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(54) **A METHOD OF MAKING A Cr-CONTAINING STEEL PIPE FOR LINEPIPE EXCELLENT IN INTERGRANULAR STRESS CORROSION CRACKING RESISTANCE OF WELDED HEAT AFFECTED ZONE**

EINE METHODE ZUR HERSTELLUNG EINES CR-HALTIGEN STAHLROHRS FÜR EIN LEITUNGSROHR MIT HERVORRAGENDER BESTÄNDIGKEIT GEGEN INTERKRISTALLINE SPANNUNGSRISSKORROSION DER WÄRMEBEEINFLUSSTEN SCHWEISZZONE

PROCÉDÈ DE FABRICATION D'UN TUBE D'ACIER CONTENANT DU Cr DESTINÉ À UN TUBE DE CANALISATION EXCELLENT EN TERMES DE RÉSISTANCE À LA FISSURATION INTERGRANULAIRE PAR CORROSION SOUS TENSION D'UNE ZONE SOUDÉE TOUCHÉE PAR LA CHALEUR

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(73) Proprietor: **JFE Steel Corporation**
Tokyo 100-0011 (JP)

(72) Inventors:
- **MIYATA, Yukio**
  Tokyo 100-0011 (JP)
- **KIMURA, Mitsuo**
  Tokyo 100-0011 (JP)

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

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Description

[Technical Field]

[0001] The present invention relates to a method of making a Cr containing steel pipe which is suitable as a steel pipe for linepipe to be used for transporting crude oil or natural gas which are produced at an oil well or a gas well, in particular, having excellent resistance to intergranular stress corrosion cracking (or resistance to IGSCC) in a welded heat affected zone.

[Background Art]

[0002] Nowadays, deep layer oil wells and gas wells to which consideration has not been given due to their great depth or oil wells and gas wells whose development was abandoned due to their intensely corrosive environment and so forth are being actively developed from the viewpoint of skyrocketing crude oil prices and the depletion of oil resources which is anticipated in the near future. Such oil wells and gas wells are generally arranged deep in the ground and in an intensely corrosive environment, for example, in a high temperature atmosphere containing carbon dioxide gas CO_2, chloride ions Cl^-, and so forth. In addition, oil wells and gas wells which are arranged in a severe drilling environment, for example, at the bottom of the ocean are also being actively developed. For pipelines transporting crude oil or natural gas produced at such oil wells or gas wells, it is required to use a steel pipe having not only high strength and high toughness but also excellent corrosion resistance, and further, excellent weldability so as to decrease the laying cost of pipelines.

[0003] In order to meet this requirement, for example, Patent Literature 1 describes a martensitic stainless steel pipe with excellent resistance to IGSCC in a welded heat affected zone which is suitably used as a linepipe without performing a post weld heat treatment. The martensitic stainless steel pipe described in Patent Literature 1 has a chemical composition containing, by mass%, C: less than 0.0100%, N: less than 0.0100%, Cr: 10% to 14%, Ni: 3% to 8%, Si: 0.05% to 1.0%, Mn: 0.1% to 2.0%, P: 0.03% or less, S: 0.010% or less, and Al: 0.001% to 0.10%, and further containing at least one selected from Cu: 4% or less, Co: 4% or less, Mo: 4% or less, and W: 4% or less, and at least one selected from Ti: 0.15% or less, Nb: 0.10% or less, V: 0.10% or less, Zr: 0.10% or less, Hf: 0.20% or less, and Ta: 0.20% or less, so that Csol (effective content of dissolved carbon) is less than 0.0050%. According to Patent Literature 1, since formation of Cr carbides at prior-austenite grain boundaries is prevented by controlling the Csol, which is effective for forming Cr carbides, to be less than 0.0050%, formation of Cr depleted zones which causes IGSCC in a welded heat affected zone is prevented without performing - a post weld heat treatment.

[0004] Patent Literature 3 describes a Cr containing steel pipe for linepipe having high strength of X65 to X80 grade, and excellent in toughness, corrosion resistance, resistance to sulfide stress cracking, and resistance to IGSCC in a welded heat affected zone. The Cr containing steel pipe for linepipe described in Patent Literature 3 has a chemical composition containing, by mass%, C: 0.001% to 0.015%, Si: 0.05% to 0.50%, Mn: 0.10% to 2.0%, Al: 0.001% to 0.10%, Cr: 15.0% to 18.0%, Ni: 2.0% to 6.0%, Mo: 1.5% to 3.5%, V: 0.001% to 0.20%, and N: 0.015% or less, under the condition that Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N is 11.5 to 13.3. With such a chemical composition, since a microstructure in a welded heat affected zone, which is subjected to heating up to a temperature range for forming ferrite single phase of 1300°C or higher and to cooling when welding is performed, is formed such that 50% or more of prior-ferrite grain boundaries, in a ratio with respect to the total length of the prior-ferrite grain boundaries, is occupied by martensite phase and/or austenite phase and formation of Cr carbide depleted zones is suppressed, a steel pipe having significantly increased resistance to IGSCC in a welded heat affected zone can be obtained, which results in a significant decrease in construction period of a welded steel pipe structure due to a post weld heat treatment being unnecessary.

