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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

HOCHFESTE STAHLPLATTE FÜR SAUERGASBESTÄNDIGES LEITUNGSROHR, VERFAHREN ZUR HERSTELLUNG DAVON UND HOCHFESTES STAHLROHR AUS HOCHFESTER STAHLPLATTE FÜR SAUERGASBESTÄNDIGES LEITUNGSROHR

PLAQUE D'ACIER HAUTE RÉSISTANCE POUR TUYAU DE CANALISATION RÉSISTANT À L'ACIDITÉ, SON PROCÉDÉ DE FABRICATION, ET TUYAU EN ACIER HAUTE RÉSISTANCE UTILISANT UNE PLAQUE D'ACIER HAUTE RÉSISTANCE POUR TUYAU DE CANALISATION RÉSISTANT À L'ACIDITÉ

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(56) References cited:

EP-A1- 2 832 889	**EP-A1- 3 081 662**
WO-A1-2017/018108	**JP-A- 2002 327 212**

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JP-A- 2003 013 138
JP-A- 2005 060 820
JP-A- 2008 056 962
JP-A- 2012 077 331
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JP-B2- 5 223 511

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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 interrupting accelerated cooling after rolling, leaving the surface recuperated, and then performing accelerated cooling again. 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.
Further steel sheets for high strength steel sheets, methods for producing the same, and steel pips using the high strength steel plate are disclosed in JP 5 223511 B2 and EP 2 832 889 A1.

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 HIC resistance and 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.

[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. That is, in the techniques described in PTLs 5 and 6, the cooling rate of the surface layer in accelerated cooling is not considered at all. Therefore, there is a possibility that the hardness of the surface layer can not be sufficiently reduced at the cooling rate for securing the tensile characteristics at mid-thickness part, and as a result, the variation in hardness occurs in the plate thickness direction.

[0012] It would thus helpful to provide a high strength steel plate for a sour-resistant line pipe that is excellent in HIC resistance and SSCC resistance under more severe corrosion environments and that is also excellent in hardness uniformity in the plate thickness direction, 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 HIC resistance and 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 0.5×10^{14} to 7.0×10^{14} (m^{-2}), and as a result the SSCC resistance of the steel pipe is improved.

[0014] In order to provide such a steel microstructure, the inventors also discovered that it is important to strictly control both the thermal hysteresis at 0.5 mm below the surface of the steel plate in controlled cooling and the average thermal hysteresis of the steel plate, and then reduce excess dislocations introduced by controlled cooling by induction heating. The inventors also discovered that the variation in hardness in the plate thickness direction can be remarkably reduced by performing induction heating under predetermined conditions taking into account T_1 and T_2 in controlled cooling, where T_1 denotes a temperature of the surface of the steel plate at the start of cooling and T_2 denotes a cooling stop temperature in terms of an average temperature of the steel plate. The present disclosure was completed based on the above discoveries.

[0015] The invention is specified in the appended claims.

(Advantageous Effect)

[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 in HIC resistance and SSCC resistance under more severe corrosion environments, and excellent in hardness uniformity in the thickness direction. 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 in HIC resistance and SSCC resistance under more severe corrosion environments and that is also excellent in hardness uniformity in the thickness direction.

BRIEF DESCRIPTION OF THE DRAWINGS

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

DETAILED DESCRIPTION

[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]

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

C: 0.02 % to 0.08 %

[0020] C 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 increases during accelerated cooling, causing deterioration in HIC resistance and SSCC 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 %

[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 %

[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 central segregation area increases during accelerated cooling, causing deterioration in 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 %

[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. 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.

S: 0.0002 % to 0.0015 %

[0024] S is an inevitable impurity element that forms MnS inclusions in the steel and degrades the HIC resistance, and hence a lower S content is preferable. However, up to 0.0015 % is acceptable. Although a lower S content is preferable, the S content is set to 0.0002 % or more from the viewpoint of the refining cost.

Al: 0.01 % to 0.08 %

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

Ca: 0.0005 % to 0.005 %

[0026] 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 %.

[0027] 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

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

Ni: 0.50 % or less

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

Cr: 0.50 % or less

[0030] 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 weldability deteriorates. Therefore, when Cr is added, the Cr content is up to 0.50 %.

Mo: 0.50 % or less

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

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

[0033] One or more selected from the group consisting of Nb: 0.005 % to 0.1 %, V: 0.005 % to 0.1 %, and Ti: 0.005 % to 0.1 %

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 %.

