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

(57) Disclosed is a high strength steel plate for a sour-resistant line pipe that is excellent not only in HIC resistance but also in SSCC resistance under more severe corrosion environments. The high strength steel plate for a sour-resistant line pipe has: 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; a steel microstructure at 0.5 mm below a surface of the steel plate being a bainite microstructure having a dislocation density of  $1.0 \times 10^{14}$  to  $7.0 \times 10^{14}$  (m<sup>-2</sup>); a variation in Vickers hardness at 0.5 mm below the surface of the steel plate being 30 HV or less at 3 $\sigma$ , where  $\sigma$  is a standard deviation; and a tensile strength being 520 MPa or more.

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**Description**

## BACKGROUND

**[0001]** This disclosure relates to a high strength steel plate for a sour-resistant line pipe that is excellent in material homogeneity in the steel plate and that is suitable for use in line pipes in the fields of construction, marine structure, shipbuilding, civil engineering, and construction industry machinery, and to a method for manufacturing the same. This disclosure also relates to a high strength steel pipe using the high strength steel plate for a sour-resistant line pipe.

## BACKGROUND

**[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 material 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. This phenomenon is considered as a problem in line pipes with a relatively low level of strength with respect to oil well pipes, and many countermeasures have been proposed. On the other hand, SSCC is generally known to occur in high strength seamless steel pipes for oil wells and in high hardness regions of welds, and has not been regarded as a problem in line pipes with relatively low hardness. However, in recent years, it has been reported that SSCC also occurs in the base metal of line pipes in environments where oil and natural gas mining environments have become increasingly severe and environments with high hydrogen sulfide partial pressure or low pH. It is also pointed out that it is important to control the hardness of the surface layer of the inner surface of a steel pipe to improve the SSCC resistance under more severe corrosion environments.

**[0004]** In general, so-called TMCP (Thermo-Mechanical Control Process) technology, which combines controlled rolling and controlled cooling, is applied when manufacturing high strength steel plates for line pipes. In order to increase the strength of steel materials using the TMCP technology, it is effective to increase the cooling rate during 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.

**[0005]** In order to solve the above problems, for example, JP3951428B (PTL 1) and JP3951429B (PTL 2) describe methods for manufacturing steel plates with a reduced material property difference in the plate thickness direction by performing high-speed controlled cooling in which the surface is recuperated before completion of bainite transformation in the surface layer after rolling. JP2002-327212A (PTL 3) and JP3711896B (PTL 4) describe methods for manufacturing steel plates for line pipes in which the hardness of the surface layer is reduced by heating the surface of a steel plate after accelerated cooling to a higher temperature than the inside using a high frequency induction heating device.

**[0006]** 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 the variation in local cooling stop temperature in the steel plate. As a result, unevenness in scale thickness causes variations in the steel plate material property in the plate width direction. On the other hand, JPH9-57327A (PTL 5) and JP3796133B (PTL 6) disclose methods for improving the shape of a steel plate by performing descaling immediately before cooling to reduce cooling unevenness caused by scale thickness unevenness.

## CITATION LIST

## Patent Literature

**[0007]**

PTL 1: JP3951428B  
 PTL 2: JP3951429B  
 PTL 3: JP2002-327212A  
 PTL 4: JP3711896B  
 PTL 5: JPH9-57327A

PTL 6: JP3796133B

## SUMMARY

## (Technical Problem)

**[0008]** According to our study, however, it turned out that the high strength steel plates obtained by the manufacturing methods described in Patent Documents 1 to 6 have room for improvement in terms of SSCC resistance under more severe corrosion environments. The following can be considered as the reason.

**[0009]** In the manufacturing methods described in PTLs 1 and 2, when the transformation behavior differs depending on the compositions of the steel plate, a sufficient material homogenization effect by heat recuperation may not be obtained. In the case where the microstructure in the surface layer of the steel plate obtained by the manufacturing methods described in PTLs 1 and 2 is a dual phase structure such as a ferrite-bainite dual phase structure, the hardness value may have a large variation in a low load micro Vickers test depending on which microstructure the indenter indents.

**[0010]** In the manufacturing methods described in PTLs 3 and 4, the cooling rate of the surface layer in accelerated cooling is so high that the hardness of the surface layer may not be sufficiently reduced only by heating the steel plate surface.

**[0011]** On the other hand, 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. This is because if the cooling rate on the surface of the steel plate varies, the hardness of the steel plate will vary. That is, at a low cooling rate, "film boiling", in which a film of air bubbles is generated between the steel plate surface and the cooling water when the steel plate surface cools, and "nucleate boiling", in which air bubbles are separated from the surface by the cooling water before forming a film, occur at the same time, causing variations in the cooling rate on the steel plate surface. As a result, the hardness of the surface of the steel plate will vary. In the techniques described in PTLs 5 and 6, however, these facts are not considered at all.

**[0012]** It would thus helpful to provide a high strength steel plate for a sour-resistant line pipe that is excellent not only in HIC resistance but also in SSCC resistance under more severe corrosion environments, together with an advantageous method for manufacturing the same. It would also be helpful to propose a high strength steel pipe using the high strength steel plate for a sour-resistant line pipe.

## (Solution to Problem)

**[0013]** The present inventors repeated many experiments and examinations about the chemical compositions, microstructures, and manufacturing conditions of steel materials in order to ensure proper SSCC resistance under more severe corrosion environments. As a result, the inventors discovered that in order to further improve the SSCC resistance of a high strength steel pipe, it is not sufficient to merely suppress the surface layer hardness as conventionally found, and in particular, that it is possible to reduce the increase in hardness in the coating process after pipe making by forming the outermost surface layer of the steel plate, specifically at 0.5 mm below the surface of the steel plate, with a bainite microstructure having a dislocation density of  $1.0 \times 10^{14}$  to  $7.0 \times 10^{14}$  ( $\text{m}^{-2}$ ), and as a result the SSCC resistance of the steel pipe is improved. In order to provide such a steel microstructure, the inventors also discovered that it is important to strictly control the cooling rate at 0.5 mm below the surface of the steel plate, and succeeded in finding the conditions. The present disclosure was completed based on the above discoveries.

