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

HOCHFESTE STAHLPLATTE FÜR SAUER GAS-RESISTENTE LEITUNGSROHRE UND VERFAHREN ZU IHRER HERSTELLUNG, UND HOCHFESTES STAHLROHR UNTER VERWENDUNG VON HOCHFESTEN STAHLPLATTEN FÜR SAUER GAS-RESISTENTE LEITUNGSROHRE

PLAQUE D'ACIER A HAUTE RESISTANCE POUR TUYAU DE LIGNE RESISTANT A L'ACIDE ET PROCEDE DE FABRICATION, ET TUYAU EN ACIER A HAUTE RESISTANCE UTILISANT UNE PLAQUE D'ACIER A HAUTE RESISTANCE POUR TUYAU DE LIGNE RESISTANT A L'ACIDE

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(73) Proprietor: **JFE Steel Corporation**

**Tokyo 100-0011 (JP)**

(72) Inventors:

- **SHIMAMURA Junji**  
Tokyo 100-0011 (JP)
- **YOKOTA Tomoyuki**  
Tokyo 100-0011 (JP)
- **UEOKA Satoshi**  
Tokyo 100-0011 (JP)
- **ISHIKAWA Nobuyuki**  
Tokyo 100-0011 (JP)

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(74) Representative: **Grünecker Patent- und  
Rechtsanwälte  
PartG mbB  
Leopoldstraße 4  
80802 München (DE)**

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**Description**

## TECHNICAL FIELD

5 **[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.

## 10 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.

15 **[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. Additionally, in environments with relatively low hydrogen sulfide partial pressure, micro-cracks called fissures may occur, which may lead to SSCC.

20 **[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.

25 **[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.

30 **[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 JP2012077331A discloses a high strength steel sheet for a sour-resistant line pipe, having effectively reduced variations in hardness in the sheet thickness direction and the sheet width direction of the steel sheet, and thereby having improved material uniformity in the steel sheet.

## 35 CITATION LIST

## Patent Literature

40 **[0007]**

PTL 1: JP3951428B

PTL 2: JP3951429B

PTL 3: JP2002-327212A

5 PTL 4: JP3711896B

PTL 5: JPH9-57327A

10 PTL 6: JP3796133B

## SUMMARY

(Technical Problem)

15 **[0008]** According to our study, however, it turned out that the high strength steel plates obtained by the manufacturing methods described in Patent Literatures 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  
20 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  
25 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  
30 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]** Further, in PTLs 1 to 6, the conditions to avoid microcracking such as fissures in environments with relatively low hydrogen sulfide partial pressure are not clear.

**[0013]** It would thus be 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 and environments with low hydrogen sulfide partial pressure below 1 bar, together with an advantageous method for manufacturing the same.  
40 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)

**[0014]** The present inventors repeated many experiments and examinations about the chemical compositions, micro-  
45 structures, 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 0.25 mm below the surface of the steel plate, with a bainite  
50 microstructure having a dislocation density of  $1.0 \times 10^{14}$  to  $7.0 \times 10^{14}$  ( $m^{-2}$ ), 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 0.25 mm below the surface of the steel plate, and succeeded in finding the conditions to be met. The inventors also found that Mo addition is effective in suppressing initial crack generation in environments with high hydrogen sulfide partial pressure above 1 bar, while suppressing Ni addition is effective in avoiding microcracking  
55 such as fissures in environments with low hydrogen sulfide partial pressure below 1 bar. The present disclosure was completed based on the above discoveries.

**[0015]** The invention is defined in the appended claims.

(Advantageous Effect)

5 [0016] 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 and environments with low hydrogen sulfide partial pressure below 1 bar. 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 and environments with low hydrogen sulfide partial pressure below 1 bar.

10 BRIEF DESCRIPTION OF THE DRAWINGS

15 [0017] FIG. 1 is a schematic view illustrating a method for obtaining test pieces for evaluation of SSCC resistance in Examples.

DETAILED DESCRIPTION

20 [0018] Hereinafter, the high strength steel plate for a sour-resistant line pipe according to the present disclosure will be described in detail.

[Chemical composition]

25 [0019] First, the chemical composition of the high strength steel plate disclosed herein and the reasons for limitation thereof will be described. When components are expressed in "%" in the following description, this refers to "mass%".

C: 0.02 % to 0.08 %

30 [0020] C effectively contributes to the improvement in strength. However, if the content is less than 0.02 %, sufficient strength cannot 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 set in a range of 0.02 % to 0.08 %.

Si: 0.01 % to 0.50 %

35 [0021] 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 %.

Mn: 0.50 % to 1.80 %

40 [0022] 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 set in a range of 0.50 % to 1.80 %.

P: 0.001 % to 0.015 %

45 [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 %. 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.

S: 0.0002 % to 0.0015 %

55 [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 the refining cost.

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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 set in a range of 0.01 % to 0.08 %.

Mo: 0.01 % to 0.50 %

10 [0026] Mo is an effective element for improving toughness and increasing strength, it is an effective element for improving SSCC resistance regardless of the hydrogen sulfide partial pressure. To obtain this effect, the Mo content needs to be 0.01 % or more, and preferably 0.10 % or more. On the other hand, 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, the Mo content is set to 0.50 % or less, and preferably 0.40 % or less.