[0034] 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. Therefore, the CP value obtained by the following Expression (1) is set to 1.00 or less. For any element not added, what is necessary is just to substitute 0.

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

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

[0035] 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.

[0036] The balance other than the above-described elements is Fe and inevitable impurities.

[Microstructure of the steel plate]

[0037] 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, 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.

[0038] 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 0.5×10^{14} to 7.0×10^{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 0.5 mm below the surface of the steel plate is 7.0×10^{14} (m^{-2}) or less. Conversely, if the dislocation density at 0.5 mm below the surface of the steel plate exceeds 7.0×10^{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 6.0×10^{14} (m^{-2}) or less in order to obtain good SSCC resistance after pipe making. On the other hand, when the dislocation density at 0.5 mm below the surface of the steel plate is less than 0.5×10^{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 1.0×10^{14} (m^{-2}) 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.

[0039] When the dislocation density at 0.5 mm below the surface of the steel plate is 7.0×10^{14} (m^{-2}) 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.

[0040] Further, in the high strength steel plate disclosed herein, in addition to the average value of Vickers hardness at 0.5 mm below the surface of the steel plate being 230 HV or less, it is also important from the viewpoint of securing the material property in the mid-thickness part while suppressing an increase in the hardness of the surface layer that the difference ΔHV between the average value of Vickers hardness at 0.5 mm below the surface of the steel plate and the average value of Vickers hardness at the mid-thickness part of the steel plate is 25 HV or less. More preferably, ΔHV is 20 HV or less.

[0041] 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]

[0042] 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 by induction heating.

[Slab heating temperature]

Slab heating temperature: 1000 °C to 1300 °C

[0043] 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]

[0044] 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 a 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, the rolling reduction ratio in a temperature range of 950 °C or lower corresponding to the austenite non-recrystallization temperature range is set to 60 % or more. The temperature of the surface of the steel plate can be measured by a radiation thermometer or the like.

$$Ar_3\ (^\circ C) = 910 - 310\,[\%C] - 80\,[\%Mn] - 20\,[\%Cu] - 15\,[\%Cr] - 55\,[\%Ni] - 80\,[\%Mo],$$

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

[Cooling start temperature in the controlled cooling]

[0045] T_1 is (Ar_3 - 10 °C) or higher, where T_1 denotes a temperature of the surface of the steel plate at the start of cooling.

[0046] 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 Ar3 transformation temperature is greater than 10 °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 °C) or higher.

[Cooling rate of the controlled cooling]

[0047] In order to reduce the variation in hardness in the steel plate and improve the material homogeneity while achieving high strength, it is necessary to secure the cooling rate in the transformation temperature zone in the mid-thickness part while suppressing the cooling rate in the surface layer (specifically, at a depth of 0.5 mm below the surface of the steel plate).

[0048] 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: 100 °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 0.5 mm below the surface of the steel plate exceeds 100 °C/s, the dislocation density at 0.5 mm below the surface of the steel plate exceeds 7.0×10^{14} (m^{-2}). 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 100 °C/s or lower. Preferably, it is 80 °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, 10 °C/s or higher is preferable.

[0049] 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 can not be obtained, causing deterioration in the strength and HIC resistance, and also causing more variations in the hardness in the plate thickness direction, and the like. Therefore, the cooling rate in terms of an average temperature of the steel plate is set to 15 °C/s or higher. From the viewpoint of 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.

[0050] Although the temperature at 0.5 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 0.5 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] T_2 is 250 °C to 550 °C, where T_2 is a cooling stop temperature 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. When the cooling stop temperature is lower than 250 °C, martensite and martensite austenite constituent (MA) are formed, and in particular, the variation in hardness in the plate thickness direction becomes significant. 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.

[Induction heating conditions]

[0053] T_3 is 550 °C to 750 °C, where T_3 denotes an induction heating temperature in terms of a temperature of the surface of the steel plate.

