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

(57) The present disclosure provides a high strength steel plate for sour-resistant line pipes that has excellent HIC resistance in which variation in the HIC resistance in the plate width direction is suppressed. A high strength steel plate for sour line pipes disclosed herein includes a chemical composition containing C, Si, Mn, P, S, Al, and Ca in predetermined amounts, with the balance being Fe and inevitable impurities, in which in a cross-section perpendicular to a rolling direction of the steel plate, the number of Mn-concentrated spots that are approximated to an elliptical shape having a major axis length

of more than 1.5 mm, in a measuring region located ± 5 mm from a plate thickness center toward a plate thickness direction, is 3 or less per 100 mm in length in a plate width direction, HIC resistance is 10 % or less in terms of CAR at a W/4 position, a W/2 position, and a 3W/4 position from one end in the plate width direction of the steel plate, where W denotes a plate width, variation in the HIC resistance in the plate width direction in terms of 3σ is 5 % or less when σ denotes a standard deviation of CARs, and a tensile strength is 520 MPa or more.

EP 3 674 433 A1

Description

TECHNICAL FIELD

5 **[0001]** This disclosure relates to a high strength steel plate for sour-resistant line pipes that is used in the field of sour-resistant line pipes and that is excellent in the uniformity of material homogeneity, in particular HIC characteristics, in the steel plate, and to a high strength steel pipe using the same.

BACKGROUND

10 **[0002]** In general, a line pipe is manufactured by forming a steel plate manufactured by a plate mill or a hot rolling mill into a steel pipe by UOE forming, press bend forming, roll forming, or the like.

[0003] The line pipe used to transport crude oil and natural gas containing hydrogen sulfide is required to have so-called sour resistance such as resistance to hydrogen-induced cracking (HIC resistance) and resistance to sulfide stress corrosion cracking (SSCC resistance), in addition to strength, toughness, weldability, and so on. Above all, in HIC, hydrogen ions caused by corrosion reaction adsorb on the steel surface, penetrate into the steel as atomic hydrogen, diffuse and accumulate around non-metallic inclusions such as MnS in the steel and the hard second phase structure, and become molecular hydrogen, thereby causing cracking due to its internal pressure.

15 **[0004]** Several methods have been proposed to prevent such HIC. JPH5-271766A (PTL 1) and JPH7-173536A (PTL 2) propose methods for suppressing central segregation in a high strength steel plate by keeping the C and Mn contents low, while performing morphological control of sulfide inclusions by keeping the S content low and adding Ca, and supplementing the decrease in strength associated therewith by adding Cr, Mo, Ni, and the like and performing accelerated cooling.

20 **[0005]** On the other hand, the demand for a steel plate with higher strength and higher toughness is increasing from the viewpoint of increasing the size of steel structures and reducing costs. For the purposes of property improvement and alloying element reduction of steel plates and elimination of heat treatment, high strength steel plates are usually manufactured by applying a so-called TMCP (Thermo-Mechanical Control Process) technique combining controlled rolling and controlled cooling.

25 **[0006]** In order to increase the strength of the steel material by using TMCP technique, it is effective to increase the cooling rate at the time of controlled cooling. However, when the control cooling is performed at a high cooling rate, the surface layer of the steel plate is rapidly cooled, and the hardness of the surface layer becomes higher than that of the inside of the steel plate, and the hardness distribution in the plate thickness direction becomes uneven. Therefore, it is a problem in terms of ensuring the material homogeneity in the steel plate.

30 **[0007]** To solve the above problems, for example, JP2002-327212A (PTL 3) and JP3711896 B (PTL 4) describe methods for producing a steel plate for line pipes in which a steel plate surface after subjection to accelerated cooling is heated to a higher temperature than the interior using a high-frequency induction heating device such that the hardness is reduced at the surface layer.

35 **[0008]** On the other hand, when the scale thickness on the steel plate surface is uneven, the cooling rate is also uneven at the underlying steel plate during cooling, causing a problem of local variation in the cooling stop temperature in the steel plate. As a result, unevenness in scale thickness causes variation in the steel plate material property in the plate width direction. On the other hand, JPH9-57327A (PTL 5) and JP3796133B (PTL 6) describe methods for improving the shape of a steel plate by performing descaling immediately before cooling to suppress cooling unevenness caused by scale thickness unevenness.

CITATION LIST

Patent Literature

45 **[0009]**

50 PTL 1: JPH5-271766A

PTL 2: JPH7-173536A

55 PTL 3: JP2002-327212A

PTL 4: JP3711896 B

PTL 5: JPH9-57327A

PTL 6: JP3796133B

SUMMARY

(Technical Problem)

[0010] However, although the techniques of PTLs 1 to 4 focus on central segregation area, none of these documents consider the uniformity of the HIC resistance in the plate width direction. Variation in central segregation in the plate width direction in a slab result in variation in the HIC resistance in the plate width direction of the rolled steel plate.

[0011] Further, according to the present inventors' study, it turned out that there is still a room for improvement in high strength steel plates obtained by the methods described in PTLs 5 and 6 in terms of uniformity of the HIC resistance in the plate width direction. The reason can be considered as follows. The methods of PTLs 5 and 6 apply descaling to reduce the surface characteristics defects due to the scale indentation during hot leveling and to reduce the variation in the cooling stop temperature of the steel plate to improve the steel plate shape. However, no consideration is given to the cooling conditions for obtaining a uniform material property.

[0012] Thus, conventionally, when combining low-cost chemical compositions and controlled cooling at a high cooling rate, it was impossible to manufacture a high strength steel plate that has both of proper material homogeneity in the steel plate and proper HIC resistance.

[0013] It would thus be helpful to provide a high strength steel plate for sour-resistant line pipes that is excellent in HIC resistance in which variation in the HIC resistance in the plate width direction is suppressed, and a high strength steel pipe using the same.

(Solution to Problem)

[0014] To solve the above problems, the present inventors made intensive studies on the chemical compositions and microstructures of steel materials and the manufacturing methods of a high strength steel plate having a strength of X65 grade in accordance with the API standard in order to prevent HIC generation from the central segregation area, suppress the variation in the HIC resistance in the plate width direction, and improve the material homogeneity in the steel plate. As a result, it was discovered that it is possible to suppress the variation in central segregation in the plate width direction of a steel plate by a combined use of secondary cooling of a cast steel (slab) under particular conditions and controlled cooling after hot rolling under particular conditions, and the present disclosure was completed based on this discovery.