[0005] In addition, Patent Literature 2 describes a high-strength stainless steel pipe for linepipe with excellent corrosion resistance. The high-strength stainless steel pipe described in Patent Literature 2 has a chemical composition containing, by mass%, C: 0.001% to 0.015%, N: 0.001% to 0.015%, Cr: 15% to 18%, Ni: 0.5% or more and less than 5.5%, Mo: 0.5% to 3.5%, V: 0.02% to 0.2%, Si: 0.01% to 0.5%, Mn: 0.1% to 1.8%, P: 0.03% or less, S: 0.005% or less, N: 0.001 to 0.015% and O: 0.006% or less, under the condition that $Cr+0.65Ni+0.6Mo+0.55Cu-20C \geq 18.5$, $Cr+Mo+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N \geq 11.5$, and $C+N \leq 0.025$ are satisfied at the same time. According to Patent Literature 2, by maintaining a ferrite-martensite dual phase microstructure containing an appropriate amount of ferrite phase and by controlling Cr content to be in a rather high range from 15% to 18%, a steel pipe having excellent hot workability, excellent low temperature toughness, and sufficient strength for linepipe, and further having excellent corrosion resistance in a corrosive high temperature environment of 200°C containing carbon dioxide gas and chloride ions is obtained.

Patent literature 4 describes a high chromium-welded steel pipe excellent in the weld zone toughness of the seam weld zone and excellent in corrosion resistance and stress corrosion cracking resistance in the carbon dioxide environment and hydrogen sulfide environment. In this high chromium welded steel pipe excellent in weld zone toughness and corrosion resistance described in patent literature 4, the weld metal of the seam weld zone has a chemical composition

of, by weight, ≤0. 02% C, ≤1.0% Si, ≤2.0% Mn, ≤0.03% P, ≤0.005% S, ≤300 ppm N, 3.0 to 7.0% Ni, 10 to 14% Cr, 200 to 400 ppm oxygen and ≤8 cc/100 g diffusible hydrogen, and the base metal has a chemical composition of ≤0.015% C, ≤1.0% Si, ≤0.50 Mn, ≤0.03% P, ≤0.005% S, ≤200 ppm N, 3.0 to 7.0% Ni and 10 to 14% Cr, and the value of M expressed by the formula, M=%Cr+%Mo×1.3-%Ni is ≤14.0.

[Citation List]

[Patent Literature]

[0006]

[PTL 1] Japanese Unexamined Patent Application Publication No. 2005-336601 (WO2005/073419 A1)
[PTL 2] Japanese Unexamined Patent Application Publication No. 2005-336599
[PTL 3] Japanese Unexamined Patent Application Publication No. 2011-241477 (WO2011/132765 A1)
[PTL 4] JP 2001-158945A

[Summary of Invention]

[Technical Problem]

[0007] However, in an intensely corrosive environment, even with the steel pipe described in Patent Literature 1, there is a problem in that IGSCC occurring in a welded heat affected zone cannot be completely suppressed, and IGSCC occurring in a welded heat affected zone is at present prevented by performing a post weld heat treatment. The steel pipe described in Patent Literature 1 was previously developed by the present inventors, and the steel pipe according to Patent Literature 1 is a martensitic stainless steel pipe whose microstructure does not include ferrite phase.

[0008] In the case of the steel pipe according to Patent Literature 2, no consideration is given to IGSCC, and despite the fact that Cr content is increased, there is a problem in that this steel pipe is rather poorer in terms of resistance to IGSCC than the steel pipe described in Patent Literature 1 which has lower Cr content and that IGSCC occurring in a welded heat affected zone cannot be completely suppressed.

[0009] In addition, in the case of the steel pipe according to Patent Literature 3, since the amount of alloy added is comparatively large, there is a problem in that there is an increase in material cost.

