect of an increase in HIC sensitivity due to a change in hardness by pipe-making. That is, from the standpoint of the hydrogen concentration, it is necessary not only to limit the hardness in the center portion of the wall thickness where crack sensitivity is high, but also to limit the hardness of the outer and inner surface layers which increases during pipe-making.

[0021] More specifically, if an upper limit to the hardness in the center portion of the wall thickness is set at 248 HV10 and an upper limit to the hardness of the outer and inner surface layers is set at 255 HV10, then the occurrence of HIC is suppressed even in UOE steel pipes having strength of not less than X80 grade of API Standard.

[0022] The UOE steel pipe for line pipe in this embodiment was completed on the basis of the above-described findings. Details of the UOE steel pipe for line pipe in this embodiment will be described below.

Chemical composition

[0023] The UOE steel pipe for line pipe in this embodiment has the following chemical composition. As described above, % related to elements means mass%.

[0024] C: 0.01 to 0.1%

Carbon (C) increases the strength of steel. However, if the C content is too high, the chemical composition of the steel is included in the peritectic region. For this reason, it becomes difficult to produce steel by continuous casting. Therefore, the C content is 0.01 to 0.1%. The lower limit to the C content is preferably higher than 0.01%, more preferably 0.03%, and still more preferably 0.04%. The upper limit to the C content is preferably less than 0.1%, more preferably 0.07%, and still more preferably 0.06%.

[0025] Si: 0.01 to 0.5%

Silicon (Si) deoxidizes steel. However, if the Si content is too high, toughness decreases. Therefore, the Si content is 0.01 to 0.5%. The lower limit to the Si content is preferably higher than 0.01%, more preferably 0.03%, and still more preferably 0.05%. The upper limit to the Si content is preferably less than 0.5%, more preferably 0.40%, and still more preferably 0.35%.

[0026] Mn: 1.0 to 1.7%

Manganese (Mn) increases the strength of steel. However, if the Mn content is too high, the Mn concentration in a normal segregation band in the center portion of the wall thickness becomes high, and HIC becomes apt to occur in a wet H_2S environment. Therefore, the Mn content is 1.0 to 1.7%. The lower limit to the Mn content is preferably higher than 1.0%, more preferably 1.1%, and still more preferably 1.2%. The upper limit to the Mn content is preferably less than 1.7%, more preferably 1.6%, and still more preferably 1.5%.

[0027] P: Not more than 0.015%

Phosphorus (P) is an impurity. Like Mn, P is apt to segregate normally in the center portion of the wall thickness and hardens a normally segregated part. The hardening of a normally segregated part induces HIC. Therefore, it is preferred that the P content be low. The P content is not more than 0.015%. The P content is preferably less than 0.015%, more preferably not more than 0.010%.

[0028] S: Not more than 0.002%

Sulfur (S) is an impurity. S forms MnS. MnS provides an initiation point of HIC. Therefore, it is preferred that the S content be as low as possible. The S content is not more than 0.002%. The S content is preferably less than 0.002%, more preferably not more than 0.001%.

[0029] Cr: 0.01 to 0.45%

Chromium (Cr) increases the strength and toughness of steel. However, if the Cr content is too high, weldability decreases and weld cracking becomes apt to occur. Therefore, the Cr content is 0.01 to 0.45%. The lower limit to the Cr content is preferably higher than 0.01%, more preferably 0.05%, and still more preferably 0.1%. The upper limit to the Cr content is preferably less than 0.45%, more preferably 0.35%, and still more preferably 0.3%.

[0030] Mo: 0.03 to 0.5%

Molybdenum (Mo) increases the hardenability of steel and increases the strength of steel. Furthermore, because the microsegregation of Mo is not apt to occur, the occurrence of HIC caused by center segregation is suppressed. However, because Mo is expensive, the manufacturing cost increases if Mo is contained excessively. Therefore, the Mo content is 0.03 to 0.5%. The lower limit to the Mo content exceeds preferably 0.03%, is more preferably 0.05%, and still more preferably 0.1%. The upper limit to the Mo content is preferably less than 0.5%, more preferably 0.4%, and still more preferably 0.3%.

[0031] Al: 0.005 to 0.05%

Aluminum (Al) deoxidizes steel. However, if the Al content is too high, cleanliness and toughness of steel decrease. Therefore, the Al content is 0.005 to 0.05%. The lower limit to the Al content is preferably higher than 0.005%, more preferably 0.01%, and still more preferably 0.015%. The upper limit to the Al content is preferably less than 0.05%, more preferably 0.045%, and still more preferably 0.04%.

[0032] The Al content in this embodiment means the content of sol. Al (acid-soluble Al).

[0033] Ca: 0.0005% to 0.0050%

Calcium (Ca) controls the shape of MnS, which provides an initiation point of HIC, to a spherical shape and suppresses the occurrence of HIC. Furthermore, Ca forms CaS and suppresses the generation of MnS. On the other hand, if Ca is contained excessively, the effect of Ca becomes saturated, resulting in an increase in the manufacturing cost. Therefore, the Ca content is 0.0005% to 0.0050%. The lower limit to the Ca content exceeds preferably 0.0005%, is more preferably 0.001% and still more preferably 0.0015%. The upper limit to the Ca content is preferably less than 0.0050%, more preferably 0.0040%, and still more preferably 0.0030%.

