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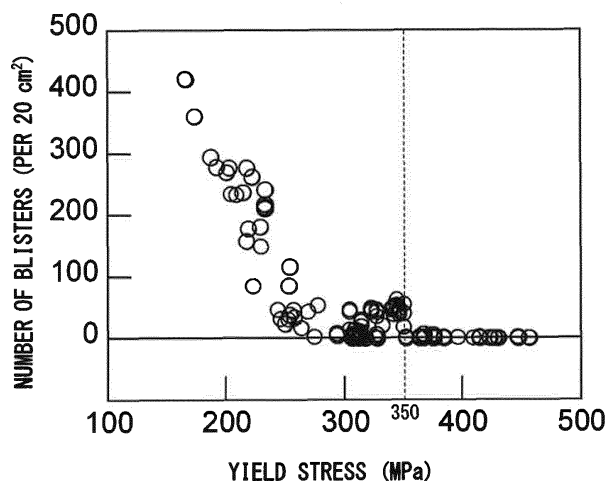
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(54) **SEAMLESS STEEL PIPE FOR LINE PIPE USED IN SOUR ENVIRONMENT**

(57) There is provided a seamless steel pipe which is used in line pipe applications, which line pipe is used in sour environments, and is not subjected to quenching and tempering treatment, and in which the occurrence of blisters can be suppressed. The seamless steel pipe according to this embodiment has a chemical composition consisting, in mass% of, C: 0.08 to 0.24%, Si: 0.10 to 0.50%, Mn: 0.3 to 2.5%, P: 0.02% or less, S: 0.006%

or less, Nb: 0.02 to 0.12%, Al: 0.005 to 0.100%, Ca: 0.0003 to 0.0050%, N: 0.0100% or less, O: 0.0050% or less, Ti: 0 to 0.1%, V: 0 to 0.03%, Cr: 0 to 0.6%, Mo: 0 to 0.3%, Ni: 0 to 0.4%, Cu: 0 to 0.3%, and B: 0 to 0.005%, the balance being Fe and impurities, has a structure consisting of ferrite and pearlite, and also has a yield strength of 350 to less than 450 MPa.

FIG. 1



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a seamless steel pipe. More particularly, it relates to a seamless steel pipe for a line pipe that is used in sour environments containing hydrogen sulfide (H₂S), which is a corrosive gas.

BACKGROUND ART

10 **[0002]** Crude oil and natural gas contain hydrogen sulfide and moisture. Such a wet hydrogen sulfide environment is called a sour environment. Line pipes are used as pipelines for transporting crude oil or natural gas produced from oil wells or gas wells. Therefore, the line pipes are used in sour environments. A line pipe used in sour environments has a problem of hydrogen embrittlement attributable to hydrogen absorbed into a steel because of corrosion in environments containing hydrogen sulfide.

15 **[0003]** The hydrogen embrittlement includes sulfide stress cracking occurring on a steel product under static external stresses and hydrogen induced cracking (hereinafter, referred to as HIC) occurring in the interior of a steel product without external stresses. The line pipe often has a problem of HIC. Therefore, a steel pipe for a line pipe is especially required to have HIC resistance.

20 **[0004]** A steel pipe for a line pipe includes a welded steel pipe and a seamless steel pipe. The welded steel pipe has a seam part (weld zone) extending in the axial direction or in a spiral form. The steel plate used for the welded steel pipe has a center segregated portion, which is produced at the time of continuous casting, in the center of plate thickness, and the center segregated portion has high HIC susceptibility. Therefore, as a steel pipe for a line pipe especially required to have HIC resistance, the seamless steel pipe is preferably used.

25 **[0005]** It is well known that, in general, HIC occurs easily with the increase in steel strength. International Application Publication No. WO2005/075694 (Patent Document 1) proposes a seamless steel pipe having a high strength and excellent HIC resistance.

30 **[0006]** Specifically, the steel product for a line pipe disclosed in Patent Document 1 has a composition consisting, in mass%, of C: 0.03 to 0.15%, Si: 0.05 to 1.0%, Mn: 0.5 to 1.8%, P: 0.015% or less, S: 0.04% or less, O: 0.01% or less, N: 0.007% or less, sol.Al: 0.01 to 0.1%, Ti: 0.024% or less, and Ca: 0.0003 to 0.02%, the balance being Fe and impurities. Further, for the above-described steel product for a line pipe, the size of TiN in the steel product is 30 μm or less. Patent Document 1 describes that since TiN is fine, excellent HIC resistance can be attained.

PRIOR ART DOCUMENTS

35 PATENT DOCUMENTS

[0007]

40 [Patent Document 1] International Application Publication No. WO2005/075694
[Patent Document 2] Japanese Patent Application Publication No. 2002-60893
[Patent Document 3] International Application Publication No. WO2011/152240

45 **[0008]** In the case where a high-strength seamless steel pipe is produced, usually, the strength of the seamless steel pipe is enhanced by quenching and tempering treatment after the hot-working. On the other hand, there is also a demand for low-strength seamless steel pipe for a line pipe that does not need high strength and has yield strength of less than 450 MPa. For such a low-strength seamless steel pipe, usually, the quenching and tempering treatment is not performed and omitted.

50 **[0009]** Conventionally, as described above, it has been thought that if the strength is low, HIC is less liable to occur. However, as the result of investigation conducted by the present inventors, it was found, as a new finding, that in the case where not only the strength is high but also the strength is low, a large number of blisters, which are one type of HIC, and fine internal cracks may be generated.

55 **[0010]** The blister is a swell that is generated in the vicinity of the surface of a steel product and extends in the axial direction of the steel product. In the HIC resistance test (for example, NACE TM0284) specified by NACE, even in the high-strength seamless steel pipe exhibiting excellent HIC resistance, the occurrence of blister may be observed. However, the case where HIC (blister) is merely a crack in the vicinity of surface does not lead to leakage or the like of a fluid being transmitted. Therefore, for the conventional high-strength seamless steel pipe, the blister has not especially posed a problem.

[0011] However, for a low-strength seamless steel pipe, and when a tensile stress is applied thereto, a plurality of

blisters and fine internal cracks in the steel may connect with each other in the wall thickness direction of the seamless steel pipe, and stress oriented hydrogen induced cracking (SOHIC) may occur.