15 Ca: 0.0005 % to 0.005 %

20 [0027] 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 %.

25 [0028] At least one selected from the group consisting of Nb: 0.005 % to 0.1 % and Ti: 0.005 % to 0.1 % Both Nb and Ti are elements effective for improving 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, at least one of Nb or Ti is added in a range of 0.005 % to 0.1 %.

[0029] 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, and Cr in the following ranges to further improve the strength and toughness of the steel plate.

30 Cu: 0.50 % or less

[0030] 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 %.

35 Ni: 0.10 % or less

40 [0031] Ni is an element effective for improving the toughness and increasing the strength. To obtain this effect, the Ni content is preferably 0.01 % or more. However, when Ni is added in excess of 0.10 %, microcracks called fissures easily occur in environments with low hydrogen sulfide partial pressure below 1 bar. Therefore, when Ni is added, the Ni content is up to 0.10 %. The Ni content is preferably 0.02 % or less.

Cr: 0.50 % or less

45 [0032] 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 %.

50 [0033] Optionally, the chemical composition of the present disclosure may further contain at least one selected from the group consisting of V, Zr, Mg, and REM in the following ranges.

[0034] At least one selected from the group consisting of V: 0.005 % to 0.1 %, Zr: 0.0005 % to 0.02 %, Mg: 0.0005 % to 0.02 %, and REM: 0.0005 % to 0.02 %

55 V is an element that can be optionally added to increase 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 %.

**[0035]** 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] represents the content by mass% of the element X in steel.

**[0036]** 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.

**[0037]** 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]

**[0038]** 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. Portions other than the surface layer also have a bainite microstructure, and the microstructure at the mid-thickness part representative of the portions may be a bainite 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.

**[0039]** 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 0.25 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  $7.0 \times 10^{14}$  ( $m^{-2}$ ). 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 0.25 mm below the surface of the steel plate is  $7.0 \times 10^{14}$  ( $m^{-2}$ ) or less. Conversely, if the dislocation density at 0.25 mm below the surface of the steel plate exceeds  $7.0 \times 10^{14}$  ( $m^{-2}$ ), 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  $6.0 \times 10^{14}$  ( $m^{-2}$ ) or less in order to obtain good SSCC resistance after pipe making. On the other hand, when the dislocation density at 0.25 mm below the surface of the steel plate is less than  $1.0 \times 10^{14}$  ( $m^{-2}$ ), 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  $2.0 \times 10^{14}$  ( $m^{-2}$ ) or more. In the high strength steel plate disclosed herein, if the dislocation density in the steel microstructure at 0.25 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 0.25 mm has an equivalent dislocation density, and consequently, the above-described SSCC resistance improving effect is obtained.

**[0040]** When the dislocation density at 0.25 mm below the surface of the steel plate is  $7.0 \times 10^{14}$  ( $m^{-2}$ ) or less, the

HV 0.1 at 0.25 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 0.25 mm below the surface of the steel plate to 230 or less, the HV 0.1 at 0.25 mm below the surface following the coating heat treatment at 250 °C for 1 hour after pipe making can be suppressed to 260 or less, and the SSCC resistance can be secured.

**[0041]** Further, in the high strength steel plate disclosed herein, it is also important that the variation in Vickers hardness at 0.25 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 0.25 mm below the surface of the steel plate is greater than 30 HV, a hardness variation in the outermost surface layer of the steel plate, i.e., the presence of a locally high hardness portion in the outermost 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.

**[0042]** With the same idea, it is also important for the high strength steel plate disclosed herein that a variation in Vickers hardness in a plate thickness direction is 30 HV or less at  $3\sigma$ , where  $\sigma$  is a standard deviation.

**[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 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; and then reheating the steel plate.

[Slab heating temperature]

**[0045]** Slab heating temperature: 1000 °C to 1300 °C

If a slab heating temperature is lower than 1000 °C, carbides do not solute sufficiently and the necessary strength cannot 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]

**[0046]** 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  $Ar_3$  transformation temperature in terms of a temperature of the surface of the steel plate. As used herein, the  $Ar_3$  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.

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

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

[Cooling start temperature in the controlled cooling]

**[0047]** Cooling start temperature is ( $Ar_3 - 10$  °C) or higher in terms of a temperature of the surface of the steel plate.

**[0048]** 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 °C, ferrite exceeding 5 % by 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 ( $A_{r3} - 10$  °C) or higher. Note that the temperature of the surface of the steel plate at the start of cooling is not higher than the rolling finish temperature.

[Cooling rate of the controlled cooling]

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**[0049]** 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 0.25 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 0.25 mm below the surface of the steel plate.

10 **[0050]** Average cooling rate in a temperature range from 750 °C to 550 °C in terms of a temperature at 0.25 mm below the surface of the steel plate: 50 °C/s or lower

When the average cooling rate in a temperature range from 750 °C to 550 °C in terms of a temperature at 0.25 mm below the surface of the steel plate exceeds 50 °C/s, the dislocation density at 0.25 mm below the surface of the steel plate exceeds  $7.0 \times 10^{14}$  (m<sup>-2</sup>). As a result, the HV 0.1 at 0.25 mm below the surface of the steel plate exceeds 230, and following the coating process after pipe making, the HV 0.1 at 0.25 mm below the surface exceeds 260, causing deterioration in the SSCC resistance of the steel pipe. Therefore, the average cooling rate is set to 50 °C/s or lower. It is preferably 45 °C/s or lower, and more preferably 40 °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 °C/s or higher is preferable.