[0015] We thus provide:

[1] A high strength steel plate for sour-resistant line pipes comprising: a chemical composition containing (consisting of), by mass%, C: 0.02 % to 0.08 %, Si: 0.01 % to 0.50 %, Mn: 0.50 % to 1.80 %, P: 0.001 % to 0.015 %, S: 0.0002 % to 0.0015 %, Al: 0.01 % to 0.08 %, and Ca: 0.0005 % to 0.005 %, with the balance being Fe and inevitable impurities, wherein in a cross-section perpendicular to a rolling direction of the steel plate, the number of Mn-concentrated spots that are approximated to an elliptical shape having a major axis length of more than 1.5 mm, in a measuring region located ± 5 mm from a plate thickness center toward a plate thickness direction, is 3 or less per 100 mm in length in a plate width direction, HIC resistance is 10 % or less in terms of CAR at a W/4 position, a W/2 position, and a 3W/4 position from one end in the plate width direction of the steel plate, where W denotes a plate width, variation in the HIC resistance in the plate width direction in terms of 3σ is 5 % or less when σ denotes a standard deviation of CARs, and a tensile strength is 520 MPa or more.

[2] The high strength steel plate for sour-resistant line pipes according to the foregoing [1], wherein the chemical composition further contains, by mass%, at least one selected from the group consisting of Cu: 0.50 % or less, Ni: 0.50 % or less, Cr: 0.50 % or less, and Mo: 0.50 % or less.

[3] The high strength steel plate for sour-resistant line pipes according to the foregoing [1] or [2], wherein the chemical composition further contains, by mass%, at least one selected from the group consisting of Nb: 0.005 % to 0.1 %, V: 0.005 % to 0.1 %, and Ti: 0.005 % to 0.1 %.

[4] A high strength steel pipe using the high strength steel plate for sour-resistant line pipes as recited in any one of the foregoing [1] to [3].

(Advantageous Effect of Invention)

[0016] The high strength steel plate for sour-resistant line pipes disclosed herein has excellent HIC resistance in which variation in the HIC resistance in the plate width direction is suppressed. Accordingly, the high strength steel pipe

disclosed herein using this high strength steel plate has excellent HIC resistance in which variation in the HIC resistance in the pipe circumferential direction is suppressed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] In the accompanying drawings:

FIG. 1 is a schematic view illustrating a C cross-section of a steel plate for explanation of the positions of EPMA analyzing regions in an example;

FIG. 2 is a schematic view illustrating a C cross-section of a steel plate for explanation of the portions for HIC test piece sampling in an example; and

FIGS. 3A and 3B are diagrams for explaining secondary cooling of cast steel in continuous casting for producing a high strength steel plate according to the present embodiment, where FIG. 3A is a schematic diagram illustrating an injection range and a water flux density distribution of coolant when the coolant is injected from one two-fluid spray nozzle, and FIG. 3B is a schematic diagram illustrating an injection range and a water flux density distribution of coolant and a lap margin of the injection range when the coolant is injected from two two-fluid spray nozzles.

DETAILED DESCRIPTION

[0018] Hereinafter, the high strength steel plate for sour-resistant line pipes according to the present disclosure will be described in detail.

[Chemical composition]

[0019] First, the chemical composition of the high strength steel plate disclosed herein and the reasons for limitation thereof will be described. Hereinbelow, all units shown by % are mass%.

C: 0.02 % to 0.08 %

[0020] C contributes effectively to the improvement of strength. However, when the content is less than 0.02 %, sufficient strength can not be secured. On the other hand, when the content is more than 0.08 %, the hardness of the surface layer is increased during accelerated cooling, and the HIC resistance deteriorates. The toughness also decreases. Therefore, the C content is set in a range of 0.02 % to 0.08 %.

Si: 0.01 % to 0.50 %

[0021] Si is added for deoxidation. However, when the content is less than 0.01 %, the deoxidizing effect is insufficient. On the other hand, when the content is more than 0.50 %, the toughness and weldability deteriorate. Therefore, the Si content is set in a range of 0.01 % to 0.50 %.

Mn :0.50 % to 1.80 %

[0022] Mn contributes effectively to the improvement of strength and toughness. However, if the content is less than 0.50 %, the addition effect is poor, while if it exceeds 1.80 %, the hardness of the surface layer is increased during accelerated cooling, and the HIC resistance deteriorates. The weldability also decreases. Therefore, the Mn content is set in a range of 0.50 % to 1.80 %.

P: 0.001 % to 0.015 %

[0023] P is an inevitable impurity element that degrades the weldability and increases the hardness of the central segregation area, causing deterioration in HIC resistance. This tendency becomes more pronounced when the content exceeds 0.015 %. Therefore, the upper limit is set at 0.015 %. The content is preferably 0.008 % or less. Although a lower P content is preferable, the P content is set to 0.001 % or more from the viewpoint of refining cost.

S: 0.0002 % to 0.0015 %

[0024] S is an inevitable impurity element that forms MnS inclusions in the steel and degrades the HIC resistance, and hence a lower S content is preferable. However, up to 0.0015 % is acceptable. Although a lower S content is

preferable, the S content is set to 0.0002 % or more from the viewpoint of refining cost.

Al: 0.01 % to 0.08 %

- 5 **[0025]** Al is added as a deoxidizing agent. However, an Al content below 0.01 % provides no addition effect, while an Al content beyond 0.08 % lowers the cleanliness of the steel and deteriorates the toughness. Therefore, the Al content is in a range of 0.01 % to 0.08 %.

Ca: 0.0005 % to 0.005 %

- 10 **[0026]** Ca is an element effective for improving HIC resistance through morphological control of sulfide inclusions. If the content is less than 0.0005 %, however, the addition effect is not sufficient. On the other hand, if the content exceeds 0.005 %, not only the addition effect saturates, but also the HIC resistance is deteriorated due to the reduction in the cleanliness of the steel. Therefore, the Ca content is in a range of 0.0005 % to 0.005 %.

- 15 **[0027]** The basic components according to the present disclosure have been described above. Optionally, however, the chemical composition according to the present disclosure may also contain at least one selected from the group consisting of Cu, Ni, Cr, and Mo in the following ranges to further improve the strength and toughness of the steel plate.