[0054] In this embodiment, after the controlled cooling, it is important to temper the steel plate to reduce the high-density dislocations introduced into the bainite due to the controlled cooling. As a result, the dislocation density at 0.5 mm below the steel plate surface becomes 7.0×10^{14} (m^{-2}) or less, and excellent SSCC resistance is obtained. In addition, the difference ΔHV between the average value of Vickers hardness at 0.5 mm below the surface of the steel plate and the average value of Vickers hardness at the mid-thickness part of the steel plate can be set to 25 HV or less. In this respect, when the induction heating temperature is below 550 °C, sufficient tempering effect can not be obtained, and even if the dislocation density of the surface layer can be set to 7.0×10^{14} (m^{-2}) or less, ΔHV can not be set to 25 HV or lower. In addition, when the induction heating temperature exceeds 750 °C, the mid-thickness part is also tempered, in which case a predetermined strength may not be obtained. Therefore, in order to secure the strength at the mid-thickness part while suppressing the deterioration of the material homogeneity in the steel plate, the end-point temperature of on-line induction heating is set to 550 °C to 750 °C in terms of a temperature of the surface of the steel plate. In this embodiment, it is important not to temper the inside of the steel plate as much as possible in order to suppress a decrease in strength, and it is important to temper only the surface layer. Therefore, heating is performed using an on-line induction heating device.

[0055] With regard to the reheating conditions, TP defined by the following Expression (2) is 0.50 or more and preferably 1.50 or less.

[0056] More preferably, it is 0.60 or more and 1.00 or less.

$$TP = (T_3 - T_2) \times T_2 / (T_1 - T_2)^2 \qquad (2)$$

TP is a relational expression of tempering to the degree of supercooling of controlled cooling. When TP satisfies 0.50 or more, the dislocations in the surface layer introduced by the accelerated cooling can be sufficiently recovered without excessive tempering at the mid-thickness part, and it is possible to significantly suppress the variation in hardness in the thickness direction. Specifically, ΔHV can be set to 20 or less.

[High strength steel pipe]

[0057] 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.

[0058] 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

[0059] The steels (Steels A to I) 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. Immediately thereafter, each steel plate was reheated by the method presented in "Heating method" in Table 2 such that the temperature of the surface of the steel plate reached "Maximum temperature in reheating" in Table 2.

[Identification of microstructure]

[0060] 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]

[0061] 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]

[0062] For a cross section perpendicular to the rolling direction, according to JIS Z 2244, Vickers hardness (HV 0.1) was measured at 20 locations at a position 0.5 mm below the surface of each steel plate, and the measurement results were averaged. Further, Vickers hardness (HV 0.1) was similarly measured at 20 locations at the mid-thickness part, and the measurement results were averaged. Then, the absolute value ΔHV of the difference between the averages was determined. 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]

[0063] 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 β of X-ray diffraction measurement. In a diffraction intensity curve obtained by ordinary X-ray diffraction, Kα1 and Ka2 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 ε, 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 ε 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 ε, the following equation was used: $p = 14.4\ \varepsilon^2/b^2$. As used herein, θ means the peak angle calculated by the θ-2θ method for X-ray diffraction, and λ means the wavelength of the X-ray used in the X-ray diffraction. b is a Burgers vector of Fe(α), which is 0.25 nm in this embodiment.

[Evaluation of SSCC resistance]

[0064] 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 × 15 mm × 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.

[Evaluation of HIC resistance]

[0065] HIC resistance was determined by performing HIC test with an immersion time of 96 hours in accordance with the NACE Standard TM-02-84. The HIC resistance was judged as "Good" when no cracks were observed, or "Poor" when cracking occurred. The results are listed in Table 2.

[0066] 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;
- the absolute value ΔHV of the difference between the hardness at 0.5 mm below the surface and the hardness at the mid-thickness part is 25 or less;
- no cracks are observed in the SSCC test in high strength steel pipe made from the corresponding steel plate; and
- no cracks are observed in the HIC test.

[0067] Example 9 is a Comparative Example (TP is too low).