20 **[0051]** 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

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 cannot 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.

25 From the viewpoint of variations 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.

**[0052]** Average cooling rate in a temperature range from 550 °C to a cooling stop temperature in terms of a temperature at 0.25 mm below the surface of the steel plate: 150 °C/s or higher

30 For cooling at a temperature of 550 °C or lower in terms of a temperature at 0.25 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 °C/s in a temperature range from 550 °C to the cooling stop temperature in terms of a temperature at 0.25 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 0.25 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 °C/s or higher. Preferably, it is 170 °C/s or higher. The upper limit of the average cooling rate is not particularly limited, yet is preferably 250 °C/s or lower in view of equipment restrictions.

35 **[0053]** Although the temperature at 0.25 mm below the surface of the steel plate and the average temperature of the steel plate cannot 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 0.25 mm below the surface of the steel plate in the temperature distribution is referred to as the "temperature at 0.25 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".

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[Cooling stop temperature]

**[0054]** Cooling stop temperature: 250 °C to 550 °C in terms of an average temperature of the steel plate

50 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 cannot 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 0.25 mm below the surface of the steel plate exceeds  $7.0 \times 10^{14}$  (m<sup>-2</sup>), 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.

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[Reheating conditions]

**[0055]** Reheating temperature: at least 50°C higher than the cooling stop temperature and in a range of 450 °C and 600 °C in terms of an average temperature of the steel plate

In the present disclosure, after the completion of rolling, the steel plate is quenched by controlled cooling to 250 °C to 550 °C which is the temperature range of bainite transformation, and then subjected to on-line reheating. The reheating brings the steel plate to a temperature higher than the cooling stop temperature such that the bainite phase is softened by tempering, and the SSCC resistance can be improved. However, if the reheating temperature is below 450 °C, the surface layer softening effect is insufficient, and if the reheating temperature is above 600 °C, the strength and the drop weight tear test (DWTT) properties are degraded. Therefore, the reheating temperature is set in a range of 450 °C and 600 °C.

**[0056]** In the present disclosure, from the viewpoint of reducing the manufacturing efficiency and the fuel cost for heat treatment, it is preferable to perform reheating immediately after the stop of the controlled cooling. As used herein, performing reheating immediately after the stop of the controlled cooling is intended to mean performing reheating within 120 seconds after the stop of the controlled cooling.

**[0057]** For softening of the surface layer, it is necessary to raise the temperature to a reheating start temperature of at least 50 °C higher than the cooling stop temperature. Basically, cooling after the reheating is preferably air cooling.

[High strength steel pipe]

**[0058]** 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.

**[0059]** 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

**[0060]** The steels (Steels A to M) 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, each steel plate was subjected to controlled cooling using a water-cooling type controlled-cooling device under the conditions listed in Table 2. Immediately thereafter, each steel plate was reheated using an on-line induction heating apparatus such that the average temperature of the steel plate was set as specified in "Reheating temp." in Table 2.

[Identification of microstructure]

**[0061]** The microstructure of each obtained steel plate was observed by an optical microscope and a scanning electron microscope. The microstructure at a position of 0.25 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]

**[0062]** 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]

**[0063]** 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 0.25 mm below the surface of each steel plate, the measurement results were averaged, and the standard deviation  $\sigma$  was determined. The average values and  $3\sigma$  values are listed in Table 2 as the average hardness and hardness variation at 0.25 mm below the surface of each steel plate. In addition, for a cross section perpendicular to the rolling direction, the Vickers hardness (HV 0.1) was measured in a region from 0.25 mm below one surface of each steel plate to 0.25 mm below the other surface of the steel plate at a pitch of 0.5 mm in

the plate thickness direction in accordance with JIS Z 2244, and the standard deviation  $\sigma$  was determined. The  $3\sigma$  values are listed in Table 2 as the hardness variation in the plate thickness direction. When Vickers hardness measurement in the plate thickness direction is continued at a pitch of 0.5 mm, after the first measurement at a position within 1.25 mm below a surface of each steel plate on the opposite side of the measurement start side, the Vickers hardness measurement is completed by measuring the Vickers hardness at a position 0.25 mm below the surface of the steel plate on the opposite side of the measurement start side. In this case, the measurement was made at HV 0.1 instead of HV 10 which is commonly used, 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]

**[0064]** 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 0.25 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). The conversion of dislocation density from strain  $\varepsilon$  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 Fe(a), and is set to 0.25 nm in this embodiment.

[Evaluation of SSCC resistance]

**[0065]** 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. In addition, at a hydrogen sulfide partial pressure of 0.1 bar and a carbon-dioxide partial pressure of 0.9 bar, evaluation was made in a similar way using a NACE standard TM0177 Solution B solution in accordance with the 4-point bending SSCC test specified by the EFC 16 standard. Furthermore, at a hydrogen sulfide partial pressure of 2 bar and a carbon dioxide partial pressure of 3 bar, evaluation was made using a NACE standard TM0177 Solution A solution 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.