Cu: 0.50 % or less

- 20 **[0028]** Cu is an element effective for improving the toughness and increasing the strength. To obtain this effect, the Cu content is preferably 0.05 % or more, yet if the content is too large, the weldability deteriorates. Therefore, when Cu is added, the Cu content is up to 0.50 %.

25 Ni: 0.50 % or less

- [0029]** Ni is an element effective for improving the toughness and increasing the strength. To obtain this effect, the Ni content is preferably 0.05 % or more, yet excessive addition of Ni is not only economically disadvantageous but also deteriorates the toughness of the heat-affected zone. Therefore, when Ni is added, the Ni content is up to 0.50 %.

30 Cr: 0.50 % or less

- [0030]** Cr, like Mn, is an effective element for obtaining a sufficient strength even at low C content. To obtain this effect, the Cr content is preferably 0.05 % or more, yet if the content is too large, the weldability deteriorates. Therefore, when Cr is added, the Cr content is up to 0.50 %.

Mo: 0.50 % or less

- 40 **[0031]** Mo is an element effective for improving the toughness and increasing the strength. To obtain this effect, the Mo content is preferably 0.05 % or more, yet if the content is too large, the weldability deteriorates. Therefore, when Mo is added, the Mo content is up to 0.50 %.

[0032] The chemical composition according to the present disclosure may further optionally contain one or more selected from the group consisting of Nb, V, and Ti in the following ranges.

- 45 **[0033]** At least one selected from the group consisting of Nb: 0.005 % to 0.1 %, V: 0.005 % to 0.1 %, Ti: 0.005 % to 0.1 % All of Nb, V, and Ti are elements that can be optionally added to enhance the strength and toughness of the steel plate. If the content of each added element is less than 0.005 %, the addition effect is poor, while if it exceeds 0.1 %, the toughness of the welded portion deteriorates. Therefore, the content of each added element is preferably in a range of 0.005 % to 0.1 %.

- 50 **[0034]** The balance other than the above-described elements is Fe and inevitable impurities. However, there is no intention in this expression of precluding the inclusion of other trace elements, without impairing the action or effect of the present disclosure.

[Mn-concentrated spots]

- 55 **[0035]** In the high strength steel plate for sour-resistant line pipes disclosed herein, it is important that in a cross-section perpendicular to a rolling direction (plate length direction) of the steel plate, the number of Mn-concentrated spots that are approximated to an elliptical shape having a major axis length of more than 1.5 mm, in a measuring region located ± 5 mm from a plate thickness center toward a plate thickness direction, is 3 or less per 100 mm in length in a

plate width direction.

[0036] As used herein, a "Mn-concentrated spot" refers to a site in which the Mn concentration is higher than the addition amount of Mn (the Mn content in the steel plate) due to segregation. This site is specifically identified as a site in which the Mn concentration is 1.60 % or more when the Mn content in the steel plate is 1.50 % or less, and as a site in which the Mn concentration is at least 0.10 % higher than the Mn content in the steel plate when the Mn content in the steel plate is more than 1.50 % and 1.80 % or less.

[0037] According to the present inventors' studies, it was revealed that HIC cracking is likely to occur from the positions of those Mn-concentrated spots having a major axis length of more than 1.5 mm among the Mn-concentrated spots specified as described above, and that HIC cracking occurs when the number of Mn-concentrated spots having a major axis length of more than 1.5 mm exceeds 3 per 100 mm in length in the plate width direction. Therefore, in the present disclosure, the number of Mn-concentrated spots having a major axis length of more than 1.5 mm is 3 or less per 100 mm in length in the plate width direction.

[0038] In the present disclosure, "the number of Mn-concentrated spots having a major axis length of more than 1.5 mm per 100 mm in length in the plate width direction" is measured as follows. First, a sample for analysis is cut out from a steel plate and polished for preparation. This setup is carried out such that the surface of the sample becomes a cross-section perpendicular to the plate length direction of the steel plate (a C cross-section). Then, as illustrated in FIG. 1, in the C cross section, Mn concentration mapping is performed using an electron probe microanalyzer (EPMA) for three regions centering on each of the three points at the plate thickness center ($t/2$ position; t is the plate thickness) of the steel plate and ranging ± 5 mm in the plate thickness direction (i.e., 10 mm thick) and ± 200 mm in the plate width direction (i.e., 400 mm wide), at a $W/4$ position, a $W/2$ position, and a $3W/4$ position from one end in the plate width direction of the steel plate, where W denotes the plate width (hereinafter, simply referred to as " $W/4$ position", " $W/2$ position", and " $3W/4$ position", respectively). Note that the three regions may be one overlapping area depending on the plate width of the steel plate. The mapping is performed using an electronic probe with an accelerating voltage of 25 kV and a diameter of 0.15 mm. In each EPMA analyzing region (10 mm thick and 400 mm wide), the number of Mn-concentrated spots having a major axis length of more than 1.5 mm is counted and converted to the number per 100 mm in length in the plate width direction.

[0039] It is preferable that the steel microstructure of the high strength steel plate for sour-resistant line pipes disclosed herein is bainite microstructure in order to have a tensile strength as high as 520 MPa or more. In this case, the bainite microstructure includes a microstructure called bainitic ferrite or granular ferrite which contributes to transformation strengthening. These microstructures appear through transformation during or after accelerated cooling. If different microstructures such as ferrite, martensite, pearlite, martensite austenite constituent, retained austenite, and the like are mixed in the bainite microstructure, a decrease in strength, a deterioration in toughness, a rise in surface hardness, and the like occur. Therefore, it is preferable that microstructures other than the bainite phase have smaller proportions. However, when the volume fraction of such microstructures other than the bainitic phase is sufficiently low, their effects are negligible, and up to a certain amount is acceptable. Specifically, in the present disclosure, if the total of the steel microstructures other than bainite (such as ferrite, martensite, pearlite, martensite austenite constituent, and retained austenite) is less than 5 % by volume fraction, there is no adverse effect, and this is acceptable.

[Uniformity of the HIC resistance in the plate width direction]

[0040] In the high strength steel plate for sour-resistant line pipes disclosed herein, it is important that the HIC resistance at a $W/4$ position, a $W/2$ position, and a $3W/4$ position is 10 % or less in terms of CAR, and that the variation in the HIC resistance in the plate width direction in terms of 3σ is 5 % or less when σ denotes a standard deviation of CARs. This means that the high strength steel plate has excellent HIC resistance in which variation in the HIC resistance in the plate width direction is suppressed. The HIC resistance at a $W/4$ position, a $W/2$ position, and a $3W/4$ position is preferably 5 % or less in terms of CAR.