[0010] An object of the present invention is, by solving the problems in conventional arts described above, to provide a method of making a Cr containing steel pipe for linepipe having desired high strength, and excellent in toughness, corrosion resistance, resistance to sulfide stress cracking, and resistance to IGSCC in a welded heat affected zone. The steel pipe which the present invention is intended for is a steel pipe of X65 to X80 grade (steel pipe having a yield strength (YS) of 448 to 651 MPa). In addition, hereinafter, "excellent toughness" refers to a case where absorbed energy E_{-40} (J) at -40°C in a Charpy impact test is 50 J or more, and "excellent corrosion resistance" refers to a case where a corrosion rate (mm/y) is 0.10 mm/y or less in a 200 g/liter NaCl aqueous solution at a temperature of 150°C in which carbon dioxide gas of 3.0 MPa is dissolved in the saturated state. Hereinafter, "steel pipe" includes not only seamless steel pipe and but also welded steel pipe.

[Solution to Problem]

[0011] The present inventors, in order to achieve the object described above, diligently conducted investigations regarding various factors having influences on resistance to IGSCC in a welded heat affected zone of a ferritic-martensitic stainless steel pipe in a corrosive high temperature environment containing carbon dioxide gas and chloride ions.

[0012] As a result, it was found that, in the case of such a ferritic-martensitic stainless steel, since ferrite grains having a large grain diameter are formed in a heating cycle when welding is performed, and since Cr carbides are precipitated at the grain boundaries of the ferrite grains having a large grain diameter in a subsequent cooling cycle, Cr depleted zones are formed at the grain boundaries, which causes IGSCC. Moreover, the present inventors found that, in the case of this kind of steel, if almost all the grain boundaries of the ferrite grains having a large grain diameter is occupied by austenite phase at least by inducing ferrite (α) to austenite (γ) transformation at the grain boundaries before Cr carbides are precipitated at the grain boundaries, precipitation of Cr carbides at the grain boundaries is prevented, and thus formation of Cr depleted zones is suppressed, which allows IGSCC to be prevented.

[0013] In addition, from the results of further investigations, it was found that, in order to prevent IGSCC by inducing α to γ transformation at the grain boundaries before Cr carbides being precipitated at the grain boundaries, it is necessary to adjust a chemical composition so that P_1 defined by equation (1) below is 11.5 to 13.3 and that P_2 defined by equation (2) below is 0 or more:

$$P_1=Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N \quad \cdots (1),$$

$$P_2=(0.5Cr+5.0)-P_1 \quad \cdots (2).$$

[0014] From the investigations by the present inventors, it was newly found that, by controlling a chemical composition so that P_1 is 13.3 or less and that P_2 is 0 or more, carbides (Cr carbides) are less likely to be precipitated at the grain boundaries, and thus Cr depleted zones are also less likely to be formed, which allows IGSCC to be prevented.

[0015] That is to say, in the case where P_1 is 13.3 or less, that is, in the case of a chemical composition in which the contents of ferrite forming elements are small, single ferrite phase microstructure having a large grain diameter is formed in a zone which is subjected to a high temperature higher than 1200°C, which is nearly equal to the melting point, in a heating process when a girth welding is performed, for example, when laying pipelines, and then, in a cooling process, α to γ transformation is induced to form γ phase at the grain boundaries or inside the grains. In such a case, since the solubility product of carbides is larger in γ phase than in α phase, carbides (Cr carbides) are less likely to be precipitated at the grain boundaries, which allows IGSCC to be prevented due to Cr depleted zones being less likely to be formed. It is needless to say that most of or all of γ phase transforms into martensite phase in the subsequent cooling process.

[0016] On the other hand, in the case where P_1 is more than 13.3, that is, in the case of a chemical composition in which the contents of ferrite forming elements are large, since α to γ transformation is not induced in the cooling process, Cr carbides are precipitated at the grain boundaries, which tends to cause IGSCC due to formation of Cr depleted zones.

[0017] From the further investigations, it was found that, even in the case where the contents of Cr and Ni are small, if it is possible to adjust a chemical composition so that P_1 is 13.3 or less and that P_2 is 0 or more, it is possible to realize the microstructure change described above, which allows IGSCC in a welded heat affected zone to be prevented.

[0018] The present invention has been completed on the basis of the findings described above and further investigations. To solve the above object, the present invention proposes a method according to claim 1.

[Advantageous Effects of Invention]

[0019] According to the present invention, a Cr containing steel pipe for linepipe excellent in resistance to IGSCC in a welded heat affected zone can be manufactured at low cost without performing a post weld heat treatment, which results in a great industrial effect. In addition, according to the present invention, since steel pipe structures such as pipelines can be constructed without performing a post weld treatment, there is also a merit of significantly decreasing construction cost due to, for example, a decrease in construction period.

[Brief Description of Drawings]

[0020]

[Fig. 1] Fig. 1 is a schematic diagram illustrating a simulated welding thermal cycle used in EXAMPLES.
[Fig. 2] Fig. 2 is a schematic diagram illustrating the test specimen bent in a U-shape using a jig for U-bent test used in EXAMPLES.