[0034] Ti: 0.005% to 0.03%

Titanium (Ti) combines with nitrogen (N) to form TiN. TiN suppresses the coarsening of austenite grains during slab heating and the HAZ (heat-affected zone) and increases the low-temperature toughness of the base metal and the HAZ. However, if the Ti content is too high, TiN is generated excessively, resulting in a decrease in toughness. Therefore, the Ti content is 0.005 to 0.03%. The lower limit to the Ti content exceeds preferably 0.005%, is more preferably 0.008%, and still more preferably 0.01%. The upper limit to the Ti content is preferably less than 0.03%, more preferably 0.025%, and still more preferably 0.02%.

[0035] N: 0.001 to 0.005%

Nitrogen (N) combines with the above-described Ti to form TiN, and increases the low-temperature toughness of the base metal and the HAZ. However, if the N content is too high, TiN is formed excessively and toughness decreases. Therefore, the N content is 0.001 to 0.005%. The lower limit to the N content is preferably higher than 0.001%, more preferably 0.0015%, and still more preferably 0.002%. The upper limit to the N content is preferably less than 0.005%, more preferably 0.0045%, and still more preferably 0.004%.

[0036] The balance of the chemical composition of the UOE steel pipe in this embodiment consists of Fe and impurities. The impurities mentioned here refer to the elements which are mixed in from ores and scraps used as the raw materials for steel or from the environment and the like of manufacturing processes.

[0037] The UOE steel pipe in this embodiment may further contain, in place of part of Fe, at least one selected from the group consisting of Cu, Ni, Nb, and V. These elements are all optional elements and increase the strength of steel.

[0038] Cu: Not more than 0.5%

Copper (Cu) is an optional element. Cu increases the hardenability of steel and increases the strength of steel. If even a small amount of Cu is contained, the above-described effects are obtained. However, if the Cu content is too high, the hot workability of steel decreases. Furthermore, the surfaces of a slab become apt to crack during continuous casting. Therefore, the Cu content is not more than 0.5%. The lower limit to the Cu content is preferably 0.05%, more preferably higher than 0.05%, and still more preferably 0.1%. The upper limit to the Cu content is preferably less than 0.5%, more preferably 0.4%, and still more preferably 0.3%.

[0039] Ni: Not more than 0.5%

Nickel (Ni) is an optional element. Ni increases the strength of steel by solid-solution strengthening. Furthermore, Ni increases the toughness of steel. If even a small amount of Ni is contained, the above-described effects are obtained. However, if the Ni content is too high, the weldability of steel decreases. Therefore, the Ni content is not more than 0.5%. The lower limit to the Ni content is preferably 0.05%, more preferably higher than 0.05%, and still more preferably 0.1%. The upper limit to the Ni content is preferably less than 0.5%, more preferably 0.4%, and still more preferably 0.3%.

[0040] Nb: Not more than 0.05%

Niobium (Nb) is an optional element. Nb forms carbides in steel. Nb carbides reduce the grain size of steel, increasing the strength and toughness of steel. If even a small amount of Nb is contained, the above-described effects are obtained. However, if the Nb content is too high, the toughness of weld zones decreases. Therefore, the Nb content is not more than 0.05%. The lower limit to the Nb content is preferably 0.005%, more preferably higher than 0.005, and still more preferably 0.01%. The upper limit to the Nb content is preferably less than 0.05%, more preferably 0.045%, and still more preferably 0.04%.

[0041] V: Not more than 0.10%

Vanadium (V) is an optional element. V dissolves in steel in a solid solution state or forms carbonitrides in steel, increasing the strength of steel. If even a small amount of V is contained, the above-described effect is obtained. However, if the V content is too high, V carbonitrides coarsen in the HAZ and HAZ toughness decreases. Therefore, the V content is not more than 0.10%. The lower limit to the V content is preferably 0.005%, more preferably higher than 0.005%, and still more preferably 0.01%. The upper limit to the V content is preferably less than 0.10%, more preferably 0.08%, and still more preferably 0.07%.

Structure

[0042] The structure of the UOE steel pipe in this embodiment is a bainite single phase. The "bainite single phase" in this specification may contain quasi-polygonal ferrite, granular bainitic ferrite, and bainitic ferrite. Although the structure of the UOE steel pipe may contain M-A constituent (MA), martensite, and pearlite, the total content rate of MA, martensite, and pearlite is not more than 2% in terms of area fraction. Hereinafter MA, martensite, and pearlite are called "hardened structures." Therefore, in this specification, the "bainite single phase" may contain hardened structures in amounts of not more than 2% in area fraction.

[0043] The structure of the UOE steel pipes is identified, for example, by the following method of microstructure observation and test. In the cross section of a UOE steel pipe, the portion at a depth of 1/4 of the wall thickness from the outer surface is etched with nital and the like. Any of 10 to 30 fields of vision (each field of vision: 8 to 24 mm^2) in the etched 1/4 portion of the wall thickness is observed. An optical microscope with a magnification of 200 times is used in the observation. Bainite, MA, martensite, and pearlite can be recognized by etching. Therefore, the area fraction of the bainite in each field of vision and the area fraction of other structures (hardened structures) can be found. The value obtained by averaging the area fraction of the hardened structures in each field of vision is defined as the area fraction (%) of hardened structures.

[0044] The structure of the UOE steel pipe may further contain inclusions and precipitates. Bainite shingle phase does not contain polygonal ferrite.

[0045] As described above, the structure of the UOE steel pipe of this embodiment is a bainite single phase, and the area fraction of hardened structures, such as MA, martensite, and pearlite, is low. For this reason, the UOE steel pipe is excellent in HIC resistance although the steel pipe has high strength.