**[0014]** The primary features of the present disclosure are as follows.

[1] A high strength steel plate for a sour-resistant line pipe, 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; a steel microstructure at 0.5 mm below a surface of the steel plate being a bainite microstructure having a dislocation density of  $1.0 \times 10^{14}$  to  $7.0 \times 10^{14}$  ( $\text{m}^{-2}$ ); a variation in Vickers hardness at 0.5 mm below the surface of the steel plate being 30 HV or less at  $3\sigma$ , where  $\sigma$  is a standard deviation; and a tensile strength being 520 MPa or more.

[2] The high strength steel plate for a sour-resistant line pipe according to [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 a sour-resistant line pipe according to [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 %, Ti: 0.005 % to 0.1 %, Zr: 0.0005 % to 0.02 %, Mg: 0.0005 % to 0.02 %, and REM: 0.0005 % to 0.02 %.

[4] A method for manufacturing a high strength steel plate for a sour-resistant line pipe, the method comprising: heating a slab to a temperature of 1000 °C to 1300 °C, the slab having 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, and then hot rolling the slab to form a steel plate; and then subjecting the steel plate to controlled cooling under a set of conditions including: a temperature of a surface of the steel plate at the start of cooling being (Ar<sub>3</sub> - 10 °C) or higher; an average cooling rate in a temperature range from 750 °C to 550 °C in terms of a temperature at 0.5 mm below the surface of the steel plate being 80 °C/s or lower; an average cooling rate in a temperature range from 750 °C to 550 °C in terms of an average temperature of the steel plate being 15 °C/s or higher; an average cooling rate in a temperature range from 550 °C to a cooling stop temperature in terms of a temperature at 0.5 mm below the surface of the steel plate being 150 °C/s or higher; and a cooling stop temperature in terms of an average temperature of the steel plate being 250 °C to 550 °C.

[5] The method for manufacturing a high strength steel plate for a sour-resistant line pipe according to [4], 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.

[6] The method for manufacturing a high strength steel plate for a sour-resistant line pipe according to [4] or [5], 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 %, Ti: 0.005 % to 0.1 %, Zr: 0.0005 % to 0.02 %, Mg: 0.0005 % to 0.02 %, and REM: 0.0005 % to 0.02 %.

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

(Advantageous Effect)

**[0015]** The high strength steel plate for a sour-resistant line pipe and the high strength steel pipe using the high strength steel plate for a sour-resistant line pipe disclosed herein are excellent not only in HIC resistance but also in SSCC resistance under more severe corrosion environments. In addition, according to the method for manufacturing a high strength steel plate for a sour-resistant line pipe disclosed herein, it is possible to manufacture a high strength steel plate for a sour-resistant line pipe that is excellent not only in HIC resistance but also in SSCC resistance under more severe corrosion environments.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0016]** FIG. 1 is a schematic view illustrating a method for obtaining test pieces for evaluation of SSCC resistance in Examples.

#### DETAILED DESCRIPTION

**[0017]** Hereinafter, the high strength steel plate for a sour-resistant line pipe according to the present disclosure will be described in detail.

[Chemical composition]

**[0018]** 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 %

**[0019]** C effectively contributes to the improvement in strength. However, if the content is less than 0.02 %, sufficient strength can not be secured, while if it exceeds 0.08 %, the hardness of the surface layer and the central segregation area increases during accelerated cooling, causing deterioration in SSCC resistance and HIC resistance. The toughness also deteriorates. Therefore, the C content is in a range of 0.02 % to 0.08 %.

Si: 0.01 % to 0.50 %

**[0020]** Si is added for deoxidation. However, if the content is less than 0.01 %, the deoxidizing effect is not sufficient, while if it exceeds 0.50 %, the toughness and weldability are degraded. Therefore, the Si content is in a range of 0.01 % to 0.50 %.

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Mn: 0.50 % to 1.80 %

5 **[0021]** Mn effectively contributes to the improvement in 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 and the central segregation area increases during accelerated cooling, causing deterioration in SSCC resistance and HIC resistance. The weldability also deteriorates. Therefore, the Mn content is in a range of 0.50 % to 1.80 %.

P: 0.001 % to 0.015 %

10 **[0022]** P is an inevitable impurity element that degrades the weldability and increases the hardness of the central segregation area, causing deterioration in HIC resistance. Since this tendency becomes remarkable when the P content exceeds 0.015 %, the upper limit is set at 0.015 %. Preferably, the P content is 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 the refining cost.

15 S: 0.0002 % to 0.0015 %

20 **[0023]** 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 the refining cost.

Al: 0.01 % to 0.08 %

25 **[0024]** 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 %

30 **[0025]** Ca is an element effective for improving the HIC resistance by morphological control of sulfide inclusions. However, if the content is less than 0.0005 %, its 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 %.

35 **[0026]** The basic components of the present disclosure have been described above. Optionally, however, the chemical composition of the present disclosure may also contain at least one selected from the group consisting of Cu, Ni, Cr, and Mo to further improve the strength and toughness of the steel plate.

Cu: 0.50 % or less

40 **[0027]** 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 %.

Ni: 0.50 % or less

45 **[0028]** 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 %.