[0041] In this disclosure, the "HIC resistance at a $W/4$ position, a $W/2$ position, and a $3W/4$ position" is evaluated as follows. As illustrated in FIG. 2, in a C-section of the steel plate, centering on the plate thickness center at a $W/4$ position, a $W/2$ position, and a $3W/4$ position (total of three points) in the plate width direction, test pieces of 20 mm thick and 20 mm wide are collected. From each of the three test pieces thus obtained, three samples are collected, and a total of nine samples are subjected to hydrogen-induced cracking (HIC) resistance examination. This examination is conducted in the Method A environment according to NACE TM0284, and the crack area ratio (CAR) is determined as a hydrogen-induced cracking criterion. In the high strength steel plate for sour-resistant line pipes disclosed herein, all nine CARs thus obtained are 10 % or less, and preferably 5 % or less.

[0042] Further, in this disclosure, the "variation in the HIC resistance in the plate width direction" is evaluated in terms of 3σ when the standard deviation of nine CARs described above is calculated as σ .

[Tensile strength]

[0043] The high strength steel plate disclosed herein is a steel plate for steel pipes having a strength of X60 grade or higher in API 5L, and thus has a tensile strength of 520 MPa or more.

[Manufacturing method]

[0044] Hereinafter, the method and conditions for manufacturing the above-described high strength steel plate for sour-resistant line pipes will be described concretely. The manufacturing method disclosed herein comprises: subjecting steel having the above chemical composition to continuous casting to prepare a cast steel (slab); heating the slab; then hot rolling the slab to obtain a steel plate; and then subjecting the steel plate to controlled cooling. At this time, by performing secondary cooling in the continuous casting under particular conditions, and by performing the slab heating and controlled cooling under particular conditions, it is possible to manufacture a high strength steel plate for sour-resistant line pipes that has excellent HIC resistance in which variation in the HIC resistance in the plate width direction is suppressed.

[Secondary cooling of a slab during continuous casting]

[0045] As illustrated in FIGS. 3A and 3B, the following secondary cooling method is used. Coolant is sprayed on a cast steel 20 in a mist form from a plurality of two-fluid spray nozzles 10A and 10B to cool the cast steel 20 while feeding the cast steel 20 in its longitudinal direction. The plurality of two-fluid spray nozzles 10A and 10B are arranged at predetermined intervals in the width direction of the cast steel 20. Regarding the two-fluid spray nozzles 10 (10A and 10B), the positions on the cast steel at which a water flux density is 50 % of the water flux density immediately below the two-fluid spray nozzles 10 are located away by a distance S (mm) from both ends of each spraying range of the coolant in the width direction of the cast steel 20. The overlapping margin between the spraying ranges of the coolant sprayed from the two-fluid spray nozzles 10A and 10B adjacent to each other is set in a range of 1.6 S to 2.4 S.

[0046] FIGS. 3A and 3B schematically illustrate the injection ranges and the water flux density distributions of the coolant injected from two-fluid spray nozzle(s). FIG. 3A illustrates a distance S from both ends of the injection range at which a ratio of a water flux density at that position to a water flux density immediately below the two-fluid spray nozzle 10 is 50 %, and FIG. 3B illustrates the overlapping margin between the injection ranges of the coolant injected from the two two-fluid spray nozzles 10A and 10B.

[0047] The distance S from both ends of the injection range of the coolant injected from the two-fluid spray nozzle 10 can be obtained as follows. First, a water flux density distribution in the width direction of the cast steel of the coolant injected from the two-fluid spray nozzle 10 is measured. The water flux density distribution can be measured by placing the two-fluid spray nozzle 10 above a group of measures finely divided in the width direction of the cast steel 1 and weighing the coolant injected from the two-fluid spray nozzle 10 for each measuring apparatus.

[0048] The reason for setting the overlapping margin in a range of 1.6 S to 2.4 S is as follows. That is, in the case of the cast steel being subjected to secondary cooling with a plurality of two-fluid spray nozzles, even if the two-fluid spray nozzles are arranged such that the water flux density of the coolant injected from each two-fluid spray nozzle is uniform in the width direction of the cast steel, the collision pressure is low at both ends of each injection range of the coolant, resulting in low ability of cooling cast steel. Thus, it is impossible to cool the cast steel uniformly in the width direction. However, if the overlapping margin is adjusted in the range of 1.6 S to 2.4 S, it is possible to uniformly cool the cast steel in the width direction, considering the collision pressure distribution in addition to the water flux density distribution in the width direction of the cast steel. That is, according to this method, it is possible to cool the cast steel without lowering the cooling ability in a region over which the injection ranges of the coolant from the adjacent two-fluid spray nozzles 10A and 10B overlap, and to suppress the surface temperature deviation in the width direction of the cast steel, enabling substantially uniform cooling. Accordingly, it is possible to prepare a slab with suppressed variation in the central segregation in the width direction.

[0049] Although FIG. 3B illustrates an example using two two-fluid spray nozzles 10A and 10B, in the case of performing secondary cooling of the cast steel with three or more two-fluid spray nozzles, the overlapping margin of the injection ranges of the coolant may be set as described above for those adjacent to each other among three or more two-fluid spray nozzles.

[0050] Further, the two-fluid spray nozzle include, but is not limited to, for example, a mist nozzle provided with a feed pipe for coolant and air, a mixing pipe, and a nozzle tip.

[Slab heating temperature]

[0051] Slab heating temperature: 1000 °C to 1300 °C

If the slab heating temperature is lower than 1000 °C, carbides do not solute sufficiently and the necessary strength can not be obtained. On the other hand, if the slab heating temperature exceeds 1300 °C, the toughness is deteriorated. Therefore, the slab heating temperature is set to 1000 °C to 1300 °C. This temperature is the temperature in the heating furnace, and the slab is heated to this temperature to the center.