Hardness and tensile strength

[0046] In the UOE steel pipe in this embodiment, the hardness of the outer and inner surface layers is 200 to 255 in terms of HV10, and the hardness of the center portion of the wall thickness is 200 to 248 in terms of HV10. The condition that this upper limit to the hardness of the center portion of the wall thickness is limited to be lower than the upper limit to the hardness of the outer and inner surface layers was found by the result of a study carried out by the inventors by trial and error.

[0047] The hardness of the outer and inner layers is measured by the following method. Figure 2 shows the cross sectional view of a UOE steel pipe (i.e., a sectional view obtained by cutting the UOE steel pipe in the radial direction). Referring to Figure 2, a UOE steel pipe 100 is divided into 20 equal parts in the direction of wall thickness t. The range from an outer surface 10 of a UOE steel pipe 100 to t/5 in the direction of an inner surface 20 is defined as an outer surface layer OL. The range from an inner surface 20 to t/5 in the direction of an outer surface 10 is defined as an inner surface layer IL. The range of t/10 in the wall thickness t direction around a center position Pc of the wall thickness t is defined as a center portion of the wall thickness CN.

[0048] The top of the cross section of the UOE steel pipe is assumed to be an origin (0 degree). The position at clockwise 90 degrees (the 90-degree position), the outer surface layer OL in the position at 180 degrees (the 180-degree position), the inner surface layer IL, and the center portion of the wall thickness CN are identified. The outer surface layer OL, the inner surface layer IL, and the center portion of the wall thickness CN are all the base metal and do not provide a weld zone.

[0049] In the identified outer surface layer OL and inner surface layer IL, the Vickers hardness test in accordance with JIS Z2244 (2009) is carried out in the radial direction (in the wall thickness t direction) with a 0.5-mm pitch. The test force is 10 kgf = 98.07 N. In the case where the test force is 10 kgf, a dent formed by the Vickers indenter covers a plurality of crystal grains.

[0050] In the outer and inner surface layers OL and IL, a maximum value and a minimum value are identified in a plurality of values obtained by the Vickers hardness test, and these are defined as the hardness of the outer and inner surface layers OL and IL (a maximum value and a minimum value).

[0051] Similarly, in the center portion of the wall thickness, a maximum value and a minimum value are identified in a plurality of values obtained by the Vickers hardness test, and these are defined as the hardness of the center portion of the wall thickness CN (a maximum value and a minimum value).

[0052] Maximum values of the hardness of the outer and inner surface layers OL and IL defined by the above-described method are not more than 255 HV10. Minimum values of the hardness of the outer and inner surface layers OL and IL are not less than 200 HV10. Similarly, maximum values of the hardness of the center portion of the wall thickness CN are not more than 248 HV10. Minimum values of the hardness of the center portion of the wall thickness CN are not less than 200 HV10. To sum up, the hardness of the outer and inner surface layers OL and IL is 200 to 255 HV10, and the hardness of the center portion of the wall thickness CN is 200 to 248 HV10.

[0053] That is, different allowable upper limits to hardness are set for the outer and inner surface layers and the center portion of the wall thickness. The reason for this is that for the occurrence of HIC in a UOE steel pipe, it is necessary to consider not only the hydrogen concentration in steel and the crack sensitivity related to the allowable hydrogen concentration, but also the synergistic effect of an increase in HIC sensitivity due to a change in hardness due to working, and it is necessary not only to limit the hardness of the center portion of the wall thickness where crack sensitivity is high from the standpoint of the hydrogen concentration, but also to limit the hardness of the outer and inner surface layers which rises during pipe-making.

[0054] In order to ensure that the tensile strength TS of the UOE steel pipe becomes not less than 625 MPa, it is necessary that the hardness of the outer and inner surface layers OL and IL and that the hardness of the center portion of the wall thickness CN become not less than 200 HV10.

Manufacturing method

[0055] An example of a manufacturing method of UOE steel pipes in this embodiment will be described. A slab is produced from a molten steel having the above-described chemical composition by the continuous casting method (the continuous casting process). A steel plate for UOE steel pipe is produced by rolling the produced slab (the rolling process). A UOE steel pipe is produced by working the produced steel plate (the pipe-making process). Each of the processes will be described in detail below.

Continuous casting process

[0056] A molten steel having above-described chemical composition is produced by refining steel. A slab is produced from the produced molten steel by the continuous casting method.

[0057] Preferably, the slab is reduced in the vicinity of a final solidification position during continuous casing. Furthermore, preferably, appropriate water cooling conditions and casting speed are selected so that remarkable solidification nonuniformity does not occur in the casting width direction, the casting length direction. In this case, the segregation of Mn, P, S and the like in the center portion of the wall thickness is suppressed. For this purpose, it is possible to increase the allowable hydrogen concentration Cth in the center portion of the wall thickness.

Rolling process

[0058] In the rolling process, the slab produced in the continuous casting process is heated in a heating furnace (the heating process). The heated slab is rolled on a rolling mill to produce a steel plate (the working process). The steel plate after rolling is immediately cooled (the cooling process). After cooling, annealing is carried out as required (the annealing process). If the rolling process is carried out on the basis of the heating process, working process, cooling process, and annealing process which are described below, a UOE steel pipe obtains the above-described structure, hardness and tensile strength.