[Description of Embodiments]

[0021] First, the reasons for limiting the chemical composition of the steel pipe according to the present invention will be described. Hereinafter, mass% will be represented simply by %, unless otherwise noted.

C: 0.001% to 0.010%

[0022] C is a chemical element which contributes to an increase in strength, and it is necessary that the C content be 0.001% or more in the present invention.

[0023] On the other hand, in the case where the C content is more than 0.015%, there is a deterioration in toughness in a welded heat affected zone. In particular, it is difficult to prevent IGSCC in a welded heat affected zone. Therefore, the C content is set to be 0.001% to 0.010%, preferably 0.002% to 0.010%.

Si: 0.05% to 0.50%

[0024] Si is a chemical element which functions as a deoxidizing agent and increases strength due to solid solution hardening, and it is necessary that the Si content be 0.05% or more in the present invention. However, in the case where the Si content is more than 0.50%, there is a deterioration in the toughness not only in a base steel but also in a welded heat affected zone. Therefore, the Si content is set to be 0.05% to 0.50%, preferably 0.10% to 0.40%.

Mn: 0.10% to 2.0%

[0025] Mn contributes to an increase in strength due to solid solution hardening and is an austenite forming element which increases the toughness in both a base steel and a welded heat affected zone by suppressing formation of ferrite phase. Although it is necessary that the Mn content be 0.10% or more in order to realize these effects, the effects become saturated in the case where the Mn content is more than 2.0% and the effect corresponding to the content cannot be expected. Therefore, the Mn content is set to be 0.10% to 2.0%, preferably 0.20% to 1.5%.

P: 0.020% or less

[0026] Since P is a chemical element which deteriorates corrosion resistances such as CO_2 corrosion resistance and resistance to sulfide stress cracking, it is preferable that the P content be as small as possible in the present invention, but there is an increase in manufacturing cost in the case where the P content is excessively decreased. As an industrially realizable range at comparatively low cost in which there is not a deterioration in corrosion resistance, the P content is set to be 0.020% or less, preferably 0.015% or less.

S: 0.010% or less

[0027] Since S is a chemical element which significantly deteriorates hot workability in a pipe manufacturing process, it is preferable that the S content is as small as possible, but, since it is possible to manufacture a pipe using an ordinary process in the case where the S content is 0.010% or less, the S content is set to be 0.010% or less, preferably 0.004% or less.

Al: 0.001% to 0.10%

[0028] Al is a chemical element which is strongly effective as a deoxidizing agent, and it is necessary that the Al content be 0.001% or more in order to realize this effect, but there is a negative effect on toughness in the case where the Al content is more than 0.10%. Therefore, the Al content is set to be 0.10% or less, preferably 0.05% or less.

Cr: more than 14% and less than 15%

[0029] Cr is a chemical element which increases corrosion resistance such as CO_2 corrosion resistance and resistance to sulfide stress cracking as a result of forming a protective surface film. It is necessary in the present invention that the Cr content be 14% or more in order to increase corrosion resistance in an intensely corrosive environment. On the other hand, in the case where the Cr content is 15% or more excessively, it is necessary that large amount of other alloy elements such as Ni be added in order to control the value of P_1 to be within the specified range, and there is a significant increase in material cost. Therefore, the Cr content is set to be more than 14% and less than 15%.

Ni: 2.0% to 5.0%

[0030] Ni is a chemical element which increases corrosion resistance such as CO_2 corrosion resistance and resistance to sulfide stress cracking as a result of strengthening a protective surface film and contributes to an increase in strength. It is necessary that the Ni content be 2.0% or more in order to realize these effects, but, in the case where the Ni content is more than 5.0%, there is a tendency for hot workability to deterioration and there is a significant increase in material cost. Therefore, the Ni content is set to be 2.0% to 5.0%, preferably 2.5% to 5.0%.

Mo: 1.5% to 3.5%

[0031] Mo is a chemical element which is effective for increasing resistance to pitting corrosion caused by Cl^- (chloride ions). It is necessary that the Mo content be 1.5% or more in order to realize this effect. On the other hand, in the case where the Mo content is more than 3.5%, there is a deterioration in hot workability and there is a significant increase in

manufacturing cost. Therefore, the Mo content is set to be 1.5% to 3.5%, preferably 1.8% to 3.0%.

V: 0.001% to 0.20%

[0032] V is a chemical element which contributes to an increase in strength and is effective for increasing resistance to stress corrosion cracking. These effects are markedly realized in the case where the V content is 0.001% or more, but there is a deterioration in toughness in the case where the V content is more than 0.20%. Therefore, the V content is set to be 0.001% to 0.20%, preferably 0.010% to 0.10%.