[0012] Therefore, for the low-strength seamless steel pipe that is not subjected to quenching and tempering treatment, it is desirable that the occurrence of blisters and fine internal cracks be suppressed. For the low-strength steel product, since the cause of the occurrence of fine internal cracks is the same as the cause of the occurrence of blisters, it is only necessary to pay attention to the blisters and to suppress the occurrence thereof.

SUMMARY OF INVENTION

[0013] An objective of the present invention is to provide a seamless steel pipe which is not subjected to quenching and tempering treatment and in which, in the case where the steel pipe is used in line pipe, which line pipe is used in sour environments, the occurrence of blisters and fine internal cracks can be suppressed.

[0014] The seamless steel pipe according to an embodiment of the present invention is used for a line pipe used in sour environments. This seamless steel pipe has a chemical composition consisting, in mass%, of C: 0.08 to 0.24%, Si: 0.10 to 0.50%, Mn: 0.3 to 2.5%, P: 0.02% or less, S: 0.006% or less, Nb: 0.02 to 0.12%, Al: 0.005 to 0.100%, Ca: 0.0003 to 0.0050%, N: 0.0100% or less, O: 0.0050% or less, Ti: 0 to 0.1%, V: 0 to 0.03%, Cr: 0 to 0.6%, Mo: 0 to 0.3%, Ni: 0 to 0.4%, Cu: 0 to 0.3%, and B: 0 to 0.005%, the balance being Fe and impurities, has a structure consisting of ferrite and pearlite, and also has a yield strength of 350 to less than 450 MPa.

[0015] For the seamless steel pipe of this embodiment, quenching and tempering treatment is not performed, and even if the strength is low, the occurrence of blisters and fine internal cracks can be suppressed.

BRIEF DESCRIPTION OF DRAWINGS

[0016]

FIG. 1 is a graph showing the relationship between the yield strength of a seamless steel pipe and the number of occurring blisters (per 20 cm²).

FIG. 2 is a photographic image of two surfaces (corresponding to the external surface and internal surface of seamless steel pipe) of a coupon test specimen after the blister number measuring test of Inventive Example of the present invention (steel A4, wall thickness: 20 mm) in Examples.

FIG. 3 is a photographic image of two surfaces (corresponding to the external surface and internal surface of seamless steel pipe) of a coupon test specimen after the blister number measuring test of Comparative Example (steel B3, wall thickness: 20 mm) in Examples.

DESCRIPTION OF EMBODIMENT

[0017] In the following, an embodiment of the present invention is explained in detail with reference to the drawings.

[0018] The present inventors examined and studied the occurrence of blisters in a low-strength seamless steel pipe that is not subjected to quenching and tempering treatment, and obtained the findings described below.

[0019] A blister occurs through the mechanism described below. Hydrogen accumulates around inclusions in the steel, and forms the starting point of hydrogen swell (blister). If the steel product yields on account of the rise in hydrogen pressure at the starting point, a crack is produced. If the crack is produced, the dislocation and hydrogen further accumulate at the edges of crack, and the crack propagates. Thereby, a blister is formed.

[0020] For the low-strength seamless steel pipe not subjected to quenching and tempering treatment, the ratio of ferrite having a low yield strength is high. Therefore, it is thought that the ferrite yields and thereby a blister is generated. For this reason, in order to suppress the occurrence of blisters, it is effective to enhance the strength of steel by strengthening the ferrite itself, or by increasing the ratio of pearlite in the steel, or by the like means.

[0021] FIG. 1 is a graph showing the relationship between the yield strength of a seamless steel pipe and the number of occurring blisters (per 20 cm²). FIG. 1 was obtained by the method described below. Seamless steel pipes having various chemical compositions were produced. At this time, each of the seamless steel pipes subjected to hot working was allowed to cool or cooled at a cooling rate of less than 5°C/s, and the quenching and tempering treatment was not performed.

[0022] For each of the produced seamless steel pipes, the yield strength was determined in the later-described yield strength test. Further, the number of blisters (per 20 cm²) occurring in each of the seamless steel pipes was determined in the later-described blister number measuring test. Thereby, FIG. 1 was created.

[0023] Referring to FIG. 1, for the seamless steel pipes, until the yield strength increased to 350 MPa, the number of blisters decreased remarkably with the increase in yield strength. On the other hand, in the case where the yield strength was 350 MPa or more, even if the yield strength increased, the number of blisters did not change so much.

[0024] In effect, the curve of FIG. 1 has an inflection point in the vicinity of the yield strength of 350 MPa. Therefore, if the yield strength is 350 MPa or more, the number of blisters can be kept small.

[0025] If the content of C is increased, the ratio of pearlite in the steel increases, and thereby the yield strength of steel is enhanced. However, if the C content increases, the weldability decreases. The seamless steel pipe for a line pipe is circumferentially welded at the site at which the line pipe is laid. If the C content increases, the toughness of the circumferentially welded joint part decreases, and also sulfide stress cracking (SSC) is liable to occur. Therefore, it is difficult to excessively increase the C content.

[0026] Also, the strength of seamless steel pipe can be enhanced by performing the quenching and tempering treatment. However, the quenching and tempering treatment of a low-strength seamless steel pipe leads to an increase in production cost.

[0027] Also, a welded steel pipe such as a UOE steel tube is subjected to cold working such as pipe making and pipe expanding. Since the strength of welded steel pipe is enhanced by cold working, the number of occurring blisters may possibly be reduced. However, as described above, the seamless steel pipe is suitable as a line pipe used in hostile sour environments. Therefore, it is difficult to raise the strength by means of cold working or the like, and considering the production cost as well, the cold working is unfavorable.

[0028] Accordingly, in this embodiment, the C content is increased, and further the Nb content is increased. Specifically, the C content is set to 0.08 to 0.24%, and the Nb content is set to 0.02 to 0.12%. In this case, even for the seamless steel pipe not subjected to quenching and tempering treatment (for which the quenching and tempering treatment is omitted), the strength thereof can be enhanced, and the occurrence of blisters can be suppressed.

[0029] Preferably, the numerical value of Nb content (mass%) is made not less than the F1 value defined by Formula (1).

$$F1 = 0.02 + (t-15) \times 0.001 \quad \dots (1)$$

where, t is the wall thickness (unit: mm) of the seamless steel pipe.