Heating process

[0059] The slab heating temperature in the heating furnace is set at 1000 to 1250°C. If the heating temperature is too high, it is impossible to reduce the size of crystal grains because austenite grains coarsen. For this reason, HIC resistance decreases. On the other hand, if the heating temperature is too low, it is impossible to cause the Nb carbonitrides formed in the slab during continuous casting to dissolve in a solid solution state, and HIC resistance decreases. Furthermore, it becomes difficult to obtain the grain refinement of the crystal grains during rolling and precipitation strengthening after rolling. By setting the heating temperature at 1000 to 1250°C, it becomes possible to suppress the coarsening of austenite grains and to cause Nb to dissolve in a solid solution state.

[0060] Preferably, the heating temperature T (°C) satisfies Expression (1) below:

[Math.1]

$$6770/(2.26 - \log (Nb \times C)) - 73 > T \geq 6770/ (2.26 \log - (Nb \times C)) - 273 \quad (1)$$

Here, the content of each element (mass%) is substituted into each chemical symbol in Expression (1).

[0061] In this case, Nb in steel is apt to dissolve in a solid solution state.

[0062] Soaking may be carried out for the slab. In this case, the segregation in the center portion of the wall thickness is suppressed. Preferred soaking temperatures are 1000 to 1300°C, and the soaking time is 20 to 50 hours. In this case, the segregation of C, Mn, P, S and the like is suppressed.

Working process

[0063] It is preferred that the surface temperature of the workpiece material during rolling be not less than the A_{r3} point. The A_{r3} point is defined by Expression (2) below:

$$A_{r3} = 910 - 310 \times C - 80 \times Mn - 20 \times Cu - 15 \times Cr - 55 \times Ni - 80 \times Mo + 0.35 - (t0 - 8) \quad (2)$$

Here, the content of each element (mass%) is substituted into each chemical symbol in Expression (2). The thickness (mm) of the steel plate after the completion of final rolling is substituted into the symbol t0.

[0064] The rolling reduction (%) is not specifically limited. In general, the rolling reduction is not less than 50%. The rolling reduction is defined by Expression (3) below:

Rolling reduction = {1-(cross-sectional area of steel plate after completion of final rolling (thickness x width) / cross-sectional area of slab (thickness x width))} x 100 (3)

Cooling process

[0065] The steel plate is cooled immediately after the completion of rolling. That is, accelerated cooling is carried out. It is preferred that the surface temperature of the steel plate at the start of cooling be not less than the A_{r3} point. If the surface temperature of the steel plate is less than the A_{r3} point, ferrite is generated and the discharge of carbon is started. HIC resistance decreases because hardened structures become apt to be formed due to the carbon discharged from the ferrite phase.

[0066] It is preferred that the cooling rate after rolling be 10 to 40°C/sec. Preferably, water cooling is carried out. If the cooling rate is too low, the diffusion of C and P is promoted. Diffused elements precipitate at the grain boundaries or on inclusions. On the other hand, because if the cooling rate is too high, hardening is carried out excessively and hardened structures are generated, with the result that the structure of steel does not easily become a bainite shingle phase.

[0067] Preferable cooling stop temperatures are 350 to 600°C. That is, when the surface temperature of the steel plate has become 350 to 600°C, the cooling at the above-described cooling rates is stopped. The diffusion of C and P is promoted in the case where the steel plate is allowed to cool immediately without cooling after rolling at the above-described cooling rates.

[0068] Natural cooling is preferable after the cooling at the above-described cooling rates is stopped at the cooling stop temperatures. This is because toughness is increased due to the annealing effect during natural cooling and the occurrence of HIC can be suppressed.

Tensile strength of steel plate after cooling and annealing process

[0069] Adjustments are made so that the tensile strength TS0 (MPa) of the steel plate after cooling satisfies Expression (4) below:

[Math.2]

$$TS0 \leq -1.11 \times (t/D \times 100)^2 + 4.32 \times (t/D \times 100) + 693 \qquad (4)$$

Here, t is the wall thickness (mm) of a UOE steel pipe to be produced, and D is the diameter (mm) of the UOE steel pipe to be produced.

[0070] Figure 3 is a diagram showing the relationship between a difference value delta of the hardness of the outer and inner surface layers of a steel plate and the hardness of the outer and inner surface layers of a UOE steel pipe and t/D (%) of the UOE steel pipe, which was obtained when the UOE steel pipe was produced from the steel plate having the above-described chemical composition. Figure 3 was obtained by the following method.

[0071] A plurality of steel plates having the above-described chemical composition were produced by the above-described manufacturing method. A plurality of UOE steel pipes having different t/D were produced from the produced steel plates by the pipe-making process which will be described later. The pipe expansion rate during pipe-making was 0.7 to 1.2%. In the steel plates before pipe-making and the UOE steel pipes, maximum values of the hardness of the outer and inner surface layers were found in accordance with the above-described Vickers hardness test. The difference value delta of hardness (HV10) was found on the basis of Expression (5) below:

delta = Maximum value of hardness of outer and inner surface layers of UOE steel pipe - maximum value of hardness of outer and inner surface layers of steel plate (5)

[0072] Figure 3 was prepared by using the obtained difference value delta.

[0073] Referring to Figure 3, the larger t/D, the larger the difference value delta. More specifically, as indicated by the curve C0 in Figure 3, the hardness of the outer and inner surface layers increases remarkably in a manner represented by a quadric function as t/D increases. Hardness and tensile strength are substantially directly proportional to each other. Specifically, when hardness increases, tensile strength also increases in a manner represented by a linear function. Expression (4) was obtained on the basis of the above-described findings.