Table 1

Steel ID	Chemical composition (mass%)														CP	Ar_3 temp. (°C)
	C	Si	Mn	P	S	Al	Cu	Ni	Cr	Mo	Nb	V	Ti	Ca		
A	0.045	0.26	1.61	0.004	0.0003	0.024								0.003	0.93	767
B	0.056	0.31	1.20	0.004	0.0008	0.028	0.31	0.40			0.020			0.003	0.89	768
c	0.040	0.30	1.35	0.005	0.0005	0.027			0.25	0.12	0.030		0.010	0.003	0.93	776
D	0.051	0.28	1.23	0.004	0.0004	0.032	0.21	0.21	0.20	0.15	0.020		0.012	0.001	0.96	765
E	0.042	0.25	1.40	0.005	0.0007	0.027			0.21	0.08	0.025	0.010		0.002	0.94	775
F	0.055	0.28	1.22	0.009	0.0008	0.027		0.16	0.18	0.22	0.024		0.012	0.001	1.07	766
G	0.061	0.12	1.82	0.005	0.0006	0.031					0.010			0.002	1.10	745
H	0.048	0.33	1.17	0.017	0.0006	0.021			0.26	0.20			0.008	0.001	1.20	782
I	0.052	0.02	1.28	0.006	0.0026	0.034		0.18	0.15	0.08	0.025	0.030	0.010	0.001	0.97	773

Note 1: The balance is Fe and inevitable impurities.
Note 2: Underlined if outside the scope of the disclosure.

Table 2

						Controlled cooling					Reheating			Microstructure								
No.	Steel ID	Plate thick-ness	Heating temp.	Rolling finish temp.	Rolling reduction ratio	Cooling start temp. T1	Cooling start temp. - Ar_3	Cooling rate in temp. range of 750 °C→ 550 °C (0.5 mm below the surface of the steel plate)	Cooling rate in temp. range of 750 °C→ 550 °C (steel plate average)	Cooling stop temp. T2	Heating method	Max. temp. T3	TP	0.5 mm below the surface of the steel plate	t/2	Tensile strength	Dislocation density at 0.5 mm below the surface of the steel plate	Average hardness HV at 0.5 mm below the surface of the steel plate	ΔHV |0.5mm below the surface of the steel plate – t/2|	SSCC resistance of the steel pipe	HIC resistance of the steel pipe	Category
		(mm)	(°C)	(°C)	(%)	(°C)	(°C)	(°C/s)	(°C/s)	(°C)		(°C)	(-)			(MPa)	(m^{-2})	(HV 0.1)	(HV 0.1)			
1	A	17.5	1100	850	75	785	18	66	75	430	induction heating	650	0.75	B	B	579	3.7E+14	211	19	Good	Good	Example
2	B	20	1080	850	75	830	62	39	37	520	induction heating	660	0.76	B	B	555	2.8E+14	201	16	Good	Good	
3	C	20	1080	880	75	820	44	63	67	425	induction heating	680	0.69	B	B	610	5.0E+14	220	18	Good	Good	
4	D	20	1050	880	75	810	45	61	54	500	induction heating	680	0.94	B	B	598	4.5E+14	209	10	Good	Good	
5	D	20	1050	850	75	785	20	64	52	500	induction heating	650	0.92	B	B	572	3.2E+14	204	15	Good	Good	
6	D	20	1050	850	75	780	15	87	68	450	induction heating	590	0.58	B	B	585	5.4E+14	208	14	Good	Good	
7	D	30	1050	850	70	815	50	35	31	495	induction heating	680	0.89	B	B	566	1.9E+14	195	7	Good	Good	
8	E	34	1150	870	70	825	50	46	23	390	induction heating	700	0.64	B	B	551	3.3E+14	206	18	Good	Good	
9	C	20	1080	880	75	820	44	68	70	430	induction heating	600	0.48	B	B	587	5.7E+14	220	24	Good	Good	

Note 1: Underlined if outside of the scope of the disclosure.
Note 2: For the microstructures, B indicates bainite, F indicates ferrite, M indicates martensite, and MA indicates martensite austenite constituent.

Table 2 (cont'd)