Cr: 0.50 % or less

50 **[0029]** Cr, like Mn, is an element effective for obtaining sufficient strength even at low C. To obtain this effect, the Cr content is preferably 0.05 % or more, yet if the content is too large, the quench hardenability becomes excessively high, causing an increase in the dislocation density to be described later and deteriorating the SSCC resistance. The weldability also deteriorates. Therefore, when Cr is added, the Cr content is up to 0.50 %.

55 Mo: 0.50 % or less

**[0030]** 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 quench hardenability becomes excessive, causing an increase in the dislocation density to be described later and deteriorating the SSCC resistance. The weldability also deteriorates. Therefore, when Mo is added, the Mo content is up to 0.50 %.

**[0031]** 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 range.

**[0032]** One or more selected from the group consisting of Nb: 0.005 % to 0.1 %, V: 0.005 % to 0.1 %, Ti: 0.005 % to 0.1 %, Zr: 0.0005 % to 0.02 %, Mg: 0.0005 % to 0.02 %, and REM: 0.0005 % to 0.02 %

Nb, V, and Ti are all 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 %. Zr, Mg, and REM are elements which can be optionally added in order to enhance the toughness through grain refinement and to improve the cracking resistance through control of the inclusion properties. Each of these elements is poor in the addition effect when the content is less than 0.0005 %, while the effect is saturated when the content is more than 0.02 %. Therefore, when added, the content of each added element is preferably in a range of 0.0005 % to 0.02 %.

**[0033]** Although the present disclosure discloses a technique for improving the SSCC resistance of the high strength steel pipe using the high strength steel plate for a sour-resistant line pipe, it goes without saying that the technique disclosed herein needs to satisfy the HIC resistance at the same time as the sour resistant performance. For example, the CP value obtained by the following Expression (1) is preferably set to 1.00 or less. For any element not added, what is necessary is just to substitute 0.

$$CP = 4.46 [\%C] + 2.37 [\%Mn] / 6 + (1.74 [\%Cu] + 1.7 [\%Ni]) / 15 + (1.18 [\%Cr] + 1.95 [\%Mo] + 1.74 [\%V]) / 5 + 22.36 [\%P] \quad (1),$$

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

**[0034]** As used herein, the CP value is a formula devised to estimate the material property at the central segregation area from the content of each alloying element, and the component concentrations of the central segregation area are higher as the CP value of Expression (1) is higher, causing a rise in the hardness of the central segregation area. Therefore, by setting the CP value obtained in Expression (1) to 1.00 or less, it is possible to suppress the occurrence of cracking in the HIC test. In addition, since the hardness of the central segregation area is lower as the CP value is lower, the upper limit for the CP value may be set to 0.95 when higher HIC resistance is required.

**[0035]** 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. For example, N is an element which is inevitably contained in the steel, and a content of 0.007 % or less, preferably 0.006 % or less, is acceptable in the present disclosure.

[Microstructure of the steel plate]

**[0036]** Next, the steel microstructure of the high strength steel plate for a sour-resistant line pipe disclosed herein will be described. In order to achieve high strength with a tensile strength of 520 MPa or more, the steel microstructure needs to be a bainite microstructure. In particular, when a hard phase such as martensite or martensite austenite constituent (MA) is generated in the surface layer, the surface layer hardness is increased, the variation in hardness in the steel plate is increased, and the material homogeneity is impaired. In order to suppress the increase in surface layer hardness, the surface layer is formed with a bainite microstructure as the steel microstructure. 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.

**[0037]** Although the bainite microstructure takes various forms according to the cooling rate, it is important for the present disclosure that the outermost surface layer of the steel plate, specifically at 0.5 mm below the surface of the steel plate, is formed with a bainite microstructure having a dislocation density of  $1.0 \times 10^{14}$  to  $7.0 \times 10^{14} \text{ (m}^{-2}\text{)}$ . Since the dislocation density decreases in the coating process after pipe making, the hardness increase due to age hardening

can be minimized if the dislocation density at 0.5 mm below the surface of the steel plate is  $7.0 \times 10^{14} \text{ (m}^{-2}\text{)}$  or less. Conversely, if the dislocation density at 0.5 mm below the surface of the steel plate exceeds  $7.0 \times 10^{14} \text{ (m}^{-2}\text{)}$ , the dislocation density does not decrease in the coating process after pipe making, and the hardness is significantly increased due to age hardening, causing deterioration in the SSCC resistance. The range of dislocation density is preferably  $6.0 \times 10^{14} \text{ (m}^{-2}\text{)}$  or less in order to obtain good SSCC resistance after pipe making. On the other hand, when the dislocation density at 0.5 mm below the surface of the steel plate is less than  $1.0 \times 10^{14} \text{ (m}^{-2}\text{)}$ , the strength of the steel plate deteriorates. In order to ensure the strength of X65 grade, it is preferable to have a dislocation density of  $2.0 \times 10^{14} \text{ (m}^{-2}\text{)}$  or more. In the high strength steel plate disclosed herein, if the dislocation density in the steel microstructure at 0.5 mm below the surface of the steel plate is in the above range, the outermost surface layer ranging from the surface of the steel plate to a depth of 0.5 mm has an equivalent dislocation density, and as a result, the above-described SSCC resistance improving effect is obtained.

**[0038]** When the dislocation density at 0.5 mm below the surface of the steel plate is  $7.0 \times 10^{14} \text{ (m}^{-2}\text{)}$  or less, the HV 0.1 at 0.5 mm below the surface is 230 or less. From the viewpoint of securing the SSCC resistance of the steel pipe, it is important to suppress an increase in the surface hardness of the steel plate. However, by setting the HV 0.1 at 0.5 mm below the surface of the steel plate to 230 or less, the HV 0.1 at 0.5 mm below the surface following the coating process after pipe making can be suppressed to 260 or less, and the SSCC resistance can be secured.