[0074] If the chemical composition and microstructure specified by the present invention are satisfied and the tensile strength TS0 of a steel plate satisfies Expression (4), then the hardness of the outer and inner surface layers of a UOE steel pipe after pipe-making satisfies 200 to 255 HV10 and the hardness of the center portion of the wall thickness satisfies 200 to 248 HV10.

[0075] In the case where the tensile strength TS0 of a steel plate after the cooling process does not satisfy Expression (4), it is ensured that the tensile strength TS0 of the steel plate satisfies Expression (4) by carrying out annealing less than the A_{c1} point. Preferable annealing temperatures are 350 to 600°C, and preferable annealing time is 30 to 90 minutes. When the tensile strength TS0 of a steel plate after cooling satisfies Expression (4), it is not necessary to carry out annealing treatment.

Pipe-making process

[0076] The produced steel plate is formed to produce an open pipe by using a C press, a U press, an O press and the like. Subsequently, both longitudinal end surfaces of the open pipe are welded by the submerged arc welding process and the like to form a welded steel pipe. The produced welded steel pipe is subjected to pipe expanding to produce a UOE steel pipe.

Examples

[0077] Slabs were produced by continuously casting the molten steel of the steel grades A to H shown in Table 1.

[0078]

[Table 1]

TABLE 1

Steel grade	Chemical composition (unit: mass%, balance: Fe and impurities)														
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Nb	V	Al	Ca	N	Ti
A	0.041	0.28	1.19	0.006	0.0004	0.45	0.27	0.47	0.25	0.036	0.07	0.05	0.0025	0.0029	0.012
B	0.05	0.29	1.26	0.005	0.0004	0.3	0.36	0.25	0.05	0.032	0.04	0.035	0.0023	0.0037	0.011
C	0.052	0.25	1.5	0.005	0.0004	0.22	0.18	0.43	0.08	0.04	0.044	0.042	0.0022	0.0036	0.012
D	0.054	0.3	1.18	0.006	0.0004	0.45	0.28	0.47	0.41	0.038	0.07	0.041	0.0023	0.0037	0.012
E	0.07	0.2	**1.78**	**0.02**	**0.03**	0.25	0.05	0.23	0.15	0.035	0.035	0.03	0.0005	0.004	0.016
F	0.052	0.27	1.35	0.005	0.0005	-	0.42	-	0.23	-	-	0.034	0.0023	0.0036	0.011
G	0.055	0.23	1.33	0.006	0.0004	-	0.4	-	0.22	0.045	0.045	0.035	0.0024	0.0035	0.012
H	0.07	0.08	1.36	0.009	0.0018	0.27	0.42	0.21	0.17	0.032	0.04	0.026	0.0023	0.0034	0.017

[0079] The chemical compositions of the steel grades A to D, F and G in Table 1 were in the range of the chemical composition of the UOE steel pipe of the present invention. On the other hand, the Mn content, P content and S content of the steel grade E exceeded the upper limits to the Mn content, P content and S content of the present invention.

[0080] The UOE steel pipes with the marks 1 to 18 shown in Table 2 were produced from a plurality of slabs of the steel grades A to H.

[0081]

[Table 2]

TABLE 2

Mark	Steel grade	Manufacturing conditions				Characteristics of steel plate		Characteristics of UOE steel pipe						Vickers hardness (HV10)				HIC test
		Slab heating temperature (°C)	Cooling start temperature (°C)	Cooling stop temperature (°C)	Annealing	TSO (MPa)	F1	Wall thickness t (mm)	Outside diameter D (mm)	t/D (%)	Structure	YS (Mpa)	TS (Mpa)	Outer and inner surface layers		Center portion of wall thickness		
														min	max	min	max	
1	A	1180	790	450	Without annealing	673	693.6	19.1	508	3.8	B	599	705	234	242	212	232	No crack
2	A	1180	790	450	Without annealing	680	697.2	19.1	914	2.1	B	627	702	227	238	205	225	No crack
3	A	1180	790	450	Without annealing	682	697.0	19.1	1219	1.6	B	612	702	224	236	208	229	No crack
4	A	1180	790	450	Without annealing	675	696.4	25.4	914	2.8	B	571	688	219	241	215	230	No crack
5	A	1180	790	450	Without annealing	664	697.2	25.4	1219	2.1	B	580	690	212	235	204	227	No crack
6	B	1180	790	450	Without annealing	641	693.6	19.1	508	3.8	B	564	633	219	219	200	204	No crack
7	C	1160	790	450	Without annealing	653	682.7	25.4	457	5.6	B	635	705	232	245	212	224	No crack
8	A	1180	790	370	With annealing	693	686.9	25.4	508	5.0	B	612	712	230	242	235	243	No crack
9	C	1160	790	450	With annealing	662	647.4	39.5	457	8.6	B	591	670	224	247	214	223	No crack
10	D	1180	790	450	With annealing	742	693.6	19.1	508	3.8	B	631	756	228	244	233	240	No crack
11	F	1180	790	450	Without annealing	643	695.6	19.1	610	3.1	B	562	653	237	249	203	231	No crack
12	G	1180	790	450	Without annealing	656	695.6	19.1	610	3.1	B	571	663	234	253	206	221	No crack
13	A	1180	790	370	Without annealing	690	686.9	25.4	508	5.0	B	622	691	240	**261**	235	243	**Cracking**
14	C	1160	790	450	Without annealing	662	647.4	39.5	457	8.6	B	630	691	251	**266**	214	223	**Cracking**
15	D	1180	790	450	Without annealing	732	693.6	19.1	508	3.8	B	631	756	231	**257**	232	241	**Cracking**
16	E	1100	770	480	Without annealing	673	688.4	25.4	533	4.8	B	601	702	208	235	209	**254**	**Cracking**
17	E	1100	770	480	With annealing	650	688.4	25.4	533	4.8	B	621	682	210	229	215	**261**	**Cracking**
18	H	1160	770	460	Without annealing	676	691.7	22.2	533	4.2	B	642	706	244	252	239	**250**	**Cracking**