[Rolling finish temperature]

[0052] In a hot rolling step, in order to obtain high toughness for base metal, a lower rolling finish temperature is preferable, yet on the other hand, the rolling efficiency is lowered. Thus, the rolling finish temperature in terms of a temperature of the surface of the steel plate needs to be set in consideration of the required toughness for base metal and rolling efficiency. From the viewpoint of improving the strength and the HIC resistance, it is preferable to set the rolling finish temperature at or above the Ar₃ transformation temperature in terms of a temperature of the surface of the steel plate. As used herein, the Ar₃ transformation temperature means the ferrite transformation start temperature during cooling, and can be determined, for example, from the components of steel according to the following equation. Further, in order to obtain high toughness for base metal, it is desirable to set the rolling reduction ratio in a temperature range of 950 °C or lower, which corresponds to the austenite non-recrystallization temperature range, to 60 % or more. The temperature of the surface of the steel plate can be measured by a radiation thermometer or the like.

$$\text{Ar}_3(^{\circ}\text{C}) = 910 - 310[\%C] - 80[\%Mn] - 20[\%Cu] - 15[\%Cr] - 55[\%Ni] - 80[\%Mo],$$

where [%X] indicates the content by mass% of the element X in steel.

[Cooling start temperature in the controlled cooling]

[0053] Cooling start temperature: (Ar₃ - 10 °C) or higher in terms of a temperature of the surface of the steel plate

[0054] If the temperature of the surface of the steel plate is low at the start of cooling, ferrite forms in a large amount before controlled cooling, in particular, when the temperature drop from the Ar₃ transformation temperature exceeds 10 °C, ferrite forms in a volume fraction of more than 5 %, causing a significant reduction in the strength and a deterioration in the HIC resistance. Therefore, the temperature of the surface of the steel plate at the start of cooling is set to (Ar₃ - 10 °C) or higher.

[Cooling rate of the controlled cooling]

[0055] Average cooling rate in a temperature range from 750 °C to 550 °C in terms of an average temperature of the steel plate: 15 °C/s or higher

[0056] If the average cooling rate in a temperature range from 750 °C to 550 °C in terms of an average temperature of the steel plate is lower than 15 °C/s, a bainite microstructure can not be obtained, causing deterioration in the strength and HIC resistance. Therefore, the cooling rate in terms of an average temperature of the steel plate is set to 15 °C/s or higher. From the viewpoint of variation in the strength and hardness of the steel plate, the steel plate average cooling rate is preferably 20 °C/s or higher. The upper limit of the average cooling rate is not particularly limited, yet is preferably 80 °C/s or lower such that excessive low-temperature transformation products will not be generated.

[Cooling stop temperature]

[0057] Cooling stop temperature: 250 °C to 550 °C in terms of an average temperature of the steel plate

[0058] After the completion of rolling, a bainite phase is generated by performing controlled cooling to quench the steel plate to a temperature range of 250 °C to 550 °C which is the temperature range of bainite transformation. When the cooling stop temperature exceeds 550 °C, bainite transformation is incomplete and sufficient strength can not be obtained. In addition, if the cooling stop temperature is lower than 250 °C, the hardness markedly increases in the surface layer. The cooling stop temperature is preferably 350 °C to 500 °C.

[0059] Although an average temperature of the steel plate can not be directly measured physically, a temperature distribution in a cross section in the plate thickness direction can be determined in real time, for example, by difference calculation using a process computer on the basis of the surface temperature at the start of cooling measured with a radiation thermometer and the target surface temperature at the end of cooling. The average value of temperatures in the plate thickness direction in the temperature distribution is referred to as the "average temperature of the steel plate" in this description.

[High strength steel pipe]

[0060] By forming the high strength steel plate disclosed herein into a tubular shape by press bend forming, roll forming, UOE forming, or the like, and then welding the butting portions, a high strength steel pipe for sour-resistant line pipes (such as a UOE steel pipe, an electric-resistance welded steel pipe, and a spiral steel pipe) that has excellent material homogeneity in the steel plate and that is suitable for transporting crude oil and natural gas can be manufactured.

[0061] For example, an UOE steel pipe is manufactured by milling and beveling the edges of a steel plate, forming the steel plate into a steel pipe shape by C press, U-ing press, and O-ing press, then seam welding the butting portions by inner surface welding and outer surface welding, and optionally subjecting it to an expansion process. Any welding method may be applied as long as sufficient joint strength and joint toughness are guaranteed, yet it is preferable to use submerged arc welding from the viewpoint of excellent weld quality and manufacturing efficiency.

EXAMPLES

[0062] Steels having the chemical compositions listed in Table 1 (Steel Sample IDs A to M) were prepared and subjected to continuous casting to obtain slabs with a slab width of 1600 mm. Secondary cooling was performed with the overlapping margin of the injection ranges of the coolant injected in a mist form from the three two-fluid spray nozzles arranged at predetermined intervals in the width direction being set as listed in Table 2. Note that a distance S from both ends of the injection range of the coolant in the width direction of the cast steel 20 to the position where the ratio of a water flux density at that position to a water flux density immediately below the two-fluid spray nozzles is 50 % was fixed to 70 mm.

[0063] Each slab thus obtained was heated to the temperature as listed in Table 2, and then hot rolled with the rolling finish temperature and the rolling reduction ratio as listed in the table, to thereby obtain a steel plate with the plate thickness as listed in the table. Then, each steel plate was subjected to controlled cooling using a water-cooling type controlled-cooling device under the conditions listed in Table 2.

Table 1

Steel sample ID	Chemical composition (mass%)														Ar ₃ Temperature (°C)
	C	Si	Mn	P	S	Al	Ca	Cu	Ni	Cr	Mo	Nb	V	Ti	
A	0.064	0.32	1.41	0.004	0.0004	0.024	0.0022					0.010			777
B	0.075	0.20	1.52	0.003	0.0005	0.032	0.0030								765
C	0.044	0.21	1.28	0.005	0.0005	0.020	0.0017	0.23	0.11		0.19	0.025			768
D	0.049	0.14	1.33	0.004	0.0004	0.019	0.0021			0.22	0.10	0.035			777
E	0.046	0.24	1.23	0.006	0.0006	0.022	0.0015			0.20	0.14	0.021		0.015	783
F	0.053	0.25	1.27	0.004	0.0008	0.025	0.0023			0.35		0.035	0.035		787
G	0.041	0.28	1.32	0.003	0.0005	0.021	0.0011			0.25	0.11	0.029		0.011	779
H	0.048	0.30	1.25	0.003	0.0004	0.020	0.0014	0.15	0.16	0.30	0.18	0.031		0.008	764
I	<u>0.086</u>	0.17	1.33	0.005	0.0006	0.021	0.0021		0.26		0.15	0.022		0.010	751
J	0.034	0.22	<u>1.88</u>	0.006	0.0008	0.025	0.0014	0.12	0.25						733
K	0.046	0.20	1.28	<u>0.018</u>	0.0004	0.023	0.0020			0.23	0.12	0.015			780
L	0.054	0.15	1.31	0.006	<u>0.0026</u>	0.022	0.0016		0.22	0.11	0.10	0.027	0.044	0.010	767
M	0.055	0.19	<u>1.44</u>	<u>0.017</u>	0.0005	0.022	0.0026								778
Note 1: Underlined if outside the scope of the disclosure.															