						Controlled cooling					Reheating			Microstructure								
No.	Steel ID	Plate thick-ness	Heating temp.	Rolling finish temp.	Rolling reduction ratio	Cooling start temp. T1	Cooling start temp. - Ar_3	Cooling rate in temp. range of 750 °C→ 550 °C (0.5 mm below the surface of the steel plate)	Cooling rate in temp. range of 750 °C→ 550 °C (steel plate average)	Cooling stop temp. T2	Heating method	Max. temp. T3	TP	0.5 mm below the surface of the steel plate	t/2	Tensile strength	Dislocation density at 0.5 mm below the surface of the steel plate	Average hardness HV at 0.5 mm below the surface of the steel plate	ΔHV |0.5mm below the surface of the steel plate – t/2|	SSCC resistance of the steel pipe	HIC resistance of the steel pipe	Category
		(mm)	(°C)	(°C)	(%)	(°C)	(°C)	(°C/s)	(°C/s)	(°C)		(°C)	(-)			(MPa)	(m^{-2})	(HV 0.1)	(HV 0.1)			
10	C	20	1080	880	75	820	44	60	43	240	induction heating	680	0.31	B+M	B+MA	616	5.0E+14	228	28	Good	Good	Comparative example
11	C	20	1080	880	75	820	44	188	71	470	induction heating	650	0.69	B+M	B	605	2.2E+15	258	58	Poor	Good	
12	C	20	1080	880	75	820	44	120	65	490	induction heating	650	0.68	B	B	601	9.6E+14	232	27	Poor	Good	
13	C	20	1080	880	75	820	44	37	6	540	induction heating	650	0.76	B	F+B	515	1.9E+14	200	29	Good	Poor	
14	C	20	1080	880	75	820	44	77	64	420	induction heating	500	0.21	B	B	603	6.1E+14	224	26	Good	Good	
15	C	20	1080	880	75	820	44	61	58	420	furnace heating	650	0.60	B	B	518	3.9E+14	204	12	Good	Good	
16	C	20	1080	880	75	820	44	64	66	420	none	-	-	B	B	586	7.8E+14	234	28	Poor	Good	
17	F	34	1150	850	65	820	68	58	20	450	induction heating	660	0.69	B	B	578	5.5E+14	207	14	Good	Poor	
18	G	34	1150	850	70	790	40	48	23	380	induction heating	630	0.57	B	B	589	3.2E+14	208	12	Good	Poor	
19	H	34	1150	860	70	820	38	52	17	490	induction heating	630	0.63	B	B	558	3.4E+14	198	12	Good	Poor	
20	I	34	1150	860	70	820	52	31	18	520	induction heating	630	0.64	B	B	534	1.8E+14	187	10	Good	Poor	

Note 1: Underlined if outside of the scope of the disclosure.
Note 2: For the microstructures, B indicates bainite, F indicates ferrite, M indicates martensite, and MA indicates martensite austenite constituent.

[0068] As can be seen from Table 2, Nos. 1 to 8 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 ΔHV was 25 or less, and hence the SSCC resistance and HIC resistance were also good in each high strength steel pipe produced using the steel plate.

[0069] In contrast, Nos. 10 to 16 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. 10, since the cooling stop temperature was low, the difference in hardness between the surface layer and the mid-thickness part was large. In Nos. 11 and 12, the controlled cooling conditions were outside the scope of the present disclosure, and the dislocation density was significantly increased in the surface layer of the steel plate, with the result that the surface hardness increased and SSCC occurred. In No. 13, the steel plate average cooling rate was not sufficiently secured, and ferrite was formed at the mid-thickness part, resulting in a decrease in strength. In No. 14, the heating temperature in the on-line induction heating was not optimal, and a difference occurred in the hardness in the plate thickness direction. In No. 15, although tempering was carried out by furnace heating, the temperature rise rate was so slow that the entire plate thickness was evenly tempered, resulting in a low strength. In No. 16, reheating was not performed, the surface layer was not softened by tempering, and thus the dislocation density of the surface layer was high and SSCC occurred. The variation in hardness in the thickness direction was also large. In Nos. 17 to 20, the chemical compositions of the steel plates were out of the range of the present disclosure, causing deterioration in the HIC resistance.

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 in HIC resistance and SSCC resistance under more severe corrosion environments and that is also excellent in hardness uniformity in the thickness direction. 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 %, optionally, 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, Mo: 0.50 % or less, Nb: 0.005 % to 0.1 %, V: 0.005 % to 0.1 %, and Ti: 0.005 % to 0.1 %, where a CP value determined by the following Expression (1) is 1.00 or less, with the balance being Fe and inevitable impurities:

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

where [%X] indicates the content by mass% of the element X in steel;
a steel microstructure at 0.5 mm below a surface of the steel plate consisting of a bainite microstructure having a dislocation density of 0.5×10^{14} to 7.0×10^{14} m^{-2} and the balance being at least one of ferrite, martensite, pearlite, martensite austenite constituent and retained austenite having a volume fraction of less than 5 %;
a difference ΔHV between an average value of Vickers hardness at 0.5 mm below the surface of the steel plate and an average value of Vickers hardness at a mid-thickness part being 25 HV or less; and
a tensile strength being 520 MPa or more, whereas the HV, the average value and the dislocation density are determined as indicated 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 %, and Ca: 0.0005 % to 0.005 %, optionally, 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, Mo: 0.50 % or less, Nb: 0.005 % to 0.1 %, V: 0.005 % to 0.1 %, and Ti: 0.005 % to 0.1 %, where a CP value determined by the following Expression (1) is 1.00 or less, with the balance being Fe and inevitable impurities, and then hot rolling the slab to form a steel plate with a rolling reduction ratio of 60 % or more:

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

where [%X] indicates the content by mass% of the element X in steel;
then subjecting the steel plate to controlled cooling under a set of conditions including:

T_1 being (Ar_3 - 10 °C) or higher, where T_1 denotes a temperature of a surface of the steel plate at the start of cooling;
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 100 °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; and
T_2 being 250 °C to 550 °C, where T_2 denotes a cooling stop temperature in terms of an average temperature of the steel plate; and

then reheating the steel plate by induction heating such that the average temperature of the steel plate is the cooling stop temperature T_2 or higher and the temperature of the surface of the steel plate is a heating temperature T_3 of 550 °C to 750 °C,
wherein the reheating is performed so as to satisfy a condition that TP defined by the following Expression (2) is 0.50 or more:

$$TP = (T_3 - T_2) \times T_2 / (T_1 - T_2)^2 \qquad (2).$$

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. Hochfeste Stahlplatte für ein sauergasbeständiges 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 % und Ca: 0,0005 % bis 0,005 %, gegebenenfalls, in Masse-%, mindestens eines, ausgewählt aus der Gruppe bestehend aus Cu: 0,50 % oder weniger, Ni: 0,50 % oder weniger, Cr: 0,50 % oder weniger, Mo: 0,50 % oder weniger, Nb: 0,005 % bis 0,1 %, V: 0,005 % bis 0,1 % und Ti: 0,005 % bis 0,1 %, wobei ein CP-Wert, der durch den folgenden Ausdruck (1) bestimmt wird, 1,00 oder weniger beträgt, wobei der Rest Fe und unvermeidliche Verunreinigungen sind:

$$CP = 4{,}46\ [\%C] + 2{,}37\ [\%Mn] / 6 + (1{,}74\ [\%Cu] + 1{,}7\ [\%Ni]) / 15 + (1{,}18\ [\%Cr] + 1{,}95\ [\%Mo] + 1{,}74\ [\%V]) / 5 + 22{,}36\ [\%P] \qquad (1),$$

wobei [%X] den Massenanteil des Elements X im Stahl angibt,
ein Stahlmikrogefüge 0,5 mm unterhalb einer Oberfläche der Stahlplatte, das aus einem Bainitmikrogefüge mit einer Versetzungsdichte von $0{,}5 \times 10^{14}$ bis $7{,}0 \times 10^{14}$ m^{-2} besteht, wobei der Rest mindestens eines von Ferrit, Martensit, Perlit, Martensit-Austenit-Bestandteil und Restaustenit mit einem Volumenanteil von weniger als 5 % ist,
eine Differenz ΔHV zwischen einem Durchschnittswert der Vickershärte bei 0,5 mm unter der Oberfläche des Stahlblechs und einem Durchschnittswert der Vickershärte bei einem Teil der mittleren Dicke, die 25 HV oder weniger beträgt, und
eine Zugfestigkeit, die 520 MPa oder mehr beträgt, wobei die HV, der Durchschnittswert und die Versetzungsdichte wie in der Beschreibung angegeben bestimmt werden.

2. Verfahren zur Herstellung einer hochfesten Stahlplatte für ein sauergasbeständiges Leitungsrohr, wobei das Verfahren umfasst:

Erhitzen einer Bramme auf eine Temperatur von 1000 °C bis 1300 °C, wobei die Bramme eine chemische Zusammensetzung aufweist, 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 % und Ca: 0,0005 % bis 0,005 %, gegebenenfalls, in Masse-%, mindestens eines aus der Gruppe bestehend aus Cu: 0,50 % oder weniger, Ni: 0,50 % oder weniger, Cr: 0,50 % oder weniger, Mo: 0,50 % oder weniger, Nb: 0,005 % bis 0,1 %, V: 0,005 % bis 0,1 %, und Ti: 0,005 % bis 0,1 %, wobei ein CP-Wert, der durch den folgenden Ausdruck (1) bestimmt wird, 1,00 oder weniger beträgt, wobei der Rest Fe und unvermeidliche Verunreinigungen sind, und dann Warmwalzen der Bramme, um eine Stahlplatte mit einem Walzreduktionsverhältnis von 60 % oder mehr zu bilden:

$$CP = 4{,}46\,[\%C] + 2{,}37\,[\%Mn]\,/\,6 + (1{,}74\,[\%Cu] + 1{,}7\,[\%Ni])\,/\,15 + (1{,}18\,[\%Cr] + 1{,}95\,[\%Mo] + 1{,}74\,[\%V])\,/\,5 + 22{,}36\,[\%P] \qquad (1),$$

wobei [%X] den Massenanteil des Elements X im Stahl angibt,
anschließendes Unterziehen der Stahlplatte einer kontrollierten Kühlung unter einer Reihe von Bedingungen, einschließlich:

T_1 ist (Ar_3 - 10 °C) oder höher, wobei T, die Temperatur einer Oberfläche der Stahlplatte zu Beginn der Kühlung bezeichnet,
eine durchschnittliche Abkühlungsgeschwindigkeit in einem Temperaturbereich von 750 °C bis 550 °C, bezogen auf eine Temperatur 0,5 mm unter der Oberfläche der Stahlplatte, beträgt 100 °C/s oder weniger,
eine durchschnittliche Abkühlungsgeschwindigkeit in einem Temperaturbereich von 750 °C bis 550 °C, bezogen auf eine durchschnittliche Temperatur der Stahlplatte, beträgt 15 °C/s oder mehr und
T_2 beträgt 250 °C bis 550 °C, wobei T_2 eine Kühlstopptemperatur, bezogen auf eine durchschnittliche Temperatur der Stahlplatte, bezeichnet, und
anschließendes Wiedererwärmen der Stahlplatte durch Induktionserwärmung, so dass die durchschnittliche Temperatur der Stahlplatte die Kühlstopptemperatur T_2 oder mehr beträgt und die Temperatur der Oberfläche der Stahlplatte eine Erwärmungstemperatur T_3 von 550 °C bis 750 °C ist,
wobei das Wiedererwärmen so durchgeführt wird, dass eine Bedingung, dass TP, definiert durch den folgenden Ausdruck (2), 0,50 oder mehr beträgt, erfüllt ist:

$$TP = (T_3 - T_2) \times T_2 / (T_1 - T_2)^2 \qquad (2).$$

3. Hochfestes Stahlrohr unter Verwendung der hochfesten Stahlplatte für ein sauergasbeständiges Leitungsrohr nach Anspruch 1.

Revendications

1. Plaque d'acier à haute résistance pour un tuyau de canalisation résistant à l'acidité, 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 %, et Ca : 0,0005 % à 0,005 %, facultativement, en % en masse, au moins l'un choisi parmi le groupe constitué de Cu : 0,50 % ou moins, Ni : 0,50 % ou moins, Cr : 0,50 % ou moins, Mo : 0,50 % ou moins, Nb : 0,005 % à 0,1 %, V : 0,005 % à 0,1 %, et Ti: 0,005 % à 0,1 %, où une valeur CP déterminée par l'Expression suivante (1) est de 1,00 ou moins, le reste étant Fe et des impuretés inévitables :

$$CP = 4{,}46\,[\%C] + 2{,}37\,[\%Mn]/6 + (1{,}74\,[\%Cu] + 1{,}7\,[\%Ni])/15 + (1{,}18\,[\%Cr] + 1{,}95\,[\%Mo] + 1{,}74\,[\%V])/5 + 22{,}36\,[\%P] \qquad (1),$$

où [%X] indique la teneur en % en masse de l'élément X dans l'acier ;

une microstructure en acier à 0,5 mm au-dessous d'une surface de la plaque d'acier constituée d'une microstructure de bainite ayant une densité de dislocations de $0{,}5 \times 10^{14}$ à $7{,}0 \times 10^{14}$ m^{-2} et le reste étant au moins l'un parmi un constituant ferrite, martensite, perlite, martensite austénite et de l'austénite retenue ayant une fraction volumique inférieure à 5 % ;
une différence ΔHV entre une valeur moyenne de dureté Vickers à 0,5 mm au-dessous de la surface de la plaque d'acier et une valeur moyenne de dureté Vickers au niveau d'une partie à mi-épaisseur étant de 25 HV ou moins ; et
une résistance à la traction étant de 520 MPa ou plus, alors que la HV, la valeur moyenne et la densité de dislocations sont déterminées comme indiqué dans la description.