**[0039]** Further, in the high strength steel plate disclosed herein, it is also important that the variation in Vickers hardness at 0.5 mm below the surface of the steel plate is 30 HV or less at  $3\sigma$ , where  $\sigma$  is a standard deviation. The reason is that if  $3\sigma$  at the time of measuring Vickers hardness at 0.5 mm below the surface of the steel plate is greater than 30 HV, a hardness variation in the surface layer of the steel plate, i.e., the presence of a locally high hardness portion in the surface layer causes deterioration in the SSCC resistance originating from that portion. Note that when calculating the standard deviation  $\sigma$ , it is preferable to measure the Vickers hardness at 100 locations or more.

**[0040]** 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]

**[0041]** Hereinafter, the method and conditions for manufacturing the above-described high strength steel plate for a sour-resistant line pipe will be described concretely. The manufacturing method according to the present disclosure comprises: heating a slab having the above-described chemical composition, and then hot rolling the slab to form a steel plate; then subjecting the steel plate to controlled cooling under predetermined conditions.

[Slab heating temperature]

Slab heating temperature: 1000 °C to 1300 °C

**[0042]** If a 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]

**[0043]** 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  $A_{r3}$  transformation temperature in terms of a temperature of the surface of the steel plate. As used herein, the  $A_{r3}$  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 corresponding 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.

$$A_{r3} \text{ (}^{\circ}\text{C)} = 910 - 310 [\%C] - 80 [\%Mn] - 20 [\%Cu] - 15 [\%Cr] - 55 [\%Ni] - 80 [\%Mo],$$

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

[Cooling start temperature in the controlled cooling]

**[0044]** Cooling start temperature is ( $Ar_3 - 10\text{ }^{\circ}\text{C}$ ) or higher in terms of a temperature of the surface of the steel plate.

**[0045]** When the temperature of the surface of the steel plate at the start of cooling is low, the amount of ferrite formation before controlled cooling increases, and in particular, if the temperature drop from the  $Ar_3$  transformation temperature is greater than  $10\text{ }^{\circ}\text{C}$ , ferrite exceeding 5 % in volume fraction is generated, causing a significant decrease 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 ( $Ar_3 - 10\text{ }^{\circ}\text{C}$ ) or higher.

[Cooling rate of the controlled cooling]

**[0046]** In order to reduce the variation in hardness in the steel plate and improve the material homogeneity while achieving high strength, it is important to control the cooling rate of the surface layer and the average cooling rate in the steel plate. In particular, in order to set the dislocation density at 0.5 mm below the surface of the steel plate and  $3\sigma$  within the ranges described above, it is necessary to control the cooling rate at 0.5 mm below the surface of the steel plate.

Average cooling rate in a temperature range from  $750\text{ }^{\circ}\text{C}$  to  $550\text{ }^{\circ}\text{C}$  in terms of a temperature at 0.5 mm below the surface of the steel plate:  $80\text{ }^{\circ}\text{C/s}$  or lower

**[0047]** When the average cooling rate in a temperature range from  $750\text{ }^{\circ}\text{C}$  to  $550\text{ }^{\circ}\text{C}$  in terms of a temperature at 0.5 mm below the surface of the steel plate exceeds  $80\text{ }^{\circ}\text{C/s}$ , the dislocation density at 0.5 mm below the surface of the steel plate exceeds  $7.0 \times 10^{14}\text{ (m}^{-2}\text{)}$ . As a result, the HV 0.1 at 0.5 mm below the surface of the steel plate exceeds 230, and following the coating process after pipe making, the HV 0.1 at 0.5 mm below the surface exceeds 260, causing deterioration in the SSCC resistance of the steel pipe. Therefore, the average cooling rate is set to  $80\text{ }^{\circ}\text{C/s}$  or lower. Preferably, it is  $50\text{ }^{\circ}\text{C/s}$  or lower. The lower limit of the average cooling rate is not particularly limited, yet if the cooling rate is excessively low, ferrite and pearlite are generated and the strength is insufficient. Therefore, from the viewpoint of preventing this,  $20\text{ }^{\circ}\text{C/s}$  or higher is preferable.

Average cooling rate in a temperature range from  $750\text{ }^{\circ}\text{C}$  to  $550\text{ }^{\circ}\text{C}$  in terms of an average temperature of the steel plate:  $15\text{ }^{\circ}\text{C/s}$  or higher

**[0048]** If the average cooling rate in a temperature range from  $750\text{ }^{\circ}\text{C}$  to  $550\text{ }^{\circ}\text{C}$  in terms of an average temperature of the steel plate is lower than  $15\text{ }^{\circ}\text{C/s}$ , 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  $15\text{ }^{\circ}\text{C/s}$  or higher. From the viewpoint of variations in the strength and hardness of the steel plate, the steel plate average cooling rate is preferably  $20\text{ }^{\circ}\text{C/s}$  or higher. The upper limit of the average cooling rate is not particularly limited, yet is preferably  $80\text{ }^{\circ}\text{C/s}$  or lower such that excessive low-temperature transformation products will not be generated.

Average cooling rate in a temperature range from  $550\text{ }^{\circ}\text{C}$  to a cooling stop temperature in terms of a temperature at 0.5mm below the surface of the steel plate:  $150\text{ }^{\circ}\text{C/s}$  or higher

**[0049]** For cooling at a temperature of  $550\text{ }^{\circ}\text{C}$  or lower in terms of a temperature at 0.5 mm below the surface of the steel plate, cooling in a stable nucleate boiling state is necessary, and it is essential to increase the water flow rate. If the average cooling rate is lower than  $150\text{ }^{\circ}\text{C/s}$  in a temperature range from  $550\text{ }^{\circ}\text{C}$  to the cooling stop temperature in terms of a temperature at 0.5 mm below the surface of the steel plate, cooling in a nucleate boiling state is not achieved, a hardness variation occurs in the outermost surface layer of the steel plate, and  $3\sigma$  at 0.5 mm below the surface of the steel plate exceeds 30 HV, resulting in deterioration in the SSCC resistance. Therefore, the average cooling rate is set to  $150\text{ }^{\circ}\text{C/s}$  or higher. Preferably, it is  $170\text{ }^{\circ}\text{C/s}$  or higher. The upper limit of the average cooling rate is not particularly limited, yet is preferably  $250\text{ }^{\circ}\text{C/s}$  or lower in view of equipment restrictions.