[0030] The wall thickness of the seamless steel pipe for a line pipe used in sour environments is, for example, 10 to 50 mm. If the wall thickness increases, the cooling condition of the seamless steel pipe after hot-working also changes. The cooling rate decreases, and the strength of steel tends to be degraded. If the Nb content is not less than the F1 value of Formula (1), the strength of steel is 350 MPa or more, and the occurrence of blisters can be suppressed.

[0031] The seamless steel pipe of this embodiment completed based on the above-described findings is as described below.

[0032] The seamless steel pipe according to this embodiment is used for a line pipe used in sour environments. This seamless steel pipe has a chemical composition consisting, in mass%, of C: 0.08 to 0.24%, Si: 0.10 to 0.50%, Mn: 0.3 to 2.5%, P: 0.02% or less, S: 0.006% or less, Nb: 0.02 to 0.12%, Al: 0.005 to 0.100%, Ca: 0.0003 to 0.0050%, N: 0.0100% or less, O: 0.0050% or less, Ti: 0 to 0.1%, V: 0 to 0.03%, Cr: 0 to 0.6%, Mo: 0 to 0.3%, Ni: 0 to 0.3%, Cu: 0 to 0.3%, and B: 0 to 0.005%, the balance being Fe and impurities, has a structure consisting of ferrite and pearlite, and also has a yield strength of 350 to less than 450 MPa.

[0033] Preferably, the numerical value of Nb content (mass%) is made not less than the F1 value defined by Formula (1).

$$F1 = 0.02 + (t-15) \times 0.001 \quad \dots (1)$$

where, t is the wall thickness (unit: mm) of the seamless steel pipe.

[0034] In the following, the seamless steel pipe of this embodiment is described in detail.

[Chemical composition]

[0035] The seamless steel pipe according to this embodiment has the chemical composition described below.

C: 0.08 to 0.24%

[0036] Carbon (C) enhances the hardenability, and enhances the strength of steel. In the case where heat treatment such as quenching and tempering is not performed after pipe making as in the case of the seamless steel pipe of this embodiment, if the C content is too low, the strength of steel decreases excessively. If the C content is too low, furthermore, excellent HIC resistance is less liable to be attained. If the C content is 0.08% or more, high-strength pearlite dispersedly precipitates in the steel. Therefore, the yield of ferrite is restrained. For this reason, excellent HIC resistance is attained, and the occurrence of blisters is suppressed. On the other hand, the seamless steel pipe of this embodiment is circum-

ferentially welded at the site as a line pipe. Therefore, if the C content is too high, the heat affected zone (HAZ) of circumferential welding hardens, and the SSC resistance decreases. Therefore, the C content is 0.08 to 0.24%. The lower limit of the C content is preferably more than 0.08%, further preferably 0.10%. The upper limit of the C content is preferably less than 0.24%, further preferably 0.15%.

Si: 0.10 to 0.50%

[0037] Silicon (Si) deoxidizes a steel. If the Si content is too low, this effect cannot be achieved. On the other hand, if the Si content is too high, the toughness of the welding heat affected zone decreases. If the Si content is too high, furthermore, the precipitation of ferrite, which is a softening phase, is promoted. Therefore, the HIC resistance decreases, and blisters are liable to occur. For these reasons, the Si content is 0.10 to 0.50%. The lower limit of the Si content is preferably more than 0.10%, further preferably 0.15%, and still further preferably 0.20%. The upper limit of the Si content is preferably less than 0.50%, further preferably 0.35%, and still further preferably 0.30%.

Mn: 0.3 to 2.5%

[0038] Manganese (Mn) enhances the hardenability of steel, and enhances the strength of steel. Furthermore, Mn enhances the toughness of steel. If the Mn content is too low, these effects cannot be achieved. On the other hand, if the Mn content is too high, HIC is liable to occur due to the hardening of steel caused by Mn segregation and due to the formation of MnS. Therefore, the Mn content is 0.3 to 2.5%. The lower limit of the Mn content is preferably more than 0.3%, further preferably 0.5%, and still further preferably 0.8%. The upper limit of the Mn content is preferably less than 2.5%, further preferably 2.0%, and still further preferably 1.8%.

P: 0.02% or less

[0039] Phosphorus (P) is an impurity. Phosphorus decreases the toughness of steel. Therefore, the P content is 0.02% or less. The P content is preferably less than 0.02%, further preferably 0.01% or less. The P content is preferably as low as possible.

S: 0.006% or less

[0040] Sulfur (S) is an impurity. Sulfur forms MnS. The MnS serves as the starting point of a blister. Therefore, the S content is preferably as low as possible. However, the decreasing of the S content incurs high costs. For the seamless steel pipe of this embodiment, in order to reduce the production cost, the S content should be 0.006% or less. For the seamless steel pipe of this embodiment, even if 0.005% or more of S is contained, excellent HIC resistance is exhibited and the occurrence of blisters is suppressed if the C content and the Nb content are proper. However, the S content is preferably as low as possible. The S content is preferably 0.003% or less.

Nb: 0.02 to 0.12%

[0041] Niobium (Nb) dissolves ferrite and enhances the strength of steel. Furthermore, Nb combines with C and N to form carbo-nitrides, and performs grain refinement of steel due to pinning hardening. By the grain refinement, the HIC resistance of steel is enhanced. Furthermore, the grain refinement enhances the toughness of steel. In the case where the seamless steel pipe is made from a steel material containing the above-described range of C and the above-described range of Mn, and not containing Nb, and thereafter heat treatment is not performed (that is, in the case where an as-rolled material, for which quenching and tempering treatment is omitted, is produced), the yield strength of the produced seamless steel pipe is about 250 MPa. However, if the above-described range of Nb is contained, the yield strength of the seamless steel pipe rises to 350 MPa or more. Therefore, the occurrence of blisters is suppressed. If the Nb content is too low, the above-described effects are not achieved. On the other hand, if the Nb content is too high, coarse Nb carbo-nitrides are formed. A coarse Nb carbo-nitride serves as the starting point of blister, and further the HIC resistance also decreases. Therefore, the Nb content is 0.02 to 0.12%.

[0042] As described above, the wall thickness of the seamless steel pipe for a line pipe used in sour environments is 10 to 50 mm. As the wall thickness of the seamless steel pipe increases, the cooling rate of the seamless steel pipe becomes low, and the ferrite grains become coarse, so that the yield strength of steel degrades. Therefore, the lower limit of the Nb content is preferably not less than the F1 value (%) defined by the following Formula (1).

$$F1 = 0.02 + (t-15) \times 0.001 \quad \dots (1)$$

where, t is the wall thickness (unit: mm) of the seamless steel pipe.