Table 2

No.	Steel sample ID	Plate thickness (mm)	Overlapping margin for secondary cooling of slab	Heating temp. (°C)	Rolling finish temperature (°C)	Rolling reduction ratio (%)	Cooling start temp. (°C)	Cooling start temp. - Ar ₃ (°C)	Cooling rate (steel plate average) (°C/s)	Cooling stop temp. (°C)	Category
1	A	34	2.0S	1150	880	70	820	43	37	480	Example
2	B	16	2.0S	1130	910	75	830	65	54	520	
3	C	25	2.1S	1080	880	75	810	42	33	510	
4	D	15	1.9S	1080	870	75	810	33	45	440	
5	E	20	2.2S	1080	850	80	790	7	31	450	
6	F	34	2.4S	1080	840	75	810	23	29	500	
7	G	34	2.0S	1080	870	70	830	51	43	390	
8	G	34	2.0S	1110	830	75	770	-9	23	460	
9	G	20	2.0S	1110	800	75	780	1	34	470	
10	G	20	2.0S	1100	850	75	810	31	31	440	
11	H	34	1.8S	1080	860	75	810	46	37	350	
12	H	25	1.6S	1150	850	75	820	56	47	500	
13	H	38	2.3S	1080	850	75	800	36	32	480	

(continued)

No.	Steel sample ID	Plate thickness (mm)	Overlapping margin for secondary cooling of slab	Heating temp. (°C)	Rolling finish temperature (°C)	Rolling reduction ratio (%)	Cooling start temp. (°C)	Cooling start temp. - Ar ₃ (°C)	Cooling rate (steel plate average) (°C/s)	Cooling stop temp. (°C)	Category
14	G	34	2.2S	970	850	75	810	31	31	480	Comparative example
15	G	34	2.0S	1080	780	75	740	-39	25	420	
16	G	34	1.9S	1080	830	75	810	31	5	500	
17	G	34	2.3S	1080	850	75	800	21	37	180	
18	G	20	2.0S	1080	850	75	830	51	13	450	
19	G	20	1.5S	1100	850	75	820	41	35	430	
20	G	34	2.5S	1130	850	75	810	31	32	450	
21	H	34	2.6S	1080	850	75	810	46	38	460	
22	B	16	1.4S	1140	910	75	830	65	52	500	
23	I	34	2.0S	1080	840	75	800	49	37	430	
24	J	34	2.0S	1080	820	75	780	47	27	520	
25	K	34	2.0S	1080	860	75	820	40	33	470	
26	L	34	2.0S	1080	850	75	810	43	32	450	
27	M	16	2.0S	1130	890	75	840	62	42	520	
Note 1: Underlined if outside the scope of the disclosure.											

EP 3 674 433 A1

[Identification of microstructure]

[0064] The microstructure of each obtained steel plate was observed with an optical microscope and a scanning electron microscope. The microstructures at the plate thickness center (i.e., $t/2$ position) of the steel plate are listed in Table 3.

[Evaluation of tensile property]

[0065] From each obtained steel plate, a full-thickness test piece (as prescribed in API-5L specification) in the transverse direction (direction orthogonal to the rolling direction) was taken and subjected to tensile test as a tensile test piece to measure the yield stress (0.5% proof stress) and the tensile strength. The target ranges were a yield stress of 450 MPa or more and a tensile strength of 520 MPa or more. The results are listed in Table 3.

[Evaluation of variation in the HIC resistance in the plate width direction]

[0066] Three samples were respectively collected from a $W/4$ position, a $W/2$ position, and a $3W/4$ position in the manner described above, and CARs were measured. The maximum value of the nine measured values thus obtained is presented in the column of "HIC resistance" in Table 3. Table 3 also lists 3σ when the standard deviation of nine CARs is calculated as σ . The target range was 10 % or less for the maximum value and 5 % or less for 3σ .

[Measurement of Mn-concentrated spots]

[0067] The number of Mn-concentrated spots having a major axis length of more than 1.5 mm was counted per 100 mm in length in the plate width direction in the manner described above. The target range was 3 or less. The results are listed in Table 3.

[DWTT test]

[0068] From each obtained steel plate, a DWTT test piece conforming to the API-5L was taken and tested at test temperatures of 0 °C to -80 °C to determine a transition temperature at which the SA value (Shear Area: percent ductile fracture) was 85 %. The target range for transition temperature was -50 °C or lower. The results are listed in Table 3.

Table 3

No.	Steel sample ID	Plate thickness (mm)	Microstructure (t/2 position)	Yield strength (MPa)	Tensile strength (MPa)	HIC resistance (%)	Variation in HIC resistance, 3 σ (%)	Mn-concentrated spots (pcs.)	DWTT 85 % SATT (°C)	Category
1	A	34	B	460	575	1	0.3	1	-50	Example
2	B	16	B	477	589	2	1.2	2	-50	
3	C	25	B	480	624	0	0	1	-60	
4	D	15	B	485	622	0	0	0	-65	
5	E	20	B	462	581	0	0	0	-55	
6	F	34	B	458	578	3	0.7	2	-50	
7	G	34	B	504	637	2	0.4	1	-50	
8	G	34	B	466	574	0	0	2	-55	
9	G	20	B	506	621	0	0	0	-60	
10	G	20	B	511	628	0	0	0	-65	
11	H	34	B	498	629	1	0.2	2	-65	
12	H	25	B	522	639	2	0.5	2	-60	
13	H	38	B	531	634	4	1	3	-60	

(continued)