**[0050]** Although the temperature at 0.5 mm below the surface of the steel plate and the an average temperature of the steel plate can not be directly measured physically, for example, a temperature distribution in a cross section in the plate thickness direction can be determined in real time by difference calculation using a process computer on the basis of the surface temperature at the start of cooling measured by a radiation thermometer and the target surface temperature at the end of cooling. As used herein, the temperature at 0.5 mm below the surface of the steel plate in the temperature distribution is referred to as the "temperature at 0.5 mm below the surface of the steel plate", and the average value of temperatures in the thickness direction in the temperature distribution as the "average temperature of the steel plate".



[Cooling stop temperature]

**[0051]** Cooling stop temperature: 250 °C to 550 °C in terms of an average temperature of the steel plate

**[0052]** 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 increase in the surface layer becomes remarkable and the dislocation density at 0.5 mm below the surface of the steel plate exceeds  $7.0 \times 10^{14}$  ( $\text{m}^{-2}$ ), causing deterioration in the SSCC resistance. In addition, the hardness of the central segregation area increases and the HIC resistance deteriorates. Therefore, in order to suppress deterioration of material homogeneity in the steel plate, the cooling stop temperature of the controlled cooling is set to 250 °C to 550 °C in terms of an average temperature of the steel plate.

[High strength steel pipe]

**[0053]** 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 a sour-resistant line pipe (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.

**[0054]** For example, an UOE steel pipe is manufactured by groove machining the ends 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

**[0055]** The steels (Steels A to K) having the chemical compositions listed in Table 1 are made into slabs by continuous casting, heated to the temperatures listed in Table 2, and then hot rolled at the rolling finish temperatures and rolling reduction ratios listed in Table 2 to obtain the steel plates of the thicknesses listed in Table 2. Then, the steel plates were subjected to controlled cooling using a water-cooled controlled cooling device under the conditions listed in Table 2.

[Identification of microstructure]

**[0056]** The microstructure of each obtained steel plate was observed by an optical microscope and a scanning electron microscope. The microstructure at a position of 0.5 mm below the surface of each steel plate and the microstructure at the mid-thickness part are listed in Table 2.

[Measurement of tensile strength]

**[0057]** Tensile test was conducted using full-thickness test pieces collected in a direction perpendicular to the rolling direction as tensile test pieces to measure the tensile strength. The results are listed in Table 2.

[Measurement of Vickers hardness]

**[0058]** For a cross section perpendicular to the rolling direction, according to JIS Z 2244, Vickers hardness (HV 0.1) was measured at 100 locations at a position 0.5 mm below the surface of each steel plate, the measurement results were averaged, and the standard deviation  $\sigma$  was determined. The average value and  $3\sigma$  are listed in Table 2. In this case, the measurement was made at HV 0.1 instead of the commonly used HV 10, because the indentation size is made smaller in measurement at HV 0.1, and it is possible to obtain hardness information at a position closer to the surface and more sensitive to the microstructure.

[Dislocation density]

**[0059]** A sample for X-ray diffraction was taken from a position having an average hardness, the sample surface was polished to remove scale, and X-ray diffraction measurement was performed at a position of 0.5 mm below the surface of the steel plate. The dislocation density was converted from the strain obtained from the half width  $\beta$  of X-ray diffraction measurement. In a diffraction intensity curve obtained by ordinary X-ray diffraction,  $K\alpha_1$  and  $K\alpha_2$  rays having different

wavelengths overlap, and are thus separated by the Rachinger's method. For extraction of strain, the Williamson-Hall method described below is used. The spread of the half width is influenced by the size  $D$  of the crystallite and the strain  $\varepsilon$ , and can be calculated by the following equation as the sum of both factors:  $\beta = \beta_1 + \beta_2 = (0.9 \lambda / (D \times \cos \theta)) + 2\varepsilon \times \tan \theta$ . Further modifying this equation, the following is derived:  $\beta \cos \theta / \lambda = 0.9 \lambda / D + 2\varepsilon \times \sin \theta / \lambda$ . The strain  $\varepsilon$  is calculated from the slope of the straight line by plotting  $\beta \cos \theta / \lambda$  relative to  $\sin \theta / \lambda$ . The diffraction lines used for the calculation are (110), (211), and (220). For conversion of the dislocation density from the strain  $\varepsilon$ , the following equation was used:  $\rho = 14.4 \varepsilon^2 / b^2$ . As used herein,  $\theta$  means the peak angle calculated by the  $\theta$ - $2\theta$  method for X-ray diffraction, and  $\lambda$  means the wavelength of the X-ray used in the X-ray diffraction,  $b$  is a Burgers vector of  $\text{Fe}(\alpha)$ , which is 0.25 nm in this embodiment.