[Evaluation of HIC resistance]

**[0066]** HIC resistance was determined by performing HIC test at a hydrogen sulfide partial pressure of 1 bar and with an immersion time of 96 hours using a NACE standard TM0177 Solution A solution. In addition, HIC resistance was determined by performing HIC test at a hydrogen sulfide partial pressure of 0.1 bar and a carbon-dioxide partial pressure of 0.9 bar and with an immersion time of 96 hours using a NACE standard TM0177 Solution B 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.

**[0067]** 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 0.25 mm below the surface and of  $t/2$ ;
- the HV 0.1 at 0.25 mm below the surface is 230 or less;
- no cracks are observed in the SSCC test in the 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 sample 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	0.042	0.30	1.24	0.005	0.0005	0.026	0.0040	0.06	0.08	0.22	0.08	0.030		0.010		0.003			0.89	782
B	0.041	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	0.065	0.32	1.44	0.005	0.0008	0.024	0.0035				0.01	0.015				0.002			0.97	774
D	0.051	0.13	1.31	0.004	0.0006	0.027	0.0038			0.22	0.10	0.040				0.002			0.93	778
E	0.048	0.25	1.29	0.004	0.0008	0.030	0.0035			0.35	0.01	0.035	0.035			0.002			0.91	786
F	0.045	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	0.93	773
G	0.040	0.28	1.30	0.004	0.0006	0.035	0.0043			0.25	0.12	0.035		0.013		0.001	0.002		0.89	780
H	0.085	0.20	1.29	0.005	0.0007	0.027	0.0034		0.05		0.15	0.025		0.012		0.001			1.06	766
I	0.051	0.23	1.83	0.005	0.0008	0.031	0.0041	0.12	0.04		0.02					0.002			1.09	742
J	0.052	0.22	1.25	0.005	0.0006	0.026	0.0035			0.90	0.02					0.001			1.06	779
K	0.047	0.15	1.30	0.006	0.0008	0.034	0.0038		0.02	0.11	0.60	0.025	0.035	0.010		0.001			1.13	741
L	0.042	0.30	1.14	0.005	0.0005	0.026	0.0040	0.20	0.27	0.08	0.030			0.010		0.003			0.83	781
M	0.042	0.30	1.35	0.004	0.0006	0.028	0.0041			0.30	0.00	0.032		0.011		0.002			0.88	784

Note 1: The balance is Fe and inevitable impurities.

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

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Table 2.

Steel sample ID	Plate thickness (mm)	Heating temp. (°C)	Rolling finish temp. (°C)	Rolling reduction ratio (%)	Cooling start temp. (°C)	Cooling rate in temp. range of 750 °C → 550 °C (°C/s)	Cooling rate in temp. range of 550 °C → lower (°C/s)	Cooling rate in temp. range of 750 °C → 550 °C (steel plate average) (°C/s)	Cooling stop temp. (°C)	Reheating temp. (°C)	Micro-structure (0.25 mm below the surface of the steel plate)	Micro-structure (at 1/2)	Tensile strength (MPa)	Average hardness (HV 0.1)	Hardness variation 3σ (0.25 mm below the surface of the steel plate)	Dislocation density (m <sup>-2</sup> )	Hardness variation 3σ (plate thickness direction) (HV 0.1)	SSCC resistance of the steel pipe		HIC resistance of the steel pipe		Category
																		Sol.A	Sol.B	Sol.A	Sol.B	
1	A	16	1100	890	75	850	50	65	180	395	500	B	579	185	23	3 × 10 <sup>14</sup>	25	Sol.A	Sol.B	Sol.A	Sol.B	Good
2	B	20	1080	890	75	850	45	55	180	300	500	B	585	189	22	3 × 10 <sup>14</sup>	24	Sol.A	Sol.B	Sol.A	Sol.B	Good
3	B	20	1080	890	75	850	50	53	170	410	500	B	596	200	18	5 × 10 <sup>14</sup>	26	Sol.A	Sol.B	Sol.A	Sol.B	Good
4	B	20	1080	890	75	850	50	56	190	300	550	B	587	191	25	6 × 10 <sup>14</sup>	22	Sol.A	Sol.B	Sol.A	Sol.B	Good
5	B	30	1080	880	75	830	40	35	180	380	550	B	599	197	19	3 × 10 <sup>14</sup>	21	Sol.A	Sol.B	Sol.A	Sol.B	Good
6	B	30	1080	880	75	860	45	38	170	350	500	B	615	195	22	2 × 10 <sup>14</sup>	18	Sol.A	Sol.B	Sol.A	Sol.B	Good
7	C	30	1080	850	80	810	35	32	190	400	500	B	605	183	24	3 × 10 <sup>14</sup>	28	Sol.A	Sol.B	Sol.A	Sol.B	Good
8	D	30	1080	870	75	840	50	28	160	300	550	B	587	184	23	5 × 10 <sup>14</sup>	27	Sol.A	Sol.B	Sol.A	Sol.B	Good
9	D	30	1080	830	75	810	45	37	180	350	500	B	612	188	22	6 × 10 <sup>14</sup>	26	Sol.A	Sol.B	Sol.A	Sol.B	Good
10	D	34	1080	850	70	810	50	33	180	390	500	B	622	193	20	5 × 10 <sup>14</sup>	25	Sol.A	Sol.B	Sol.A	Sol.B	Good
11	D	34	1080	870	70	840	40	35	200	420	500	B	596	193	21	4 × 10 <sup>14</sup>	26	Sol.A	Sol.B	Sol.A	Sol.B	Good
12	E	34	1080	870	75	820	45	36	190	380	500	B	582	190	24	4 × 10 <sup>14</sup>	19	Sol.A	Sol.B	Sol.A	Sol.B	Good
13	E	20	1080	890	75	850	45	55	150	340	500	B	576	189	24	3 × 10 <sup>14</sup>	28	Sol.A	Sol.B	Sol.A	Sol.B	Good
14	F	20	1080	890	75	850	45	55	180	320	500	B	587	187	24	4 × 10 <sup>14</sup>	27	Sol.A	Sol.B	Sol.A	Sol.B	Good
15	G	20	1080	890	75	850	45	55	180	320	500	B	587	187	24	4 × 10 <sup>14</sup>	27	Sol.A	Sol.B	Sol.A	Sol.B	Good