[0082] The slabs with all of the marks were heated in a heating furnace. The heating temperatures (°C) were as shown in Table 2. The slabs after heating were rolled to produce steel plates. Each of the steel plates was water-cooled immediately after rolling. Cooling rates by water cooling were in the range of 10 to 40°C/sec. The cooling start temperatures (°C) of the steel plates with all of the marks were as shown in Table 2. Furthermore, water cooling was stopped at the cooling stop temperatures (°C) shown in Table 2. The steel plates after the stop of water cooling were allowed to cool.

[0083] Tensile test specimens were taken from part of the steel plates after natural cooling and the tensile test was carried out at normal temperature (25°C) to find the tensile strength TS0 (MPa). Furthermore, the value F1 was found on the basis of Expression (6) below:

$F1 = -1.11 \times (t/D \times 100)^2 + 4.32 \times (t/D \times 100) + 693$ (6)

That is, the value F1 is the right side of Expression (4).

[0084] In the marks 8 to 10 and 13 to 15, the yield strength TS0 of the steel plates after cooling exceeded the value F1. For this reason, the steel plates of the marks 8 to 10 were subjected to annealing. The annealing temperatures were in the range of 350 to 600°C and the annealing time was 30 to 90 minutes. The tensile strength TS0 (MPa) of the marks 8 to 10 in Table 2 are values obtained before annealing. As not shown in Table 2, the tensile strength Th0 (MPa) of the mark 8 to 10 after annealing were not more than the value of F1. The steel plates of marks other than the marks 8 to 10 and 17 were not subjected to annealing.

[0085] Incidentally, in the marks 8 and 13, the manufacturing conditions other than whether or not annealing was carried out and the steel grade were the same. Similarly, for the marks 9 and 14, and the marks 10 and 15, the manufacturing conditions other than whether or not annealing was carried out and the steel grade were the same. As described above, for the marks 13 to 15, annealing was not carried out.

[0086] After the production of the steel plates by the above-described processes, UOE steel pipes were produced by subjecting the steel plates of all marks to pipe-making by the above-described method. The wall thickness t (mm) and outside diameter D (mm) of the produced UOE steel pipes were measured. Tensile test specimens were taken from the UOE steel pipes and the tensile test was carried out at normal temperature (25°C) to find the yield strength YS (MPa) and tensile strength TS (MPa).

Observation of microstructure

[0087] On the basis of the above-described method of microstructure observation, the structure of each mark was observed. In the case where the area fraction of hardened structures is not more than 2%, it was judged that the structure of that mark is a bainite shingle phase. Table 2 shows the result of the structure observation. "B" in the column "Structure" of Table 2 means that the structure of the corresponding mark is a bainite single phase.

Vickers hardness test

[0088] In the UOE steel pipes of all marks, maximum values and minimum values (HV10) of the hardness of the outer and inner surface layers and maximum values and minimum values (HV10) of the hardness of the center portion of the wall thickness were found on the basis of the above-described Vickers hardness test.

HIC test

[0089] Test specimens (thickness: 10 mm, width: 20 mm, length: 100 mm) were taken from the UOE steel pipes of all marks. The HIC test was conducted with the aid of the taken test specimens. The test specimens were subjected to the NACE test specified in NACE TM-02-84 as the HIC test, and by the ultrasonic flaw detection method a judgment was made as to whether or not HIC occurred in each of the test specimens after the test.

Test results

[0090] Table 2 shows the test results. The "min" column of "Outer and inner surface layers" of "Vickers hardness" of Table 2 indicates a minimum value (HV10) of the hardness of the outer and inner surface layers of a UOE steel pipe of a corresponding mark. The "max" column indicates a maximum value (HV10) of the hardness of the outer and inner surface layers of a UOE steel pipe. Similarly, the "min" column of "Center portion of wall thickness" of "Vickers hardness" indicates a minimum value (HV10) of the hardness of the center portion of the wall thickness of a UOE steel pipe, and the "max" column indicates a maximum value of the hardness of the center portion of the wall thickness.

[0091] Furthermore, "No crack" of the "HIC test" column in Table 2 means that HIC was not observed in a UOE steel pipe of a corresponding mark. "Cracking" means that HIC was observed.

[0092] Referring to Table 2, the chemical compositions of the marks 1 to 12 were in the range of the present invention. Furthermore, the tensile strength was not less than 625 MPa and the UOE steel pipes had strength of not less than X80 grade of API standard. Furthermore, the maximum values and minimum values of the hardness of the outer and inner surface layers of the UOE steel pipes were all in the range (200 to 255) of the present invention. Also the maximum values and minimum values of the hardness of the center portion of the wall thickness were in the range (200 to 248) of the present invention. For this reason, HIC did not occur in the UOE steel pipes of the marks 1 to 12.