[Evaluation of SSCC resistance]

**[0060]** The SSCC resistance was evaluated for a pipe made from a part of each steel plate. Each pipe was manufactured by groove machining the ends of a steel plate, and 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 on the inner and outer surfaces by submerged arc welding, and subjecting it to an expansion process. As illustrated in FIG. 1, after a coupon cut out from each obtained steel pipe was flattened, an SSCC test piece of 5 mm  $\times$  15 mm  $\times$  115 mm was collected from the inner surface of the steel pipe. At this time, the inner surface to be tested was left intact without removing the scale in order to leave the state of the outermost layer. Each collected SSCC test piece was loaded with 90 % stress of the actual yield strength (0.5 % YS) of the corresponding steel pipe, and evaluation was made using a NACE standard TM0177 Solution A solution, at a hydrogen sulfide partial pressure of 1 bar, in accordance with the 4-point bending SSCC test specified by the EFC 16 standard. After immersion for 720 hours, the SSCC resistance was judged as "Good" when no cracks were observed, or "Poor" when cracking occurred. The results are listed in Table 2.

**[0061]** HIC resistance was determined by performing HIC test with an immersion time of 96 hours using a NACE standard TM0177 Solution A solution. The HIC resistance was judged as "Good" when the crack length ratio (CLR) was 15 % or less in the HIC test, or "Poor" when the CLR exceeded 15 %.. The results are listed in Table 2.

**[0062]** The target ranges of the present disclosure were as follows:

- the tensile strength is 520 MPa or more as a high strength steel plate for a sour-resistant line pipe;
- the microstructure is a bainite microstructure at both positions of 0.5 mm below the surface and of  $t/2$ ;
- the HV 0.1 at 0.5 mm below the surface is 230 or less;
- no cracks are observed in the SSCC test in high strength steel pipe made from the corresponding steel plate; and
- the crack length ratio (CLR) is 15 % or less in the HIC test.

Table 1

Steel ID	Chemical composition (mass%)																	CP	Ar <sub>3</sub> temp. (°C)	
	C	Si	Mn	P	S	Al	N	Cu	Ni	Cr	Mo	Nb	V	Ti	Zr	Ca	Mg			REM
A	0.040	0.30	1.14	0.005	0.0005	0.026	0.0040	0.16	0.27	0.22	0.08	0.030		0.010		0.003			0.87	779
B	0.040	0.30	1.31	0.004	0.0004	0.035	0.0040			0.27	0.12	0.030		0.011		0.001			0.90	779
C	0.067	0.32	1.44	0.005	0.0008	0.024	0.0035									0.002			0.98	774
D	0.052	0.13	1.31	0.004	0.0006	0.027	0.0038			0.22	0.10					0.002			0.93	778
E	0.050	0.25	1.29	0.004	0.0008	0.030	0.0035			0.35		0.035	0.035			0.002			0.92	786
F	0.042	0.31	1.35	0.004	0.0006	0.033	0.0037			0.22	0.15	0.030		0.012	0.002	0.001		0.004	0.92	774
G	0.043	0.28	1.30	0.004	0.0006	0.035	0.0043			0.25	0.12	0.035		0.013		0.001	0.002		0.90	779
H	<u>0.085</u>	0.18	1.29	0.005	0.0007	0.027	0.0034		0.25		0.15	0.025		0.012		0.001			1.09	755
I	0.050	0.23	<u>1.83</u>	0.005	0.0008	0.031	0.0041	0.12	0.24							0.002			1.10	733
J	0.047	0.22	1.25	0.005	0.0006		0.0035			<u>0.9</u>						0.001			1.03	782
K	0.050	0.15	1.30	0.006	0.0008	0.034	0.0038		0.022	0.11	<u>0.60</u>	0.025	0.035	0.010		0.001			1.15	740

Note 1: The balance is Fe and inevitable impurities.

Note 2: Underlined if outside the scope of the disclosure.

Table 2

No.	Steel ID	Plate thickness (mm)	Heating temp. (°C)	Rolling finish temp. (°C)	Rolling reduction ratio (%)	Cooling start temp. (°C)	Cooling start temp. - A <sub>3</sub> (°C)	Cooling rate in temp. range of 750 °C → 550 °C (°C/s)	Cooling rate in temp. range of 550 °C → 750 °C or lower (°C/s)	Cooling rate in temp. range of 750 °C → 550 °C (°C/s)	Cooling rate in temp. range of 550 °C or lower (°C/s)	Micro-structure (0.5 mm below the surface of the steel plate)	Micro-structure (at t/2)	Tensile strength (MPa)	Average hardness (HV 0.1) (0.5 mm below the surface of the steel plate)	Hardness variation 3σ (HV 0.1) (0.5 mm below the surface of the steel plate)	Dislocation density (0.5 mm below the surface of the steel plate) (m <sup>-2</sup> )	SSCC resistance of the steel pipe	HIC resistance of the steel pipe	Category
1	A	17.5	1100	890	75	850	71	55	65	180	495	B	B	575	210	25	3×10 <sup>14</sup>	Good	Good	Example
2	B	20	1080	890	75	850	71	45	55	180	500	B	B	583	210	24	3×10 <sup>14</sup>	Good	Good	
3	B	20	1080	890	75	850	71	50	53	170	410	B	B	586	215	20	5×10 <sup>14</sup>	Good	Good	
4	B	20	1080	890	75	850	71	50	56	190	300	B	B	602	220	27	6×10 <sup>14</sup>	Good	Good	
5	B	34	1080	880	75	830	51	40	35	180	480	B	B	586	215	21	3×10 <sup>14</sup>	Good	Good	
6	B	34	1080	880	75	860	81	45	38	170	450	B	B	612	220	24	2×10 <sup>14</sup>	Good	Good	
7	C	34	1080	850	80	810	36	35	32	190	500	B	B	615	225	26	3×10 <sup>14</sup>	Good	Good	
8	D	34	1080	870	75	840	62	50	28	160	400	B	B	597	207	25	5×10 <sup>14</sup>	Good	Good	
9	D	34	1080	830	75	810	32	65	37	180	350	B	B	626	212	24	6×10 <sup>14</sup>	Good	Good	
10	D	34	1080	850	70	810	32	70	33	180	390	B	B	611	210	22	5×10 <sup>14</sup>	Good	Good	
11	D	34	1080	850	70	810	32	80	33	180	390	B	B	647	218	22	6×10 <sup>14</sup>	Good	Good	
12	E	34	1080	870	70	840	54	50	35	200	420	B	B	586	205	23	4×10 <sup>14</sup>	Good	Good	
13	E	34	1080	870	75	820	34	45	36	190	480	B	B	592	210	26	4×10 <sup>14</sup>	Good	Good	
14	F	20	1080	890	75	850	76	45	55	150	500	B	B	576	208	26	3×10 <sup>14</sup>	Good	Good	
15	G	20	1080	890	75	850	71	45	55	180	500	B	B	577	205	26	4×10 <sup>14</sup>	Good	Good	