[0043] In the case where the seamless steel pipe satisfies Formula (1), not only in the base metal but also in the welding heat affected zone formed by circumferential welding between the seamless steel pipes, a sufficient yield strength can be assured, and the occurrence of blisters is suppressed. The welding heat affected zone includes a hardened zone in which the cooling rate after heating is high and which is hardened, and a softened zone in which the cooling rate is low and which is softened by undergoing thermal effects repeatedly. In the case where Formula (1) is satisfied, in the softened zone, a sufficient yield strength is assured.

[0044] The lower limit of the Nb content is preferably more than 0.02%, further preferably 0.03%, and still further preferably 0.04%. The upper limit of the Nb content is preferably less than 0.12%, further preferably 0.10%, and still further preferably 0.08%.

Al: 0.005 to 0.100%

[0045] Aluminum (Al) deoxidizes a steel. If the Al content is too low, this effect cannot be achieved. On the other hand, if the Al content is too high, coarse cluster-form alumina inclusion particles are formed when the circumferential welding is performed, and thereby the toughness in the welding heat affected zone (HAZ) is decreased. Therefore, the Al content is 0.005 to 0.100%. The lower limit of the Al content is preferably more than 0.005%, further preferably 0.010%, and still further preferably 0.020%. The upper limit of the Al content is preferably less than 0.100%, further preferably 0.060%, and still further preferably 0.040%. In this description, the Al content means the content of acid-soluble Al (sol.Al).

Ca: 0.0003 to 0.0050%

[0046] Calcium (Ca) suppresses the clogging of a tundish nozzle when casting is performed. Furthermore, Ca suppresses the formation of MnS, which serves as the starting point of HIC, a blister, and a fine internal crack. Therefore, Ca suppresses the occurrence of blisters and fine internal cracks. If the Ca content is too low, these effects are insufficient. On the other hand, if the Ca content is too high, inclusions form a cluster, and the toughness and HIC resistance of steel are decreased. Therefore, the Ca content is 0.0003 to 0.0050%. The lower limit of the Ca content is preferably more than 0.0003%, further preferably 0.0010%, and still further preferably 0.0015%. The upper limit of the Ca content is preferably less than 0.0050%, further preferably 0.0040%, and still further preferably 0.0030%.

N: 0.0100% or less

[0047] Nitrogen (N) is an impurity. Nitrogen forms coarse nitrides, and decreases the toughness and SSC resistance of steel. Therefore, the N content is preferably as low as possible. For this reason, the N content is 0.0100% or less. The N content is preferably 0.0080% or less, further preferably 0.0060% or less.

O: 0.0050% or less

[0048] Oxygen (O) is an impurity. Oxygen forms coarse oxides or a cluster of oxides, and decreases the toughness and HIC resistance of steel. Therefore, the O content is preferably as low as possible. For this reason, the O content is 0.0050% or less. The O content is preferably 0.0040% or less, further preferably 0.0030% or less.

[0049] The balance of chemical composition of the seamless steel pipe of this embodiment is Fe and impurities. The impurities referred to in this description mean elements that are mixed from ore and scrap used as steel raw materials or from the environment in the production process or the like.

[Concerning optional elements]

[0050] Furthermore, the seamless steel pipe of this embodiment may contain one or more types of elements selected from a group consisting of Ti, V, Cr, Mo, Ni, Cu, and B. Any of these elements enhances the strength of steel.

Ti: 0 to 0.1%

[0051] Titanium (Ti) is an optional element. Like Nb, Ti combines with C and N to form carbo-nitrides, and performs grain refinement of steel due to pinning hardening. On the other hand, if the Ti content is too high, this effect is saturated.

Therefore, the Ti content is 0 to 0.1%. The lower limit of the Ti content is preferably 0.002%, further preferably 0.005%. The upper limit of the Ti content is preferably less than 0.1%, further preferably 0.05%.

V: 0 to 0.03%

[0052] Vanadium (V) is an optional element. Vanadium forms carbides to strengthen a steel. On the other hand, if the V content is too high, coarse carbides are formed, and SSC is liable to occur. Therefore, the V content is 0 to 0.03%. The lower limit of the V content is preferably 0.01%, further preferably 0.015%. The upper limit of the V content is preferably less than 0.03%, further preferably 0.025%.

Cr: 0 to 0.6%

Mo: 0 to 0.3%

Ni: 0 to 0.4%

Cu: 0 to 0.3%

[0053] All of chromium (Cr), molybdenum (Mo), nickel (Ni), and copper (Cu) are optional elements. Any of these elements enhances the hardenability of steel to strengthen the steel, and enhances the HIC resistance for a low-strength steel. On the other hand, if the content of any of these elements is too high, a hardened structure may be formed locally, or uneven corrosion may be caused on the surface of steel. Therefore, the Cr content is 0 to 0.6%, the Mo content is 0 to 0.3%, the Ni content is 0 to 0.4%, and the Cu content is 0 to 0.3%. The lower limit of the Cr content is preferably 0.01%, further preferably 0.05%. The lower limit of the Mo content is preferably 0.01%, further preferably 0.05%. The lower limit of the Ni content is preferably 0.01%, further preferably 0.05%. The lower limit of the Cu content is preferably 0.01%, further preferably 0.05%. The upper limit of the Cr content is preferably less than 0.6%, further preferably 0.5%. The upper limit of the Mo content is preferably less than 0.3%, further preferably 0.25%. The upper limit of the Ni content is preferably less than 0.4%, further preferably 0.3%, and still further preferably 0.25%. The upper limit of the Cu content is preferably less than 0.3%, further preferably 0.25%.

[0054] Preferably, the total content of Cr, Mo, Ni and Cu satisfies the following Formula (2).

$$(Cr+Mo)/5 + (Cu+Ni)/15 < 0.10 \quad \dots (2)$$

where, each of the element symbols in the formula is the content (mass%) of the corresponding element.

[0055] If Cr, Mo, Ni and Cu satisfy Formula (2), even for a large-thickness seamless steel pipe, the yield strength is less than 450 MPa.