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

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

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Table 2 (cont'd)

Steel sample ID	Plate thickness (mm)	Heating temp. (°C)	Rolling finish temp. (°C)	Rolling reduction ratio (%)	Cooling start temp. (°C)	Cooling rate in temp. range of 750 °C → 550 °C (°C/s)	Cooling rate in temp. range of 550 °C → lower. (°C/s)	Cooling rate in temp. range of 750 °C → 550 °C (steel plate average) (°C/s)	Cooling rate in temp. range of 550 °C or lower. (°C/s)	Reheating temp. (°C)	Micro-structure (0.25 mm below the surface of the steel plate)	Micro-structure (at t/2)	Tensile strength (MPa)	Average hardness (0.25 mm below the surface of the steel plate) (HV 0.1)	Hardness variation 3σ (0.25 mm below the surface of the steel plate) (HV 0.1)	Dislocation density (0.25 mm below the surface of the steel plate) (m <sup>-2</sup> )	Hardness variation 3σ (plate thickness direction) (HV 0.1)	SSCC resistance of the steel pipe		HIC resistance of the steel pipe		Category
																		0.1 bar H <sub>2</sub> S + 0.9 bar CO <sub>2</sub>	1 bar H <sub>2</sub> S + 0.9 bar CO <sub>2</sub>	0.1 bar H <sub>2</sub> S + 2 bar H <sub>2</sub> S	1 bar H <sub>2</sub> S + 0.9 bar CO <sub>2</sub>	
16 B	20	980	880	75	840	51	160	51	160	320	B	B	512	198	2.5	3 × 10 <sup>14</sup>	(HV 0.1)	Sol.A	Sol.A	Sol.B	Good	Good
17 B	20	1080	780	75	730	53	170	53	170	350	F+B	F+B	508	200	2.2	2 × 10 <sup>14</sup>	25	Good	Good	Good	Good	Good
18 B	20	1080	840	75	810	5	160	5	160	370	B	F+P	515	192	2.5	1 × 10 <sup>14</sup>	26	Good	Good	Good	Good	Good
19 B	20	1080	850	75	810	55	180	55	180	200	B	B	629	240	2.6	9 × 10 <sup>14</sup>	33	Poor	Poor	Poor	Poor	Poor
20 B	20	1080	870	75	840	90	190	55	190	450	B	B	592	235	2.2	9 × 10 <sup>14</sup>	24	Poor	Poor	Poor	Good	Good
21 B	20	1080	860	75	840	52	110	52	110	430	B	B	586	220	3.8	5 × 10 <sup>14</sup>	33	Poor	Poor	Poor	Good	Good
22 B	20	1080	860	75	840	45	135	52	135	430	B	B	590	217	3.3	5 × 10 <sup>14</sup>	38	Poor	Poor	Poor	Good	Good
23 C	34	1080	890	75	850	29	170	29	170	360	B	B	584	245	1.8	10 × 10 <sup>14</sup>	22	Poor	Poor	Poor	Poor	Poor
24 H	34	1080	890	75	850	40	180	30	180	460	B	B	615	250	2.0	11 × 10 <sup>14</sup>	24	Poor	Poor	Poor	Poor	Poor
25 I	34	1080	820	75	800	45	160	36	160	500	B	B	625	235	2.5	9 × 10 <sup>14</sup>	25	Poor	Poor	Poor	Poor	Poor
26 J	34	1080	840	75	810	50	190	36	190	350	B	B	637	230	2.4	9 × 10 <sup>14</sup>	26	Poor	Poor	Poor	Poor	Poor
27 K	34	1080	860	75	810	50	200	38	200	430	B	B	611	252	2.2	11 × 10 <sup>14</sup>	26	Poor	Poor	Poor	Poor	Poor
28 L	34	1080	860	75	810	45	200	38	200	430	B	B	608	195	2.2	3 × 10 <sup>14</sup>	28	Good	Good	Good	Good	Good
29 M	34	1080	860	75	810	51	180	51	180	320	B	B	606	199	2.7	6 × 10 <sup>14</sup>	28	Good	Good	Good	Good	Good
30 B	20	1080	890	75	850	40	190	55	190	360	B	B	588	200	2.6	5 × 10 <sup>14</sup>	31	Good	Good	Good	Good	Good
31 B	20	1080	870	75	840	55	190	55	190	450	B	B	588	232	2.2	8 × 10 <sup>14</sup>	24	Good	Good	Good	Good	Good

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

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

**[0068]** As can be seen from Table 2, Nos. 1 to 15 are our examples in which the chemical compositions 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 0.25 mm below the surface and of t/2 was a bainite microstructure, the HV 0.1 at 0.25 mm below the surface was 230 or less, and hence the SSCC resistance and HIC resistance were also good in the high strength steel pipe made from the steel plate.