No.	Steel sample ID	Plate thickness (mm)	Microstructure (t/2 position)	Yield strength (MPa)	Tensile strength (MPa)	HIC resistance (%)	Variation in HIC resistance, 3σ (%)	Mn-concentrated spots (pcs.)	DWTT 85 % SATT (°C)	Category	
14	G	34	B	415	505	4	2	2	-60	Comparative example	
15	G	34	F+B	420	510	12	8	5	-65		
16	G	34	F+P	410	513	15	7	6	-70		
17	G	34	B+M	541	654	14	6	5	-30		
18	G	20	F+P	430	511	12	6	4	-50		
19	G	20	B	482	632	22	7	8	-60		
20	G	34	B	476	639	18	8	8	-60		
21	H	34	B	489	644	27	8	12	-35		
22	B	16	B	468	597	8	6	4	-55		
23	I	34	B	510	647	22	8	6	-30		
24	J	34	B	516	650	16	6	6	-65		
25	K	34	B	501	614	14	7	5	-60		
26	L	34	B	483	620	12	8	6	-60		
27	M	16	B	503	616	13	7	5	-60		
Note 1: Undefined if outside the scope of the disclosure.											
Note 2: For microstructure, B denotes bainite, F denotes ferrite, M denotes martensite, and P denotes pearlite.											

[0069] For Nos. 1 to 13, which are our examples, the chemical compositions were within the scope of the present disclosure and the manufacturing conditions were within the range suitable for obtaining steel plates according to the present disclosure. All of our samples had a yield stress of 450 MPa or more, a tensile strength of 520 MPa or more, a 85 % SATT of -50 °C or lower in the DWTT test, and small variation in the HIC resistance in the plate width direction, any of which properties were considered good.

[0070] In contrast, for Nos. 14 to 22, which are comparative examples, although the chemical compositions were within the scope of the present disclosure, the manufacturing conditions were outside the scope of the preferred conditions for obtaining steel plates according to the present disclosure. For No. 14, the slab heating temperature was low, the homogenization of the microstructure and the solid solution state of carbides were insufficient, and the strength was low. For No. 15, since ferrite generated excessively due to the low cooling start temperature, the strength was low and the HIC resistance was inferior.

For Nos. 16 and 18, since pearlite excessively generated as a microstructure in the mid-thickness part due to the controlled cooling condition outside the suitable range, the strength was low and the HIC resistance was inferior.

For No. 17, since hard phases such as martensite and martensite austenite constituent (MA) were formed due to the low cooling stop temperature, the DWTT property and the HIC resistance were inferior.

For Nos. 19 to 22, since the secondary cooling conditions of the slabs were outside the suitable range, Mn concentration in the central segregation area was high, variation in the HIC resistance in the plate width direction was large, and the HIC resistance was inferior.

For Nos. 23 to 27, since the chemical compositions were outside the scope of the present disclosure, Mn concentration in the central segregation area was high, variation in the HIC resistance in the plate width direction was large, and the HIC resistance was inferior.

INDUSTRIAL APPLICABILITY

[0071] The high strength steel plates for sour-resistant line pipes according to the present disclosure have excellent HIC resistance in which variation in the HIC resistance in the plate width direction is suppressed. Therefore, steel pipes (such as electric-resistance welded steel pipes, spiral steel pipes, and UOE steel pipes) manufactured by cold-forming the disclosed steel plate can be suitably used for transportation of crude oil and natural gas that contain hydrogen sulfides where sour resistance is required.

REFERENCE SIGNS LIST

[0072]

10, 10A, 10B two-fluid spray nozzle
20 cast steel

Claims

1. A high strength steel plate for sour-resistant line pipes comprising: a chemical composition containing, by mass%, C: 0.02 % to 0.08 %, Si: 0.01 % to 0.50 %, Mn: 0.50 % to 1.80 %, P: 0.001 % to 0.015 %, S: 0.0002 % to 0.0015 %, Al: 0.01 % to 0.08 %, and Ca: 0.0005 % to 0.005 %, with the balance being Fe and inevitable impurities, wherein in a cross-section perpendicular to a rolling direction of the steel plate, the number of Mn-concentrated spots that are approximated to an elliptical shape having a major axis length of more than 1.5 mm, in a measuring region located ± 5 mm from a plate thickness center toward a plate thickness direction, is 3 or less per 100 mm in length in a plate width direction,
HIC resistance is 10 % or less in terms of CAR at a W/4 position, a W/2 position, and a 3W/4 position from one end in the plate width direction of the steel plate, where W denotes a plate width,
variation in the HIC resistance in the plate width direction in terms of 3σ is 5 % or less when σ denotes a standard deviation of CARs, and
a tensile strength is 520 MPa or more.
2. The high strength steel plate for sour-resistant line pipes according to claim 1, wherein the chemical composition further contains, by mass%, at least one selected from the group consisting of Cu: 0.50 % or less, Ni: 0.50 % or less, Cr: 0.50 % or less, and Mo: 0.50 % or less.
3. The high strength steel plate for sour-resistant line pipes according to claim 1 or 2, wherein the chemical composition

EP 3 674 433 A1

further contains, by mass%, at least one selected from the group consisting of Nb: 0.005 % to 0.1 %, V: 0.005 % to 0.1 %, and Ti: 0.005 % to 0.1 %.

4. A high strength steel pipe using the high strength steel plate for sour-resistant line pipes as recited in any one of claims 1 to 3.