Note 1: Underlined if outside of the scope of the disclosure.

Note 2: For the microstructures, B indicates bainite and F indicates ferrite.

Table 2 (cont'd)

No.	Steel ID	Plate thickness (mm)	Heating temp. (°C)	Rolling finish temp. (°C)	Rolling reduction ratio (%)	Cooling start temp. (°C)	Cooling start temp. - Ar <sub>3</sub> (°C)	Cooling rate in temp. range of 750 °C → 550 °C (°C/s)	Cooling rate in temp. range of 550 °C → 750 °C or lower (°C/s)	Cooling stop temp. (°C)	Micro-structure (0.5 mm below the surface of the steel plate)	Micro-structure (at 1/2)	Tensile strength (MPa)	Average hardness (HV0.1) (0.5 mm below the surface of the steel plate)	Hardness variation 3σ (0.5 mm below the surface of the steel plate) (HV0.1)	Dislocation density (0.5 mm below the surface of the steel plate) (m <sup>-2</sup> )	SSCC resistance of the steel pipe	HIC resistance of the steel pipe	Category
16	B	20	980	880	75	840	61	50	51	160	500	B	508	203	27	3x10 <sup>14</sup>	Good	Good	
17	B	20	1080	780	75	720	49	45	53	170	450	F+B	513	205	24	2x10 <sup>14</sup>	Good	Poor	
18	B	20	1080	840	75	810	31	40	5	160	470	B	505	197	27	1x10 <sup>14</sup>	Good	Poor	
19	B	20	1080	850	75	810	31	60	55	180	200	B	639	245	28	9x10 <sup>14</sup>	Poor	Poor	
20	B	20	1080	870	75	840	61	90	55	190	450	B	582	240	24	9x10 <sup>14</sup>	Poor	Good	
21	B	20	1080	860	75	840	61	55	52	110	430	B	576	225	40	5x10 <sup>14</sup>	Poor	Good	
22	B	20	1080	860	75	840	61	55	52	135	430	B	580	222	35	5x10 <sup>14</sup>	Poor	Good	
23	C	34	1080	890	75	850	76	105	29	170	360	B	594	250	20	10x10 <sup>14</sup>	Poor	Poor	
24	H	34	1080	890	75	850	95	45	30	180	460	B	605	255	22	11x10 <sup>14</sup>	Poor	Poor	
25	I	34	1080	820	75	800	68	40	36	160	500	B	615	240	27	9x10 <sup>14</sup>	Poor	Poor	
26	J	34	1080	840	75	810	28	50	36	190	350	B	627	235	26	8x10 <sup>14</sup>	Poor	Poor	
27	K	34	1080	860	75	810	70	45	38	200	430	B	621	257	24	11x10 <sup>14</sup>	Poor	Poor	

Note 1: Underlined if outside of the scope of the disclosure.

Note 2: For the microstructures, B indicates bainite and F indicates ferrite.

[0063] As can be seen from Table 2, Nos. 1 to 15 are our examples in which the chemical composition and the production conditions satisfy the appropriate ranges of the present disclosure. In any of these cases, the tensile strength

as a steel plate was 520 MPa or more, the microstructure at both positions of 0.5 mm below the surface and of t/2 was a bainite microstructure, the HV 0.1 at 0.5 mm below the surface was 230 or less, and hence the SSCC resistance and HIC resistance were also good in each high strength steel pipe produced using the steel plate.

**[0064]** In contrast, Nos. 16 to 23 are comparative examples whose chemical compositions are within the scope of the present disclosure but whose production conditions are outside the scope of the present disclosure. In No. 16, since 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. In No. 17, since the cooling start temperature was low and the microstructure was formed in a layered manner with precipitation of ferrite, the low strength was low and the HIC resistance after pipe formation deteriorated. In No. 18, since the controlled cooling conditions were outside the scope of the present disclosure and a bainite microstructure was not obtained at the mid-thickness part, but instead a ferrite + pearlite microstructure was obtained as the microstructure, the strength was low and the HIC resistance after pipe formation deteriorated. In No. 19, since the cooling stop temperature was low, the dislocation density at 0.5 mm below the surface increased, and the HV 0.1 exceeded 230, the SSCC resistance after pipe formation was inferior. In addition, the hardness of the central segregation area also increased, and the HIC resistance also deteriorated. In Nos. 20 and 23, since the average cooling rate in a temperature range from 750 °C to 550 °C at 0.5 mm below the surface of the steel plate exceeded 80 °C/s, the dislocation density at 0.5 mm below the surface increased, and the HV 0.1 exceeded 230, and the SSCC resistance after pipe formation was inferior. In No. 23, the HIC resistance in the surface layer also deteriorated. In No. 21 and No. 22, since the average cooling rate in a temperature range of 550 °C or lower at 0.5 mm below the surface of the steel plate was lower than 150 °C/s, uneven cooling of the steel plate was remarkable, and although the HV 0.1 was 230 on average, the variation in hardness was large and a locally high hardness portion was generated, and hence the SSCC resistance after pipe formation was inferior. In Nos. 24 to 27, since the compositions of the steel plates were outside the scope of the present disclosure, the dislocation density at 0.5 mm below the surface was high, and the HV 0.1 exceeded 230, the SSCC resistance after pipe formation was inferior. In addition, in Nos. 24 to 27, the HIC resistance was also inferior because the hardness of the central segregation area increased.