[0093] On the other hand, in the marks 13 to 15, the tensile strength TS0 of the steel plates was higher than F1 although the chemical compositions were in the range of the present invention. For this reason, the maximum value of the hardness of the outer and inner surface layers of the UOE steel pipes exceeded the upper limit (255) to the hardness of the outer and inner surface layers of the present invention. For this reason, HIC was observed in the HIC test.

[0094] The Mn contents, P contents and S contents of the marks 16 and 17 all exceeded the upper limits of the present invention. For this reason, the maximum values of hardness in the center portion of the wall thickness of the UOE steel pipes exceeded the upper limit (248) to the hardness in the center portion of the wall thickness of the present invention. For this reason, HIC was observed. It seems that the hardness of the center portion of the wall thickness increased excessively because of the excessive segregation of Mn, P, and S in the center portion of the wall thickness.

[0095] In the mark 18, an appropriate reduction was not given to the slab in continuous casting and the control to suppress center segregation was insufficient although the chemical composition was in the range of the present invention. For this reason, the maximum value of hardness in the center portion of the wall thickness of the UOE steel pipes exceeded the upper limit (248) of the preset invention and HIC was observed.

[0096] The embodiment of the present invention was described above. However, the above-described embodiment is illustrative only for carrying out the present invention. Therefore, the present invention is not limited by the above-described embodiment, and the present invention can be carried out by appropriately modifying the above-described embodiment so long as the gist of the invention is not departed from thereby.

Claims

[Claim 1] A UOE steel pipe for line pipe containing, by mass%, C: 0.01 to 0.1%, Si: 0.01 to 0.5%, Mn: 1.0 to 1.7%, P: at most 0.015%, S: at most 0.002%, Cr: 0.01 to 0.45%, Mo: 0.03 to 0.5%, Al: 0.005 to 0.05%, Ca: 0.0005 to 0.0050%, N: 0.001 to 0.005%, and Ti: 0.005 to 0.03%, the balance being Fe and impurities, and having a bainite single-phase structure,

wherein the hardness of outer and inner surface layers of the UOE steel pipe is 200 to 255 in terms of HV10,

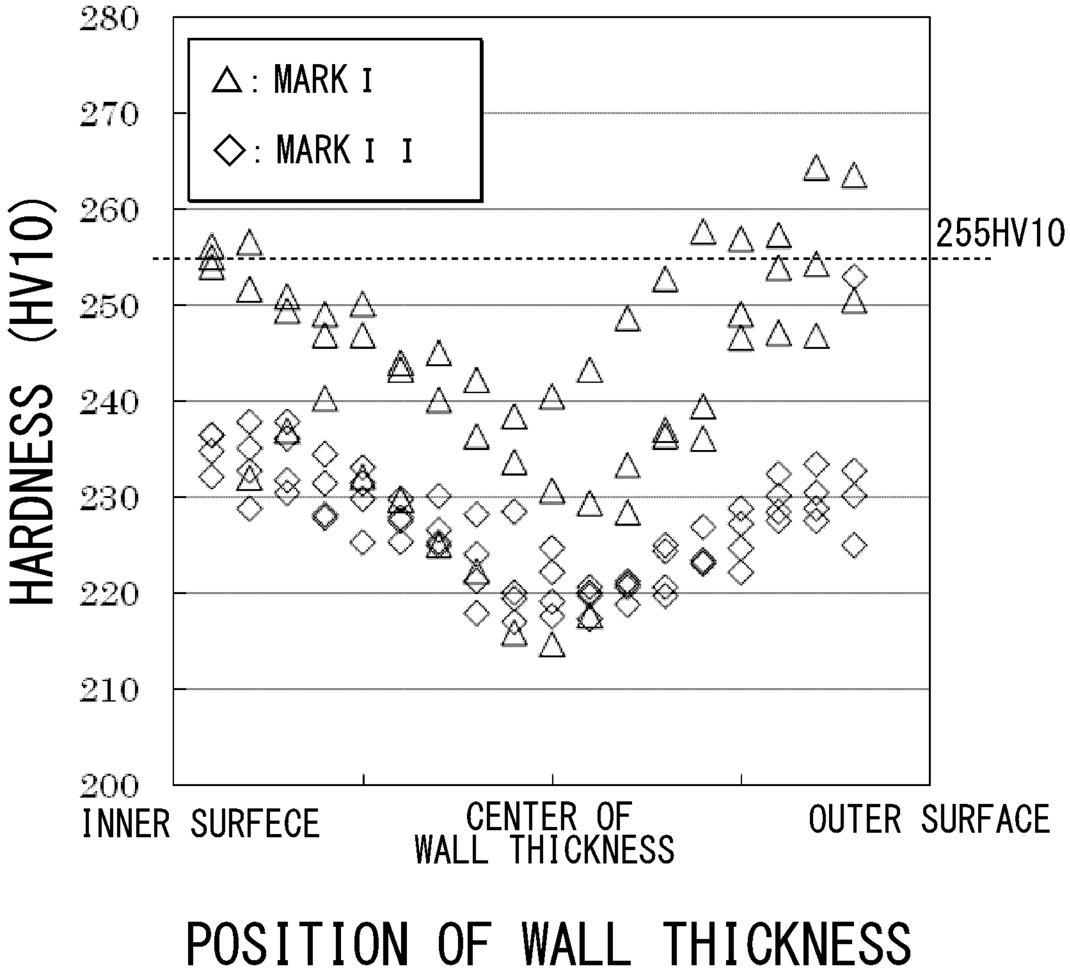
the hardness of a center potion of wall thickness of the UOE steel pipe is 200 to 248 in terms of HV10, and

the tensile strength is not less than 625 MPa.