B: 0 to 0.005%

[0056] Boron (B) is an optional element. Boron enhances the hardenability of steel for a low-strength seamless steel pipe, and enhances the HIC resistance for a low-strength steel. On the other hand, if the B content is too high, the SSC resistance of steel decreases. Therefore, the B content is set to 0 to 0.005%. The lower limit of the B content is preferably 0.0001% or more, further preferably 0.0003%. The upper limit of the B content is preferably less than 0.005%, further preferably 0.003%.

[Structure and strength]

[0057] The seamless steel pipe of this embodiment is not subjected to quenching and tempering treatment after pipe making. That is to say, the seamless steel pipe of this embodiment is a so-called as-rolled material for which the quenching and tempering treatment is omitted. As described later, the seamless steel pipe having been made is allowed to cool or is cooled at a cooling rate of less than 2°C/s. Therefore, the structure of the seamless steel pipe of this embodiment consists of ferrite and pearlite. Most part of the structure is ferrite, and the remaining part thereof is pearlite. The structure referred to in this description means a matrix structure not containing inclusions and precipitates.

[0058] Even if being cooled at so low a cooling rate as described above, the seamless steel pipe of this embodiment has a yield strength of 350 MPa or more. In this description, the yield strength means a 0.2% yield stress. The preferable yield strength of the seamless steel pipe is 400 MPa or more. For the seamless steel pipe of this embodiment, the yield

strength is less than 450 MPa.

[Manufacturing method]

[0059] There is now explained one example of the manufacturing method for the seamless steel pipe for a line pipe used in sour environments according to the embodiment.

[0060] A steel having the above-described chemical composition is melted, and is refined by the well-known method. Successively, the molten steel is cast into a continuously cast material by the continuous casting process. The continuously cast material is, for example, a slab, a bloom, or a billet. Also, the molten steel may be made an ingot by the ingot-making process.

[0061] The slab or bloom of the continuously cast material or the ingot is hot-worked to produce a billet. For example, a slab, bloom or an ingot is rolled into a billet using a blooming mill.

[0062] Successively, the produced billet is hot-rolled to produce a seamless steel pipe. Specifically, the billet is heated in a heating furnace. If the heated billet is hot-rolled in the state in which coarse Nb inclusions remain therein, at the cooling time after hot rolling, the strengthening due to Nb cannot be attained sufficiently. In this embodiment, therefore, the billet is heated to a further high temperature as compared with the time of production of the ordinary seamless steel pipe. Specifically, at the heating time, the billet is heated to a temperature of 1250°C or more.

[0063] The billet extracted from the heating furnace is hot-worked to produce a seamless steel pipe. Specifically, piercing-rolling based on the Mannesmann process is performed to produce a hollow shell. The produced hollow shell is further subjected to elongation rolling and sizing by using a mandrel mill, a reducer, a sizing mill, or the like to produce a seamless steel pipe.

[0064] The produced seamless steel pipe is cooled. At this time, the cooling rate in a high-temperature region of 500°C or more, in which Nb carbo-nitrides precipitate, is preferably higher. Therefore, until the temperature of seamless steel pipe decreases to 500°C, the seamless steel pipe is cooled at a cooling rate of 0.5 to 5°C/s, and subsequently, it is cooled at a cooling rate of less than 2°C. The cooling at a cooling rate of less than 2°C/s includes the allowing to cool.

[0065] The cooling rate can be controlled, for example, by regulating the spacing between the adjacent seamless steel pipes at the time of allowing to cool. For example, until the temperature of seamless steel pipe decreases to 500°C, the spacing between the adjacent seamless steel pipes is made distance D1, and at a temperature of 500°C or less, the spacing is regulated to distance D2, which is shorter than distance D1. Thereby, a gentle two-stage cooling rate can be realized.

[0066] In the above-described production method, the seamless steel pipe after hot-working is not subjected to quenching and tempering treatment.

[Number of blisters]

[0067] For the seamless steel pipe produced by the manufacturing method, the occurrence of blisters can be suppressed. In particular, in the case where the Nb content (%) is not less than the F1 value defined by Formula (1), the number of blisters in the surface is less than 10 per 20 cm². The number of blisters can be determined by the blister number measuring test described below.

[Blister number measuring test]

[0068] Based on NACE TM0284-2011 specified by NACE (National Association of Corrosion Engineers) International, a HIC test using a wet hydrogen sulfide environment (sour environment) is conducted. Specifically, a coupon test specimen measuring plate thickness x 20 mm wide x 100 mm long (length in the axial direction of seamless steel pipe) is sampled. This coupon test specimen has a pair of surfaces corresponding to the external surface and internal surface of the seamless steel pipe.

[0069] In conformity to NACE TM0284, there is prepared a 25°C test bath in which 100% H₂S gas is saturated in (5%NaCl + 0.5%CH₃COOH) aqueous solution under the atmospheric pressure. The coupon test specimen is immersed in the test bath for 96 hours. After the 96-hour immersion, the surfaces (two surfaces each measuring 20 mm wide x 100 mm long corresponding to the external surface and internal surface of seamless steel pipe) of the coupon test specimen are observed visually. Then, the total number of blisters occurring in the surfaces is counted to determine the number of blisters (per 20 cm²).

[0070] As described above, for the seamless steel pipe according to this embodiment, by enhancing the yield strength to 350 MPa or more by means of C and Nb, the occurrence of blisters can be suppressed. Therefore, the HIC resistance is excellent, and furthermore, when a tensile stress is applied, SOHIC is less liable to occur.

EXAMPLES

[0071] Ingots of steels A1 to A15 and B1 to B6 given in Table 1 were produced.
[0072] [Table 1]