**[0069]** 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 strength was low and the HIC resistance after pipe making 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 making deteriorated. In No. 19, since the cooling stop temperature was low, the dislocation density at 0.25 mm below the surface increased, and the HV 0.1 exceeded 230, the SSCC resistance after pipe making 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 0.25 mm below the surface of the steel plate exceeded 50 °C/s, the dislocation density at 0.25 mm below the surface increased, and the HV 0.1 exceeded 230, and the SSCC resistance after pipe making 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 0.25 mm below the surface of the steel plate was lower than 150 °C/s, uneven cooling of the steel plate was remarkable. In addition, although the HV 0.1 was 230 or less on average, the variation in hardness was large and a locally high hardness portion was generated. Accordingly, the SSCC resistance after pipe making 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 0.25 mm below the surface was high, and the HV 0.1 exceeded 230, the SSCC resistance after pipe making was inferior. In addition, in Nos. 24 to 27, the HIC resistance was also inferior because the hardness of the central segregation area increased. In No. 28, the amount of Ni in the steel plate was excessive, and the SSCC resistance in environments with low hydrogen sulfide partial pressure deteriorated. In No. 29, the steel plate was Mo-free, and the SSCC resistance deteriorated in a very severe corrosion environment with a hydrogen sulfide partial pressure of 2 bar. In No. 30, since reheating was not performed, there was no effect of surface layer softening, and the SSCC resistance deteriorated in some cases under a very severe corrosive environment with a hydrogen sulfide partial pressure of 2 bar. In No. 31, the average cooling rate in a temperature range from 750 °C to 550 °C in terms of a temperature at 0.25 mm below the surface of the steel plate exceeded 50 °C/s, and the SSCC resistance deteriorated in some cases under a very severe corrosion environment with a hydrogen sulfide partial pressure of 2 bar.

## INDUSTRIAL APPLICABILITY

**[0070]** 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 and environments with low hydrogen sulfide partial pressure below 1 bar. 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.

## 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 %, Mo: 0.01 % to 0.50 %, Ca: 0.0005 % to 0.005 %, at least one selected from the group consisting of Nb: 0.005 % to 0.1 % and Ti: 0.005 % to 0.1 %, and optionally one or more of Cu: 0.50 % or less, Ni: 0.10 % or less, Cr: 0.50 % or less, V: 0.005 % to 0.1 %, Zr: 0.0005 % to 0.02 %, Mg: 0.0005 % to 0.02 %, and REM: 0.0005 % to 0.02 %, with the balance being Fe and inevitable impurities;

a steel microstructure at 0.25 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 0.25 mm below the surface of the steel plate being 30 HV or less at  $3\sigma$ , where

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$\sigma$  is a standard deviation;

a variation in Vickers hardness in a plate thickness direction being 30 HV or less at  $3\sigma$ , where  $\sigma$  is a standard deviation; and

a tensile strength being 520 MPa or more;

where the tensile strength is measured using a full-thickness test piece collected in a direction perpendicular to the rolling direction and the Vickers hardness HV 0.1 is measured for a cross section perpendicular to the rolling direction according to JIS Z 2244 as defined in the description.

### 2. 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 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 %, Mo: 0.01 % to 0.50 %, Ca: 0.0005 % to 0.005 %, at least one selected from the group consisting of Nb: 0.005 % to 0.1 % and Ti: 0.005 % to 0.1 %, and optionally one or more of Cu: 0.50 % or less, Ni: 0.10 % or less, Cr: 0.50 % or less, V: 0.005 % to 0.1 %, Zr: 0.0005 % to 0.02 %, Mg: 0.0005 % to 0.02 %, and REM: 0.0005 % to 0.02 %, 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 ( $Ar_3 - 10$  °C) or higher;

an average cooling rate in a temperature range from 750 °C to 550 °C in terms of a temperature at 0.25 mm below the surface of the steel plate being 50 °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 0.25 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; and

then reheating the steel plate with an average temperature of the steel plate being at least 50 °C higher than the cooling stop temperature and in a range of 450 °C to 600 °C.

### 3. A high strength steel pipe using the high strength steel plate for a sour-resistant line pipe as recited in claim 1.

## Patentansprüche

### 1. Hochfestes Stahlblech für ein säurebeständiges Leitungsrohr, umfassend:

eine chemische Zusammensetzung, die in Masse-% enthält: C: 0,02 % bis 0,08 %, Si: 0,01 % bis 0,50 %, Mn: 0,50 % bis 1,80 %, P: 0,001 % bis 0,015 %, S: 0,0002 % bis 0,0015 %, Al: 0,01 % bis 0,08 %, Mo: 0,01 % bis 0,50 %, Ca: 0,0005 % bis 0,005 %, mindestens eines, ausgewählt aus der Gruppe bestehend aus Nb: 0,005 % bis 0,1 % und Ti: 0,005 % bis 0,1 % und wahlweise eines oder mehrere aus Cu: 0,50 % oder weniger, Ni: 0,10 % oder weniger, Cr: 0,50 % oder weniger, V: 0,005 % bis 0,1 %, Zr: 0,0005 % bis 0,02 %, Mg: 0,0005 % bis 0,02 %, und REM: 0,0005 % bis 0,02 %, wobei der Rest Fe und unvermeidliche Verunreinigungen sind,