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

chauffer une brame jusqu'à une température de 1 000°C à 1 300°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 %, et Ca : 0,0005 % à 0,005 %, facultativement, en % en masse, au moins l'un choisi parmi le groupe constitué de Cu : 0,50 % ou moins, Ni : 0,50 % ou moins, Cr: 0,50 % ou moins, Mo : 0,50 % ou moins, Nb : 0,005 à 0,1 %, V: 0,005 % à 0,1 %, et Ti: 0,005 à 0,1 %, où une valeur CP déterminée par l'Expression (1) suivante est de 1,00 ou moins, le reste étant Fe et des impuretés inévitables, puis laminer à chaud la brame pour former une plaque d'acier ayant un taux de réduction de laminage de 60 % ou plus :

$$CP = 4{,}46\,[\%C] + 2{,}37\,[\%Mn]/6 + (1{,}74\,[\%Cu] + 1{,}7\,[\%Ni])/15 + (1{,}18\,[\%Cr] + 1{,}95\,[\%Mo] + 1{,}74\,[\%V])/5 + 22{,}36\,[\%P] \qquad (1),$$

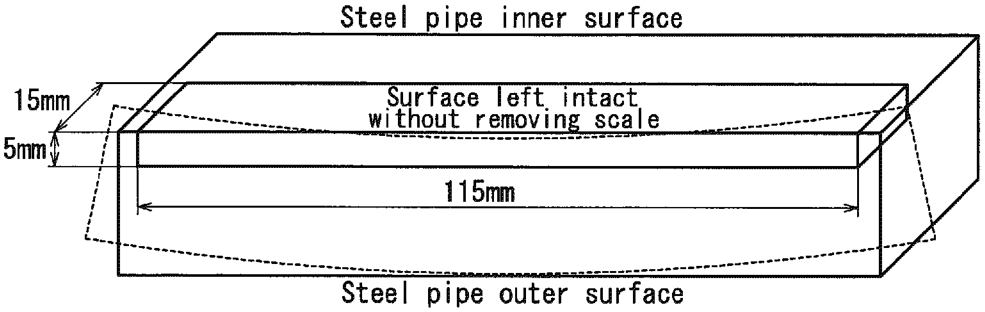
où [%X] indique la teneur en % en masse de l'élément X dans l'acier ;
puis soumettre la plaque d'acier à un refroidissement régulé sous un ensemble de conditions comprenant :

T_1 étant (Ar_3 - 10°C) ou plus, où T_1 désigne une température d'une surface de la plaque d'acier au début du refroidissement ;
une vitesse de refroidissement moyenne dans une plage de température de 750°C à 550°C en termes de température à 0,5 mm au-dessous de la surface de la plaque d'acier étant de 100°C/s ou moins ;
une vitesse de refroidissement moyenne dans une plage de température de 750°C à 550°C en termes de température moyenne de la plaque d'acier étant de 15°C/s ou plus; et
T_2 étant de 250°C à 550°C, où T_2 désigne une température d'arrêt de refroidissement en termes de température moyenne de la plaque d'acier ; et réchauffer alors la plaque d'acier par chauffage par induction de telle sorte que la température moyenne de la plaque d'acier est la température d'arrêt de refroidissement T_2 ou plus et la température de la surface de la plaque d'acier est une température de chauffage T_3 de 550°C à 750°C,
dans lequel le réchauffage est effectué de manière à satisfaire à une condition telle que TP définie par l'Expression suivante (2) est de 0,50 ou plus :

$$TP = (T_3 - T_2) \times T_2/(T_1 - T_2)^2 \qquad (2).$$

3. Tuyau en acier à haute résistance utilisant la plaque d'acier à haute résistance pour un tuyau de canalisation résistant à l'acidité telle que définie dans la revendication 1.

FIG. 1


Steel pipe inner surface
15mm
Surface left intact without removing scale
5mm
115mm
Steel pipe outer surface

REFERENCES CITED IN THE DESCRIPTION

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]**
- JP 5223511 B **[0006]**
- EP 2832889 A1 **[0006]**