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Table 1

Steel	Chemical composition (unit: mass%, balance being Fe and impurities)																F2	
	C	Si	Mn	P	S	Nb	Al	Ca	Ti	V	Cr	Mo	Ni	Cu	B	N		O
A1	0.20	0.20	1.00	0.01	0.005	0.030	0.037	0.0017	-	-	-	-	-	-	-	0.0010	0.0020	-
A2	0.20	0.20	0.99	0.01	0.005	0.069	0.034	0.0018	-	-	-	-	-	-	-	0.0010	0.0020	-
A3	0.10	0.19	0.98	0.01	0.004	0.050	0.034	0.0025	-	-	-	-	-	-	-	0.0010	0.0020	-
A4	0.10	0.19	0.98	0.01	0.004	0.098	0.032	0.0023	-	-	-	-	-	-	-	0.0010	0.0010	-
A5	0.11	0.20	0.99	0.01	0.006	0.044	0.038	0.0016	-	-	-	-	-	-	-	0.0020	0.0020	-
A6	0.13	0.28	1.19	0.01	0.005	0.045	0.034	0.0018	0.013	-	-	-	-	-	0.001	0.0010	0.0030	-
A7	0.12	0.30	1.23	0.01	0.006	0.045	0.035	0.0015	-	0.02	-	-	-	-	-	0.0020	0.0020	-
A8	0.12	0.30	1.21	0.01	0.006	0.046	0.041	0.0020	-	-	0.23	0.18	-	-	-	0.0020	0.0020	0.082
A9	0.12	0.29	1.20	0.01	0.006	0.044	0.033	0.0017	-	-	-	-	0.19	0.19	-	0.0020	0.0030	0.025
A10	0.09	0.11	0.61	0.01	0.004	0.021	0.031	0.0023	-	-	-	-	-	-	-	0.0010	0.0030	-
A11	0.10	0.13	0.60	0.01	0.004	0.033	0.032	0.0019	-	-	-	-	-	-	-	0.0010	0.0030	-
A12	0.20	0.21	1.01	0.01	0.004	0.049	0.035	0.0020	-	-	-	-	-	-	-	0.0020	0.0030	-
A13	0.11	0.19	1.00	0.01	0.005	0.050	0.032	0.0015	-	-	-	-	-	-	-	0.0020	0.0030	-
A14	0.11	0.21	1.29	0.01	0.003	0.043	0.038	0.0016	0.019	-	0.11	0.01	0.36	0.24	0.001	0.0040	0.0020	0.064
A15	0.12	0.18	1.33	0.01	0.004	0.045	0.034	0.0021	0.011	-	0.24	0.02	0.34	0.25	0.001	0.0010	0.0020	0.091
B1	0.19	0.20	0.98	0.01	0.006	-	0.033	0.0020	-	-	-	-	-	-	-	0.0020	0.0020	-
B2	0.20	0.19	1.00	0.01	0.005	0.011	0.036	0.0019	-	-	-	-	-	-	-	0.0020	0.0030	-
B3	0.10	0.19	1.00	0.01	0.005	-	0.036	0.0025	-	-	-	-	-	-	-	0.0010	0.0010	-
B4	0.01	0.19	0.99	0.01	0.005	0.045	0.045	0.0013	-	-	-	-	-	-	-	0.0020	0.0030	-
B5	0.05	0.18	1.01	0.01	0.005	0.046	0.039	0.0015	-	-	-	-	-	-	-	0.0020	0.0020	-
B6	0.11	0.21	1.31	0.01	0.005	0.046	0.035	0.0022	0.013	-	0.42	0.02	0.34	0.23	0.001	0.0020	0.0030	0.126

[0073] The symbol "-" in Table 1 indicates that the content is substantially "0" (impurity level). The F2 value in Table 1 is defined as described below.

$$F2 = (Cr+Mo)/5 + (Cu+Ni)/15$$

In effect, F2 is the left side of Formula (2).

[0074] Referring to Table 1, the chemical compositions of steels A1 to A15 were within the range of chemical composition of the seamless steel pipe of this embodiment. On the other hand, steels B1 and B3 did not contain Nb, and the Nb content of steel B2 was less than the lower limit of the Nb content of the seamless steel pipe of this embodiment. The C content of each of steels B4 and B5 was less than the lower limit of the C content of the seamless steel pipe of this embodiment. The F2 value of steel B6 did not satisfy Formula (2).

[0075] The ingots of the steels were hot-forged to produce a plurality of billets of the steels. After each of the billets had been heated at the heating temperature given in Table 2, the billet is piercing-rolled by using a piercing mill (piercer) to produce a seamless steel pipe. At this time, for each steel, three kinds of seamless steel pipes having wall thicknesses of 12.7 mm, 25.4 mm, and 38.1 mm were produced. Each of the produced seamless steel pipes was cooled at the first cooling rate given in Table 2 until the temperature of seamless steel pipe decreases to 500°C, and was cooled at the second cooling rate subsequently.

[0076] [Table 2]

Table 2

Steel	Heating temperature (°C)	No content (%)	Wall thickness t=12.7 mm					Wall thickness t=25.4 mm					Wall thickness t=38.1 mm				
			F1 value	1st cooling rate	2nd cooling rate	YS (MPa)	Number of blisters	F1 value	1st cooling rate	2nd cooling rate	YS (MPa)	Number of blisters	F1 value	1st cooling rate	2nd cooling rate	YS (MPa)	Number of blisters
A1	1260	0.030	0.018	3.0	1.0	411	1	0.030	1.5	0.5	382	0	0.043	1.0	Less than 0.5	349	10
A2	1260	0.069	0.018	3.0	1.0	442	0	0.030	1.5	0.5	419	1	0.043	1.0	Less than 0.5	389	0
A3	1280	0.050	0.018	3.5	1.5	424	1	0.030	2.0	1.0	402	0	0.043	1.5	0.5	383	0
A4	1280	0.098	0.018	3.5	1.5	438	0	0.030	2.0	1.0	426	0	0.043	1.5	0.5	402	0
A5	1250	0.044	0.018	2.0	1.0	418	0	0.030	1.0	0.5	399	1	0.043	1.0	Less than 0.5	381	0
A6	1250	0.045	0.018	2.0	1.0	433	0	0.030	1.0	0.5	415	0	0.043	1.0	Less than 0.5	398	0
A7	1250	0.045	0.018	2.0	1.0	421	2	0.030	1.0	0.5	410	3	0.043	1.0	Less than 0.5	388	1
A8	1250	0.046	0.018	2.0	1.0	435	1	0.030	1.0	0.5	412	2	0.043	1.0	Less than 0.5	398	1
A9	1250	0.044	0.018	2.0	1.0	446	0	0.030	1.0	0.5	423	0	0.043	1.0	Less than 0.5	405	0
A10	1250	0.021	0.018	2.0	1.0	372	0	0.030	1.0	0.5	348	10	0.043	1.0	Less than 0.5	329	18
A11	1250	0.033	0.018	2.0	1.0	392	0	0.030	1.0	0.5	368	0	0.043	1.0	Less than 0.5	344	11
A12	1160	0.049	0.018	3.0	1.0	331	32	0.030	1.5	0.5	318	41	0.043	1.0	Less than 0.5	299	39
A13	1260	0.05	0.018	Less than 0.5	Less than 0.5	349	12	0.030	Less than 0.5	Less than 0.5	340	15	0.043	Less than 0.5	Less than 0.5	328	19
A14	1250	0.043	0.018	2.0	1.0	423	0	0.030	1.0	0.5	408	1	0.043	1.0	Less than 0.5	391	1