## INDUSTRIAL APPLICABILITY

**[0065]** According to the present disclosure, it is possible to provide a high strength steel plate for a sour-resistant line pipe that is excellent not only in HIC resistance but also in SSCC resistance under more severe corrosion environments. 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 sulfide and require sour resistance.

## Claims

1. A high strength steel plate for a sour-resistant line pipe, 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;

a steel microstructure at 0.5 mm below a surface of the steel plate being a bainite microstructure having a dislocation density of  $1.0 \times 10^{14}$  to  $7.0 \times 10^{14}$  (m<sup>-2</sup>);

a variation in Vickers hardness at 0.5 mm below the surface of the steel plate being 30 HV or less at  $3\sigma$ , where  $\sigma$  is a standard deviation; and

a tensile strength being 520 MPa or more.

2. The high strength steel plate for a sour-resistant line pipe 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 a sour-resistant line pipe according to claim 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 %, Ti: 0.005 % to 0.1 %, Zr: 0.0005 % to 0.02 %, Mg: 0.0005 % to 0.02 %, and REM: 0.0005 % to 0.02 %.

4. A method for manufacturing a high strength steel plate for a sour-resistant line pipe, the method comprising:

heating a slab to a temperature of 1000 °C to 1300 °C, the slab having a chemical composition containing, by

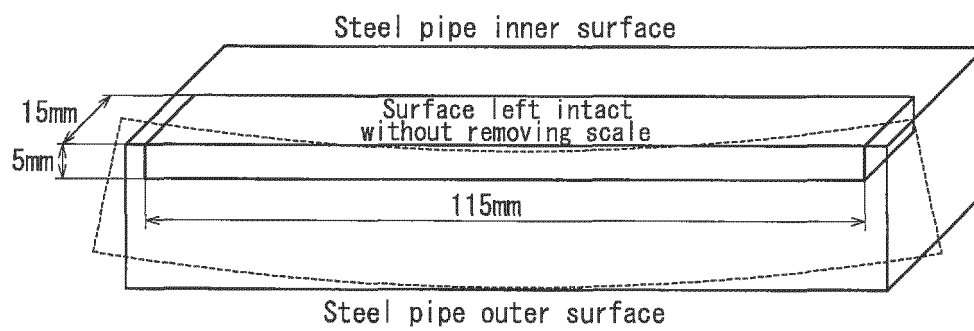
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mass%, C: 0.02 % to 0.08 %, Si: 0.01 % to 0.50 %, Mn: 0.50 % to 1.80 %, P: 0.001 % to 0.015 %, S: 0.0002 % to 0.0015 %, Al: 0.01 % to 0.08 %, and Ca: 0.0005 % to 0.005 %, with the balance being Fe and inevitable impurities, and then hot rolling the slab to form a steel plate;  
then subjecting the steel plate to controlled cooling under a set of conditions including:

a temperature of a surface of the steel plate at the start of cooling being ( $A_{r3} - 10$  °C) or higher;  
an average cooling rate in a temperature range from 750 °C to 550 °C in terms of a temperature at 0.5 mm below the surface of the steel plate being 80 °C/s or lower;  
an average cooling rate in a temperature range from 750 °C to 550 °C in terms of an average temperature of the steel plate being 15 °C/s or higher;  
an average cooling rate in a temperature range from 550 °C to a cooling stop temperature in terms of a temperature at 0.5 mm below the surface of the steel plate being 150 °C/s or higher; and  
a cooling stop temperature in terms of an average temperature of the steel plate being 250 °C to 550 °C.

5. The method for manufacturing a high strength steel plate for a sour-resistant line pipe according to claim 4, 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.
6. The method for manufacturing a high strength steel plate for a sour-resistant line pipe according to claim 4 or 5, 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 %, Ti: 0.005 % to 0.1 %, Zr: 0.0005 % to 0.02 %, Mg: 0.0005 % to 0.02 %, and REM: 0.0005 % to 0.02 %.
7. A high strength steel pipe using the high strength steel plate for a sour-resistant line pipe as recited in any one of claims 1 to 3.

*FIG. 1*





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/034800

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C38/00 (2006.01) i, C21D8/02 (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. C22C38/00-38/60, C21D8/02

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2017

Registered utility model specifications of Japan 1996-2017

Published registered utility model applications of Japan 1994-2017

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-77331 A (JFE STEEL CORPORATION) 19 April 2012 (Family: none)	1-7
A	JP 2013-139630 A (JFE STEEL CORPORATION) 18 July 2013 (Family: none)	1-7
A	WO 2016/056216 A1 (JFE STEEL CORPORATION) 14 April 2016 (Family: none)	1-7



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

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Date of the actual completion of the international search  
13.12.2017

Date of mailing of the international search report  
26.12.2017

Name 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/JP2017/034800

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006/003775 A1 (SUMITOMO METAL INDUSTRIES, LTD.) 12 January 2006 & US 2007/0137736 A1 & EP 1785501 A1 & CA 2569907 A1 & EA 200700026 A1 & CN 1969053 A & UA 81878 C2	1-7

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**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 3951428 B [0005] [0007]
- JP 3951429 B [0005] [0007]
- JP 2002327212 A [0005] [0007]
- JP 3711896 B [0005] [0007]
- JP H957327 A [0006] [0007]
- JP 3796133 B [0006] [0007]