N: 0.015% or less

[0033] Although N is effective for increasing pitting corrosion resistance, since N is a chemical element which significantly deteriorates weldability, it is preferable that the N content be as small as possible in the present invention. However, there is an increase in manufacturing cost in the case where the N content is excessively decreased. As an industrially realizable range at comparatively low cost in which there is not a deterioration in weldability, the N content is set to be 0.015% or less.

[0034] Although the chemical composition described above is a basic chemical composition, in addition to the basic chemical composition, at least one selected from Cu: 0.01% to 3.5% and W: 0.01% to 3.5%; and/or at least one selected from Ti: 0.01% to 0.20%, Nb: 0.01% to 0.20%, and Zr: 0.01% to 0.20%; and/or at least one selected from Ca: 0.0005% to 0.0100% and REM: 0.0005% to 0.0100% may be selectively added if necessary.

At least one selected from Cu: 0.01% to 3.5% and W: 0.01% to 3.5%

[0035] Since Cu and W are both chemical elements which increase CO_2 corrosion resistance, these chemical elements may be selectively added if necessary.

[0036] Cu is, moreover, also a chemical element which contributes to an increase in strength. It is preferable that the Cu content be 0.01% or more in order to realize these effects, but, since the effects become saturated in the case where the Cu content is more than 3.5%, effects corresponding to the content cannot be expected, which results in an economic disadvantage. Therefore, in the case where Cu is added, it is preferable that the Cu content be 0.01% to 3.5%, more preferably 0.30% to 2.0%.

[0037] W is, moreover, also a chemical element which increases resistance to stress corrosion cracking, resistance to sulfide stress cracking, and pitting corrosion resistance. It is preferable that the W content be 0.01% or more in order to realize these effects, but, since the effects become saturated in the case where the W content is more than 3.5%, effects corresponding to the content cannot be expected, which results in an economic disadvantage. Therefore, in the case where W is added, it is preferable that the W content be 0.01% to 3.5%, more preferably 0.30% to 2.0%.

At least one selected from Ti: 0.01% to 0.20%, Nb: 0.01% to 0.20%, and Zr: 0.01% to 0.20%

[0038] Since Ti, Nb, and Zr are all chemical elements which tend to form carbides more than Cr, these chemical elements are effective for suppressing Cr carbides from being precipitated at the grain boundaries in a cooling process. Therefore, at least one of these chemical elements may be selectively added if necessary. It is preferable that the contents of these chemical elements be respectively Ti: 0.01% or more, Nb: 0.01% or more, and Zr: 0.01% or more in order to realize this effect, but there is a deterioration in weldability and toughness in the case where the contents of these chemical elements are respectively Ti: more than 0.20%, Nb: more than 0.20%, and Zr: more than 0.20%. Therefore, in the case where these chemical elements are added, it is preferable that the contents of these chemical elements be respectively Ti: 0.01% to 0.20%, Nb: 0.01% to 0.20%, and Zr: 0.01% to 0.20%, more preferably Ti: 0.020% to 0.10%, Nb: 0.020% to 0.10%, and Zr: 0.020% to 0.10%.

At least one selected from Ca: 0.0005% to 0.0100% and REM: 0.0005% to 0.0100%

[0039] Since Ca and REM are both chemical elements which increase hot workability and manufacturing stability in a continuous casting process as a result of controlling the form of inclusions, these chemical elements may be selectively added if necessary. It is preferable that the contents of these chemical elements be respectively Ca: 0.0005% or more and REM: 0.0005% or more in order to realize these effects, but there is an increase in the amount of inclusions in the case where the contents of these chemical elements are respectively Ca: more than 0.0100% and REM: more than 0.0100%, which results in a deterioration in the cleanliness of steel. Therefore, in the case where these chemical elements are added, it is preferable that the contents of these chemical elements be respectively Ca: 0.0005% to 0.0100% and REM: 0.0005% to 0.0100%, more preferably Ca: 0.0010% to 0.0050% and REM: 0.0010% to 0.0050%.

[0040] In the present invention, within the range of the chemical composition described above, the contents of chemical elements are controlled under the condition that P_1 defined by equation (1) below is 11.5 or more and 13.3 or less and that P_2 defined by equation (2) below is 0 or more :

$$P_1=Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N \quad \cdots (1),$$

(where Cr, Mo, W, Si, C, Mn, Ni, Cu, N: the contents (mass%) of the chemical elements represented respectively by the corresponding atomic symbols),

$$P_2=(0.5Cr+5.0)-P_1 \quad \cdots (2),$$

(where Cr: Cr content (mass%)).