(continued)

Steel	Heating temperature (°C)	No content (%)	Wall thickness t=12.7 mm					Wall thickness t=25.4 mm					Wall thickness t=38.1 mm				
			F1 value	1st cooling rate	2nd cooling rate	YS (MPa)	Number of blisters	F1 value	1st cooling rate	2nd cooling rate	YS (MPa)	Number of blisters	F1 value	1st cooling rate	2nd cooling rate	YS (MPa)	Number of blisters
A15	1250	0.045	0.018	2.0	1.0	448	0	0.030	1.0	0.5	438	0	0.043	1.0	Less than 0.5	424	0
B1	1260	-	0.018	3.0	1.0	300	33	0.030	1.5	0.5	269	62	0.043	1.0	Less than 0.5	253	91
B2	1260	0.011	0.018	3.0	1.0	349	11	0.030	1.5	0.5	340	13	0.043	1.0	Less than 0.5	325	25
B3	1250	-	0.018	3.5	1.5	286	24	0.030	2.0	1.0	260	78	0.043	1.5	0.5	238	112
B4	1250	0.045	0.018	2.0	1.0	321	38	0.030	1.0	0.5	298	42	0.043	1.0	Less than 0.5	278	58
B5	1250	0.046	0.018	2.0	1.0	348	10	0.030	1.0	0.5	324	28	0.043	1.0	Less than 0.5	311	32
B6	1250	0.046	0.018	2.0	1.0	466	0	0.030	1.0	0.5	459	0	0.043	1.0	Less than 0.5	452	0

[Micro-structure observing test]

[0077] Each of the seamless steel pipes having three kinds of wall thicknesses that had been produced for each steel was subjected to a micro-structure observing test. In the transverse cross section (the surface perpendicular to the axial direction of seamless steel pipe) of each seamless steel pipe, the wall thickness central portion was etched by using nital or the like. One optional visual field (visual field area: 40,000 μm^2) of the etched wall thickness central portion was observed. For the observation, an optical microscope having a magnification of x500 was used.

[0078] As the result of the micro-structure observing test, each of all the seamless steel pipes had a structure consisting of ferrite and pearlite.

[Yield strength test]

[0079] From each of the three kinds of seamless steel pipes of each steel, a round-bar tensile test specimen having a parallel part measuring 6 mm in outside diameter and 40 mm in length was sampled. The parallel part was parallel to the axial direction of the seamless steel pipe. By using the sampled round-bar tensile test specimen, a tension test was conducted at normal temperature (25°C) to determine the yield strength YS (0.2% yield stress) (MPa).

[Blister number measuring test]

[0080] Each of the three kinds of seamless steel pipes of each steel was subjected to the above-described blister number measuring test to determine the number of blisters.

[Test results]

[0081] Table 2 gives the test results. FIG. 2 is a photographic image of two surfaces (corresponding to the external surface and internal surface of seamless steel pipe) of the coupon test specimen after the blister number measuring test of steel A4 (wall thickness: 20 mm), and FIG. 3 is a photographic image of two surfaces of the coupon test specimen after the blister number measuring test of steel B3 (wall thickness: 20 mm). In FIGS. 2 and 3, the upper surface corresponds to the external surface of seamless steel pipe, and the lower surface corresponds to the internal surface of seamless steel pipe.

[0082] Referring to Table 2, the chemical compositions of steels A1 to A11, A14 and A15 were proper. Therefore, each of the 12.7-mm seamless steel pipes of these steels, which had a wall thickness of 15 mm or less, had a yield strength YS of 350 to less than 450 MPa. For this reason, as shown in FIG. 2, the occurrence of blisters in the surface was suppressed, and the number of blisters was less than 10 per 20 cm^2 .

[0083] Furthermore, for the 25.4-mm seamless steel pipes, the Nb content of each of steels A1 to A9, A11, A14 and A15 was not less than the F1 value defined by Formula (1). Therefore, even for the seamless steel pipes having a wall thickness of more than 15 mm, a yield strength of 350 to less than 450 MPa was attained, and the number of blisters was less than 10 per 20 cm^2 .

[0084] Furthermore, for the 38.1-mm seamless steel pipes, the Nb content of each of steels A2 to A9, A14 and A15 was not less than the F1 value. Therefore, even for the seamless steel pipes having a wall thickness of more than 35 mm, a yield strength of 350 to less than 450 MPa was attained, and the number of blisters was less than 10 per 20 cm^2 .

[0085] On the other hand, although the chemical compositions of steels A12 and A13 were proper, steel A12 had a too low heating temperature and steel A13 had a too low first cooling rate. Therefore, the yield strength YS was less than 350 MPa, and for the seamless steel pipes having any wall thickness, the number of blisters was not less than 10 per 20 cm^2 .

[0086] On the other hand, the Nb content of each of steels B1 to B3 was too low. Therefore, even for the seamless steel pipes each having a wall thickness of less than 20mm, the yield strength was less than 350 MPa. As the result, many blisters occurred in the surface as shown in FIG. 3, and the number of blisters was not less than 10 per 20 cm^2 .

[0087] Also, the C content of each of steels B4 and B5 was too low. Therefore, even for the seamless steel pipes each having a wall thickness of less than 20mm, the yield strength was less than 350 MPa, and the number of blisters was not less than 10 per 20 cm^2 .

[0088] The F2 value of steel B6 did not satisfy Formula (2). Therefore, the yield strength of steel B6 was more than 450 MPa.

[0089] The above is an explanation of the embodiment of the present invention, and the embodiment is merely an illustration for carrying out the present invention. Therefore, the present invention is not limited to the embodiment, and the embodiment can be carried out by being modified or changed as appropriate without departing from the spirit and scope of the present invention.