ein Stahlmikrogefüge bei 0,25 mm unterhalb einer Oberfläche des Stahlblechs, welches ein Bainitmikrogefüge mit einer Versetzungsdichte von  $1,0 \times 10^{14}$  bis  $7,0 \times 10^{14} \text{ m}^{-2}$  ist,

eine Variation der Vickershärte bei 0,25 mm unterhalb der Oberfläche des Stahlblechs von 30 HV oder weniger bei  $3\sigma$ , wobei  $\sigma$  eine Standardabweichung ist,

eine Variation der Vickershärte in Richtung der Blechdicke von 30 HV oder weniger bei  $3\sigma$ , wobei  $\sigma$  eine Standardabweichung ist, und

eine Zugfestigkeit von 520 MPa oder mehr,

wobei die Zugfestigkeit unter Verwendung eines Prüfstücks über die gesamte Dicke in einer Richtung senkrecht zur Walzrichtung gemessen wird und die Vickershärte HV 0,1 für einen Querschnitt senkrecht zur Walzrichtung gemäß JIS Z 2244, wie in der Beschreibung definiert, gemessen wird.

### 2. Verfahren zum Herstellen eines hochfesten Stahlblechs für ein säurebeständiges Leitungsrohr, wobei das Verfahren umfasst:



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Erhitzen einer Bramme auf eine Temperatur von 1000 °C bis 1300 °C, wobei die Bramme eine chemische Zusammensetzung aufweist, welche, in Masse-%, enthält: C: 0,02 % bis 0,08 %, Si: 0,01 % bis 0,50 %, Mn: 0,50 % bis 1,80 %, P: 0,001 % bis 0,015 %, S: 0,0002 % bis 0,0015 %, Al: 0,01 % bis 0,08 %, Mo: 0,01 % bis 0,50 %, Ca: 0,0005 % bis 0,005 %, mindestens eines, ausgewählt aus der Gruppe bestehend aus Nb: 0,005 % bis 0,1 % und Ti: 0,005 % bis 0,1 % und wahlweise eines oder mehrere aus Cu: 0,50 % oder weniger, Ni: 0,10 % oder weniger, Cr: 0,50 % oder weniger, V: 0,005 % bis 0,1 %, Zr: 0,0005 % bis 0,02 %, Mg: 0,0005 % bis 0,02 %, und REM: 0,0005 % bis 0,02 %, wobei der Rest Fe und unvermeidliche Verunreinigungen sind, und dann Warmwalzen der Bramme, um ein Stahlblech zu bilden, und anschließendes Unterziehen des Stahlblechs einem kontrollierten Abkühlen unter einer Reihe von Bedingungen, einschließlich:

einer Oberflächentemperatur des Stahlblechs, die zu Beginn des Abkühlens ( $Ar_3 - 10\text{ °C}$ ) oder mehr beträgt, einer durchschnittlichen Abkühlungsgeschwindigkeit in einem Temperaturbereich von 750 °C bis 550 °C, bezogen auf eine Temperatur bei 0,25 mm unter der Oberfläche des Stahlblechs, welche 50 °C/s oder weniger beträgt, einer durchschnittlichen Abkühlungsgeschwindigkeit in einem Temperaturbereich von 750 °C bis 550 °C, bezogen auf eine durchschnittliche Temperatur der Stahlplatte, welche 15 °C/s oder mehr beträgt, einer durchschnittlichen Abkühlungsgeschwindigkeit in einem Temperaturbereich von 550 °C bis zu einer Abkühlungsstoptemperatur, bezogen auf eine Temperatur bei 0,25 mm unter der Oberfläche des Stahlblechs, welche 150 °C/s oder mehr beträgt, einer Abkühlungsstoptemperatur, bezogen auf eine durchschnittliche Temperatur der Stahlplatte, welche 250 °C bis 550 °C beträgt, und anschließendes Wiedererwärmen der Stahlplatte mit einer Durchschnittstemperatur der Stahlplatte, die mindestens 50 °C höher ist als die Kühlstoptemperatur und in einem Bereich von 450 °C bis 600 °C liegt.

3. Hochfestes Stahlrohr unter Verwendung des hochfesten Stahlblechs für ein säurebeständiges Leitungsrohr wie in Anspruch 1 angegeben.