[0041] P_1 is an index for evaluating hot workability and resistance to IGSCC, and in the present invention, the contents of chemical elements are controlled to be within the ranges described above so that P_1 is 11.5 to 13.3. In the case where P_1 is less than 11.5, since hot workability is insufficient for the manufacture of seamless steel pipes, it is difficult to manufacture seamless steel pipes. On the other hand, in the case where P_1 is more than 13.3, there is a deterioration in resistance to IGSCC as described above. Similarly, in the case where P_2 is less than 0, there is a deterioration in resistance to IGSCC. Therefore, the contents of chemical elements are to be controlled to be within the ranges described above and to satisfy the conditions that P_1: 11.5 to 13.3 and P_2: 0 or more.

[0042] The balance of the chemical composition other than the chemical elements described above consists of Fe and inevitable impurities. Among inevitable impurities, O: 0.010% or less is acceptable.

[0043] The steel pipe according to the present invention has the chemical composition described above, and, moreover, has a microstructure including martensite phase as a base phase and including, at volume percentage, 10% to 35% of ferrite phase and 30% or less of austenite phase. Here, the martensite phase includes tempered martensite phase. It is preferable that the volume percentage of martensite phase be 40% or more in order to achieve desired strength. In addition, since ferrite phase is soft and effective for increasing workability, it is preferable that the volume percentage of ferrite phase be 10% or more in order to increase workability. On the other hand, in the case where the volume percentage of ferrite phase is more than 35%, it is impossible to achieve desired high strength (X65). In addition, austenite phase increases toughness. It is preferable that the volume percentage of austenite phase be 15% or more in order to achieve sufficient toughness. However, in the case where the volume percentage of austenite phase is more than 30%, it is difficult to achieve sufficient strength.

[0044] Note that regarding austenite phase, there is a case where austenite phase does not altogether undergo transformation to martensite phase when quenching is performed and some portion of austenite phase is retained, and there is a case where some portions of martensite phase and ferrite phase undergo reverse transformation when tempering is performed and are stabilized so as to be retained as austenite phase even after cooling.

[0045] In the case of the steel pipe according to the present invention having the chemical composition described above and the microstructure described above, if a welded zone is formed, a microstructure in a welded heat affected zone, which is subjected to heating up to a temperature range for forming ferrite single phase of 1300°C or higher and to cooling when welding is performed, is formed such that 50% or more of prior-ferrite grain boundaries, in a ratio with respect to the total length of the prior-ferrite grain boundaries, is occupied by martensite phase. As a result, since precipitation of Cr carbides at grain boundaries of prior-ferrite grains having a large grain diameter can be prevented, the occurrence of IGSCC can be suppressed, which results in an increase in resistance to IGSCC in a welded heat affected zone.

[0046] Subsequently, a preferable method for manufacturing the steel pipe according to the present invention will be described in the case of a seamless steel pipe as an example.

[0047] First, it is preferable that molten steel having the chemical composition described above be smelted with an ordinary smelting method such as one using a converter, an electric furnace, or a vacuum melting furnace and that the molten steel be made into a steel material such as a billet with an ordinary method such as a continuous casting method or a slabbing mill method for rolling an ingot. Subsequently, the steel material is heated and hot rolled into a seamless steel pipe having a desired size using a Mannesmann-plug mill method or a Mannesmann-mandrel mill method. It is preferable that the seamless steel pipe after hot rolling be cooled down to a room temperature by an accelerated cooling at a cooling rate equal to or larger than an air-cooling rate, preferably at an average cooling rate of 0.5°C/s or more from 800°C to 500°C. With this method, for the steel pipe having a chemical composition according to the present invention, a microstructure having martensite phase as a base phase as described above can be obtained. In the case where the cooling rate is less than 0.5°C/s, a microstructure having martensite phase as a base phase as described above cannot

be obtained. Here, "a microstructure having martensite phase as a base phase" means a microstructure in which martensite has the largest volume percentage or in which martensite has almost the same volume percentage as another phase which has the largest volume percentage.

[0048] Note that instead of performing accelerated cooling after hot rolling as described above, reheating followed by quenching and tempering may be performed. Regarding quenching, it is preferable that the seamless steel pipe be reheated up to a temperature of 800°C or higher and held for 10 minutes or more and that the reheated pipe be cooled down to a temperature of 100°C or lower at a cooling rate equal to or larger than an air-cooling rate or at an average cooling rate of 0.5°C/s or more from 800°C to 500°C. In the case where the reheating temperature is lower than 800°C, desired microstructure having martensite phase as a base phase cannot be achieved.