[Claim 2] The UOE steel pipe according to claim 1, further containing, in place of part of Fe, at least one selected from the group consisting of Cu: at most 0.5%, Ni: at most 0.5%, Nb: at most 0.05%, and V: at most 0.10%.

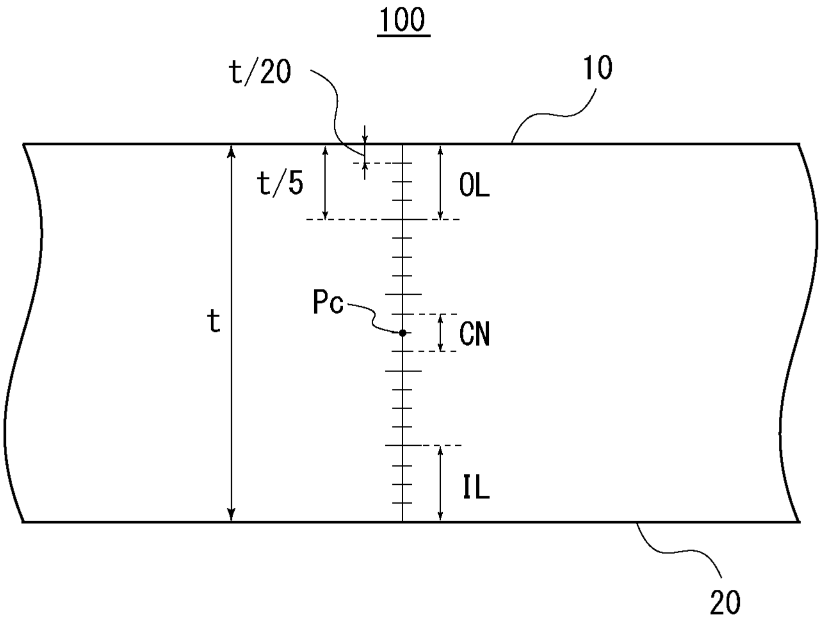
[Fig. 1]

FIG. 1



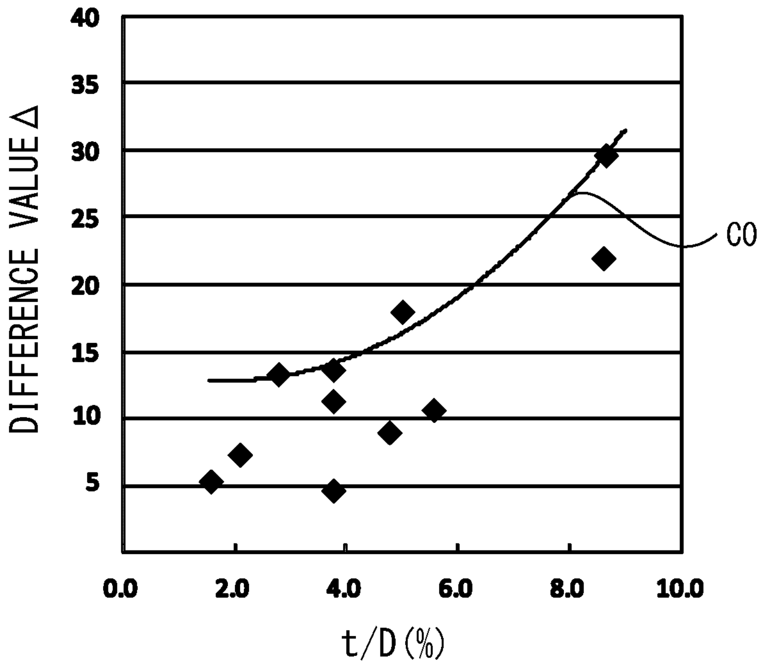
[Fig. 2]

FIG. 2



[Fig. 3]

FIG. 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2012/008456

A. CLASSIFICATION OF SUBJECT MATTER
INV. B21C37/06 C21D9/08 C21D1/18 C22C38/00 C22C38/02
C22C38/04 C22C38/06 C22C38/14 C22C38/18 C22C38/22
C22C38/28

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)
B21C C21D C22C

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 407 570 A1 (SUMITOMO METAL IND [JP]) 18 January 2012 (2012-01-18) paragraph [0032] - paragraph [0035] paragraph [0059] - paragraph [0068] examples 5, 14; table 1 abstract -----	1,2
X	WO 2011/142172 A1 (KOBE STEEL LTD [JP]; TAKAOKA HIROYUKI; TAMURA EIICHI) 17 November 2011 (2011-11-17) example 24; tables 1, 5 -----	1,2
X	JP 2009 235524 A (JFE STEEL CORP) 15 October 2009 (2009-10-15) example B; tables 1,3 -----	1,2

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 11 April 2013	Date of mailing of the international search report 19/04/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Huber, Gerrit

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2012/008456

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2407570 A1	18-01-2012	CA 2755271 A1	16-09-2010
		CN 102421926 A	18-04-2012
		EP 2407570 A1	18-01-2012
		KR 20110123807 A	15-11-2011
		US 2012121453 A1	17-05-2012
		WO 2010104165 A1	16-09-2010
WO 2011142172 A1	17-11-2011	CN 102884217 A	16-01-2013
		KR 20130006508 A	16-01-2013
		WO 2011142172 A1	17-11-2011
JP 2009235524 A	15-10-2009	JP 5146051 B2	20-02-2013
		JP 2009235524 A	15-10-2009