### Revendications

1. Plaque d'acier à haute résistance pour un tuyau de ligne résistant à l'acide, comprenant :

une composition chimique contenant, en % en masse, C : 0,02 % à 0,08 %, Si : 0,01 % à 0,50 %, Mn : 0,50 % à 1,80 %, P : 0,001 % à 0,015 %, S : 0,0002 % à 0,0015 %, Al : 0,01 % à 0,08 %, Mo : 0,01 % à 0,50 %, Ca : 0,0005 % à 0,005 %, au moins l'un choisi dans le groupe constitué de Nb : 0,005 % à 0,1 % et Ti : 0,005 % à 0,1 %, et facultativement un ou plusieurs parmi Cu : 0,50 % ou moins, Ni : 0,10 % ou moins, Cr : 0,50 % ou moins, V : 0,005 % à 0,1 %, Zr : 0,0005 % à 0,02 %, Mg : 0,0005 % à 0,02 %, et REM : 0,0005 % à 0,02 %, le reste étant Fe et des impuretés inévitables ; une microstructure d'acier à 0,25 mm sous une surface de la plaque d'acier étant une microstructure de bainite ayant une densité de dislocation de  $1,0 \times 10^{14}$  à  $7,0 \times 10^{14} \text{ m}^{-2}$  ; une variation de dureté Vickers à 0,25 mm sous la surface de la plaque d'acier étant de 30 HV ou moins à  $3\sigma$ , où  $\sigma$  est un écart type ; une variation de dureté Vickers dans une direction d'épaisseur de plaque étant de 30 HV ou moins à  $3\sigma$ , où  $\sigma$  est un écart type ; et une résistance à la traction étant de 520 MPa ou plus ; où la résistance à la traction est mesurée à l'aide d'une pièce test pleine épaisseur prélevée dans une direction perpendiculaire à la direction de laminage et la dureté Vickers HV 0,1 est mesurée pour une section transversale perpendiculaire à la direction de laminage selon la norme JIS Z 2244 telle que définie dans la description.

2. Procédé de fabrication d'une plaque d'acier à haute résistance pour un tuyau de ligne résistant à l'acide, le procédé comprenant les étapes consistant à :

chauffer une brame à une température allant de 1000 °C à 1300 °C, la brame ayant une composition chimique contenant, en % en masse, C : 0,02 % à 0,08 %, Si : 0,01 % à 0,50 %, Mn : 0,50 % à 1,80 %, P : 0,001 % à 0,015 %, S : 0,0002 % à 0,0015 %, Al : 0,01 % à 0,08 %, Mo : 0,01 % à 0,50 %, Ca : 0,0005 % à 0,005 %, au moins l'un choisi dans le groupe constitué de Nb : 0,005 % à 0,1 % et Ti : 0,005 % à 0,1 %, et facultativement un ou plusieurs parmi Cu : 0,50 % ou moins, Ni : 0,10 % ou moins, Cr : 0,50 % ou moins, V : 0,005 % à 0,1 %, Zr : 0,0005 % à 0,02 %, Mg : 0,0005 % à 0,02 %, et REM : 0,0005 % à 0,02 %, le reste étant Fe et des impuretés

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inévitables, puis laminier à chaud la brame pour former une plaque d'acier ;  
soumettre ensuite la plaque d'acier à un refroidissement régulé sous un ensemble de conditions comprenant :

- 5                    une température d'une surface de la plaque d'acier au début du refroidissement étant de ( $A_{r3} - 10$  °C) ou plus ;  
                      une vitesse de refroidissement moyenne dans une plage de températures de 750 °C à 550 °C en termes  
                      d'une température à 0,25 mm sous la surface de la plaque d'acier étant de 50 °C/s ou moins ;  
                      une vitesse de refroidissement moyenne dans une plage de températures de 750 °C à 550 °C en termes  
                      d'une température moyenne de la plaque d'acier étant de 15 °C/s ou plus ;  
10                    une vitesse de refroidissement moyenne dans une plage de températures de 550 °C à une température  
                      d'arrêt de refroidissement en termes d'une température à 0,25 mm sous la surface de la plaque d'acier  
                      étant de 150 °C/s ou plus ; et  
                      une température d'arrêt de refroidissement en termes d'une température moyenne de la plaque d'acier  
                      étant de 250 °C à 550 °C ; et
- 15                    réchauffer ensuite la plaque d'acier avec une température moyenne de la plaque d'acier qui est au moins 50  
                      °C supérieure à la température d'arrêt de refroidissement et dans une plage de 450 °C à 600 °C.

3. Tuyau en acier à haute résistance utilisant la plaque d'acier à haute résistance pour un tuyau de ligne résistant à  
l'acide selon la revendication 1.

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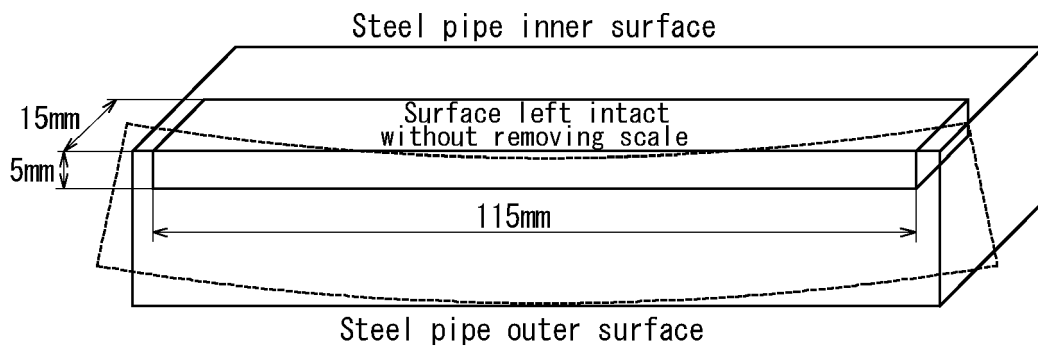
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*FIG. 1*



**REFERENCES CITED IN THE DESCRIPTION**

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