Claims

1. A seamless steel pipe for a line pipe used in sour environments comprising:

a chemical composition consisting, in mass% of,

C: 0.08 to 0.24%,
 Si: 0.10 to 0.50%,
 Mn: 0.3 to 2.5%,
 P: 0.02% or less,
 S: 0.006% or less,
 Nb: 0.02 to 0.12%,
 Al: 0.005 to 0.100%,
 Ca: 0.0003 to 0.0050%,
 N: 0.0100% or less,
 O: 0.0050% or less,
 Ti: 0 to 0.1 %,
 V: 0 to 0.03%,
 Cr: 0 to 0.6%,
 Mo: 0 to 0.3%,
 Ni: 0 to 0.4%,
 Cu: 0 to 0.3%, and
 B: 0 to 0.005%,
 the balance being Fe and impurities;

a structure consisting of ferrite and pearlite; and
 a yield strength of 350 to less than 450 MPa.

2. The seamless steel pipe according to claim 1, wherein the content (mass%) of Nb is not less than F1 value defined by Formula (1).

$$F1 = 0.02 + (t-15) \times 0.001 \quad \dots (1)$$

where, t is the wall thickness (unit: mm) of the seamless steel pipe.

FIG. 1

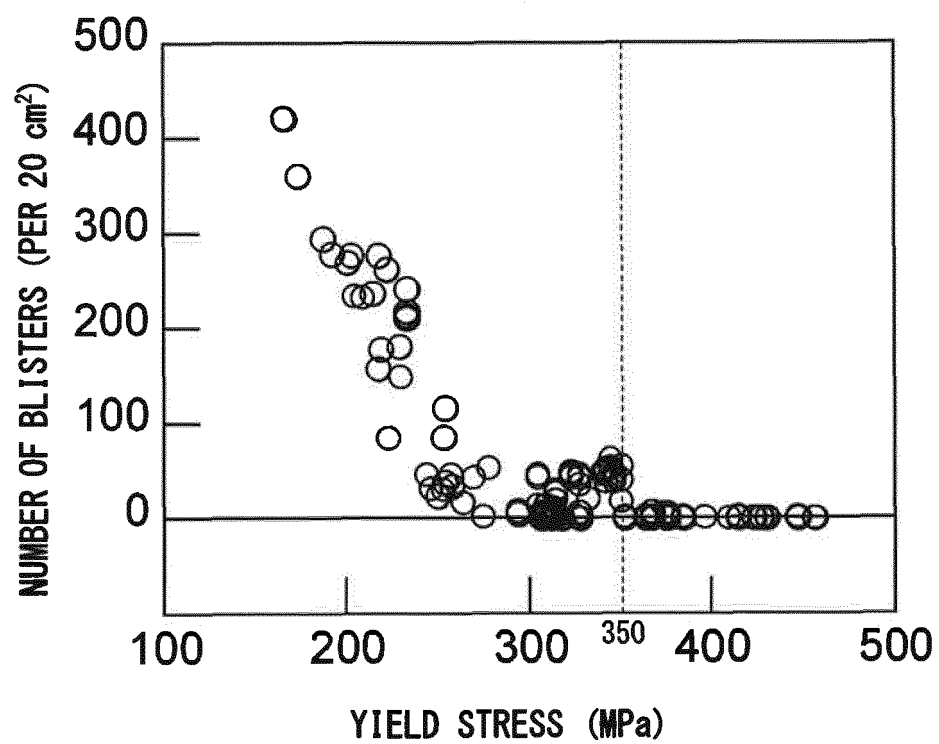


FIG. 2

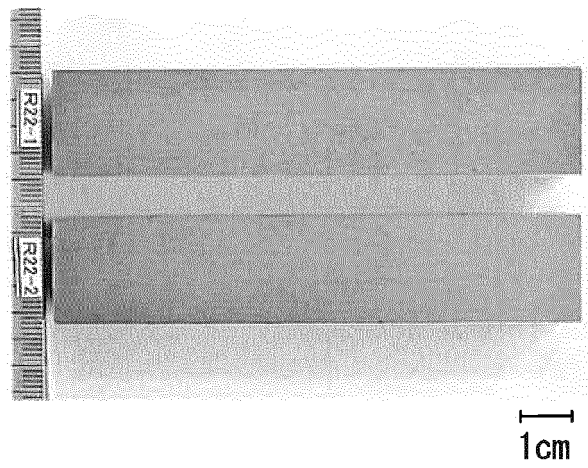
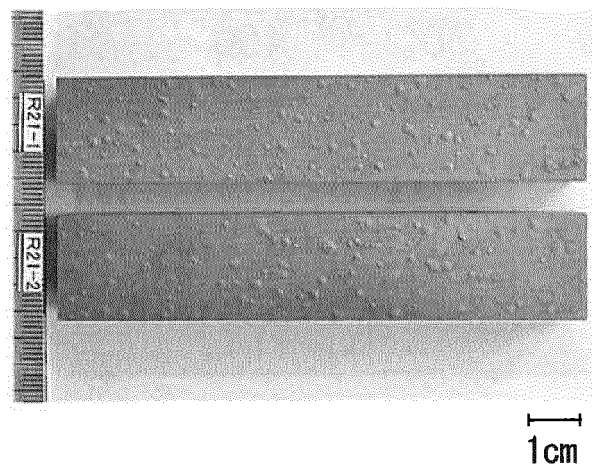


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/002662

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D8/10(2006.01)i, C22C38/58(2006.01)i

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)

C22C38/00-38/60, C21D8/10

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014

Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 63-250418 A (Nippon Steel Corp.),	1, 2
Y	18 October 1988 (18.10.1988), pages 3, 4 (Family: none)	1, 2
X	JP 1-234521 A (Nippon Steel Corp.),	1, 2
Y	19 September 1989 (19.09.1989), page 4, lower left column, line 20 to page 6, lower left column, line 16; pages 7, 8 (Family: none)	1, 2
Y	JP 59-150066 A (Sumitomo Metal Industries, Ltd.), 28 August 1984 (28.08.1984), page 1, right column, lines 10 to 17; page 3, upper left column, line 18 to page 5 (Family: none)	1, 2

☒ 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

14 July, 2014 (14.07.14)

Date of mailing of the international search report

29 July, 2014 (29.07.14)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/002662

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-509398 A (Voestalpine Tubulars GmbH & Co. KG), 19 April 2012 (19.04.2012), paragraphs [0009], [0012] & US 2011/0272067 A1 & EP 2682485 A1 & WO 2010/057235 A1 & CN 102224265 A & KR 10-2011-0095376 A	1, 2

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2005075694 A [0005] [0007]
- JP 2002060893 A [0007]
- WO 2011152240 A [0007]