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FIG. 1

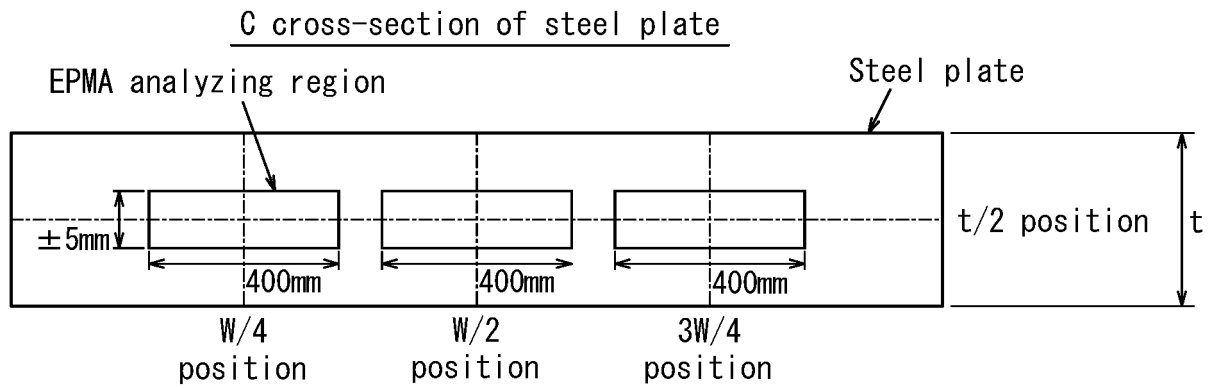


FIG. 2

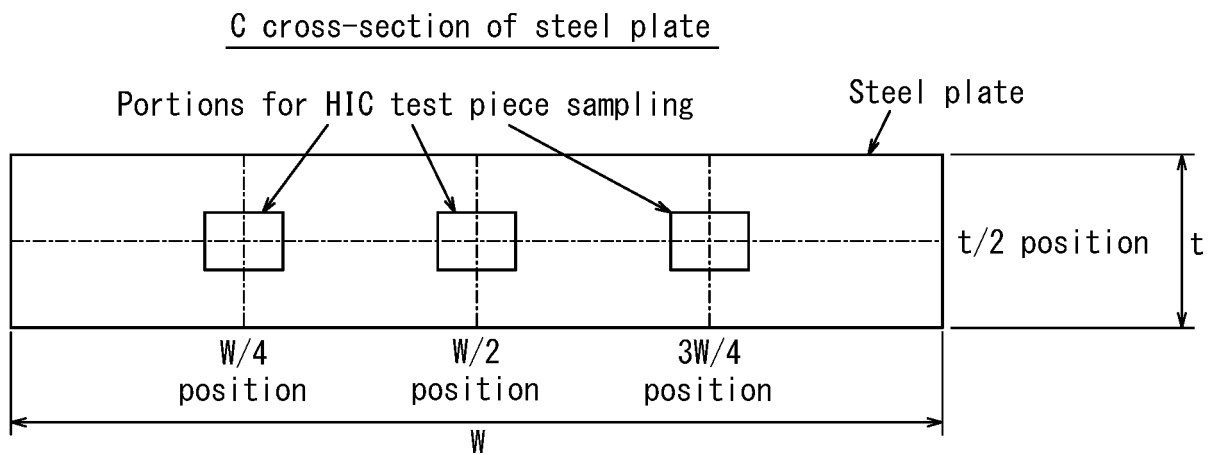
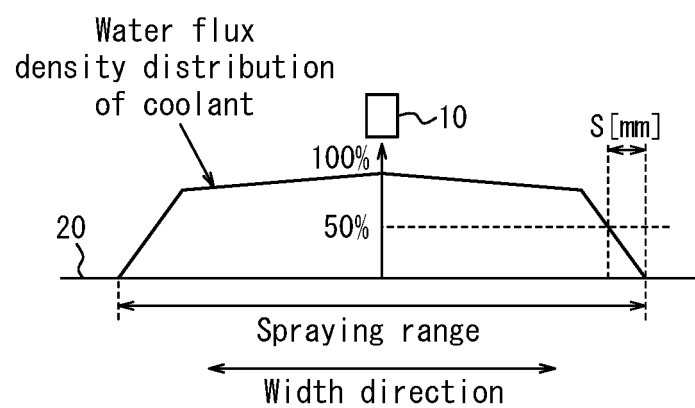
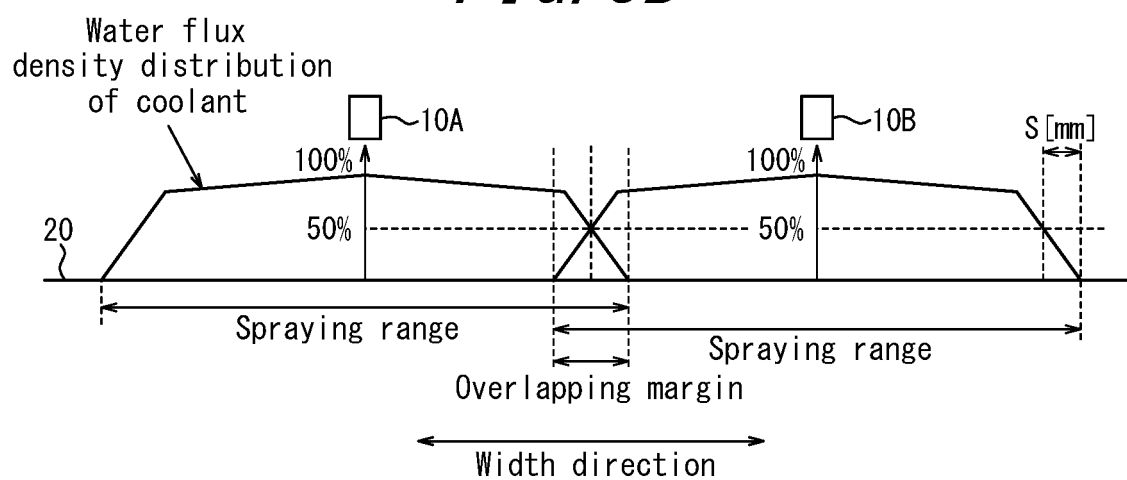


FIG. 3A*FIG. 3B*

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/037891

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. C22C38/00 (2006.01) i, C22C38/06 (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)

Int. Cl. C22C38/00, C22C38/06, C22C38/58

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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.
Y	JP 2013-124398 A (JFE STEEL CORP.) 24 June 2013, claim 3, paragraphs [0002]-[0004], [0013], [0022]-[0060] (Family: none)	1-4
Y	WO 2011/030768 A1 (NIPPON STEEL CORP.) 17 March 2011, paragraph [0055] & CN 102482744 A	1-4
Y	JP 2013-145221 A (JFE STEEL CORP.) 25 July 2013, paragraph [0080] (Family: none)	1-4
Y	JP 2014-208892 A (KOBE STEEL, LTD.) 06 November 2014, paragraphs [0030], [0037]-[0038], [0056] & EP 2980238 A1, paragraphs [0030], [0036]-[0038], [0057] & WO 2014/157165 A1 & KR 10-2015-0121193 A & CN 105102652 A	1-2, 4



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
09.01.2018Date of mailing of the international search report
23.01.2018Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2017/037891
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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 2014-77642 A (JFE STEEL CORP.) 01 May 2014 (Family: none)	1-4

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REFERENCES CITED IN THE DESCRIPTION

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- JP 3711896 B [0007] [0009]
- JP 3796133 B [0008] [0009]