[0049] Regarding tempering, it is preferable that the quenched pipe be heated up to a temperature of 500°C or higher and 700°C or lower, preferably 500°C or higher and 680°C or lower, and held for a specified time and that the heated pipe be air-cooled. With this method, desired high strength, desired high toughness, and desired excellent corrosion resistance are achieved at the same time.

[0050] Although a method for manufacturing a steel pipe has been described in the case of a seamless steel pipe as an example, the present invention is not limited to this. Using a steel material (steel plate) having the chemical composition described above, an electric resistance welded steel pipe or a UOE steel pipe may be manufactured using an ordinary process and used as a steel pipe for linepipe. In the case of an electric resistance welded steel pipe or a UOE steel pipe, also it is preferable that the quenching and tempering described above be performed to have the microstructure described above.

[0051] In addition, a welded structure (steel pipe structure) may be constructed by welding the steel pipes according to the present invention described above. Note that welding of the steel pipes according to the present invention includes welding of the steel pipes according to the present invention with other kinds of steel pipes. Such a welded structure which is constructed by welding the steel pipes according to the present invention, have a welded zone in which a welded heat affected zone, which is subjected to heating when welding is performed, preferably up to a temperature range for forming ferrite single phase of 1300°C or higher and to cooling, has a microstructure in which 50% or more of prior-ferrite grain boundaries, in a ratio with respect to the total length of the prior-ferrite grain boundaries, is occupied by martensite phase and/or austenite phase. With this, since IGSCC is suppressed, there is an increase in resistance to IGSCC in a welded heat affected zone without performing a post weld heat treatment.

[0052] Hereafter, the present invention will be further described on the basis of EXAMPLES.

[EXAMPLES]

[0053] After molten steels having a chemical composition given in Table 1-1 and Table 1-2 had been smelted using a vacuum melting furnace and degassed, the degassed molten steels were cast into billets of 100 kgf, and then the billets were made into steel pipe materials having specified sizes by hot forging. These steel pipe materials were subjected to heating and pipe making in a hot working process using a model seamless mill (small-scale experimental seamless mil) to obtain seamless steel pipes (having an outer diameter of 72 mmϕ and a thickness of 5.5 mm).

[0054] Regarding the obtained seamless steel pipe in the cooled state after pipe making, it was investigated by performing a visual test whether or not there were cracks on the inner and outer surfaces to evaluate hot workability. Here, a case where there was a crack having a length of 5 mm or more in the longitudinal end of the pipe was evaluated as "with crack: $\times$" and other case was evaluated as "without crack: $\bigcirc$".

[0055] Subsequently, a test sample (steel pipe) was cut out of the obtained seamless steel pipe, and the test sample (steel pipe) was subjected to quenching and tempering under the conditions given in Table 2.

[0056] Test specimens were cut out of the test sample (steel pipe) which had been subjected to quenching and tempering, and were subjected to microstructure observation, tensile test, impact test, corrosion test, sulfide stress test and U-bent test. The microstructure observation and the test methods will be described hereafter.

(1) Microstructure observation

[0057] A test specimen for microstructure observation was cut out of the obtained test sample (steel pipe). After polishing and etching the test specimen, the microstructure was identified by taking photographs using an optical microscope (at a magnification ratio of 1000 times), and then the percentages of ferrite phase and martensite phase of the base steel were determined using an image analyzer. Here, the amount of γ phase was determined using an X-ray diffraction method.

(2) Tensile test

[0058] An arc-shaped test specimen for a tensile test specified in the API standards was cut out of the obtained test

sample (steel pipe) such that the tensile direction was the direction of the pipe axis. After performing a tensile test using the test specimen, tensile property (yield strength YS and tensile strength TS) was determined in order to evaluate the strength of the base steel.

(3) Impact test

[0059] A V-notch test specimen having a thickness of 5.0 mm was cut out of the obtained test sample (steel pipe) in accordance with JIS Z 2242. After performing a Charpy impact test using the test specimen, absorbed energy $_vE_{-40}$ (J/cm^2) at -40°C was determined in order to evaluate the toughness of the base steel.

(4) Corrosion test

[0060] A test specimen for a corrosion test having a thickness of 3 mm, a width of 25 mm, and a length of 50 mm was cut out of the obtained test sample (steel pipe) by performing mechanical working. After performing a corrosion test using the test specimen, corrosion resistance (CO_2 corrosion resistance and pitting corrosion resistance) was evaluated. In the corrosion test, a 200 g/liter NaCl aqueous solution of a temperature of 150°C in which carbon dioxide gas of 3.0 MPa was dissolved in the saturated state was contained in an autoclave, and the test specimen was immersed in the aqueous solution for 30 days. After the corrosion test, by determining the weight of the test specimen, and by calculating a corrosion rate based on a change in weight (reduction in weight) before and after the corrosion test, CO_2 corrosion resistance was evaluated. In addition, after the corrosion test, the test specimen was observed using a loupe at a magnification ratio of 10 times in order to investigate whether or not pitting corrosion occurred on the surface of the test specimen. A case where pitting occurred was evaluated as ×, and a case where pitting did not occur was evaluated as ○.

(5) Sulfide stress cracking (SSC) test

[0061] A four-point bending test specimen having a thickness of 4 mm, a width of 15 mm, and a length of 115 mm was cut out of the obtained test sample (steel pipe). After performing a four-point bending test in accordance with EFC (European Federation of Corrosion) No. 17 using the test specimen, resistance to sulfide stress cracking (resistance to SSC) was evaluated by observing where or not cracks occurred. Here, a test solution consisting of 50 g/liter NaCl + $NaHCO_3$ (pH: 4.5) was used, and a mixed gas consisting of 1 vol% H_2S + 99 vol% CO_2 was flowed during the test. Further, Applied stress was equal to the YS (yield strength) of the base steel and the test period was 720 hours (hereinafter, abbreviated as h). A case where cracks occurred was evaluated as ×, and a case where cracks did not occur was evaluated as ○.

(6) U-bent test

[0062] A test specimen having a thickness of 4 mm, a width of 15 mm, and a length of 115 mm was cut out of the obtained test sample (steel pipe), and the welding thermal cycle illustrated in Fig. 1 was applied to the central portion of the test specimen. After applying the welding thermal cycle, the test specimen was polished and etched for micro-structure observation in order to investigate whether or not there were transformation phases (martensite phase and/or austenite phase) produced from prior-a grain boundaries. And determining the length of the prior-a grain boundaries occupied by the transformation phases (martensite phase and/or austenite phase), a grain boundary occupancy ratio was calculated with respect to the total length of the prior-a grain boundaries.

[0063] Moreover, a test specimen having a thickness of 2 mm, a width of 15 mm, and a length of 75 mm was cut out of the central portion of the specimen which had been subjected to the welding thermal cycle, and subjected to a U-bent test using the jig illustrated in Fig. 2. In the U-bent test, as illustrated in Fig. 2, the test specimen was bent in a U-shape having an internal radius of 8.0 mm and immersed in a corrosive solution. Two kinds of corrosive solution below were used:

① 50 g/liter NaCl solution of temperature: 100°C, CO_2 pressure: 0.1 MPa, pH: 2.0, and
② 200 g/liter NaCl solution of temperature: 150°C, CO_2 pressure: 0.1 MPa, pH: 2.0.

[0064] Further, the test period was 168 h.

[0065] After the U-bent test, the cross section of the test specimen was observed using an optical microscope at a magnification ratio of 100 times in order to investigate whether or not cracks occurred. And resistance to IGSCC in a welded heat affected zone (resistance to IGSCC in HAZ) was evaluated. A case where cracks occurred was evaluated as ×, and a case where cracks did not occur was evaluated as ○.

[0066] The obtained results are given in Table 3.

[0067] All of the examples of the present invention (pipe Nos. 1 through 11, 13 through 16 and 19) were excellent in

terms of hot workability, and had high strength, that is, YS: 450 MPa or more, high toughness, that is, ${}_{v}E_{-40}$: 50 J/cm^2 or more, high corrosion resistance, that is, corrosion rate: 0.10 mm/y or less, and further, had no SSC and no IGSCC in HAZ which had been subjected to heating up to a temperature of 1300°C or higher, which means that these pipes were excellent in terms of resistance to IGSCC in HAZ.

[0068] In the case of the comparative examples (pipe Nos. 20 through 30), there was a deterioration in hot workability, toughness, corrosion resistance, resistance to SSC, or resistance to IGSCC in HAZ.

[0069] Specifically, in the case of pipe Nos. 20 through 23, since P2 was out of the range according to the present invention, there was a deterioration in resistance to IGSCC in HAZ.

[0070] In the case of pipe Nos. 24 and 25, since P1 was out of the range according to the present invention, there was a deterioration in hot workability.

[0071] In the case of pipe No. 26, since the C content was more than the upper limit according to the present invention, there was a deterioration in toughness.

[0072] In the case of pipe Nos. 28 through 30 which respectively corresponded to steel Nos. F, K and M in Patent Literature 1, since the Cr content was less than the lower limit according to the present invention, since the Ni content was more than the upper limit according to the present invention, and since P1 was less than the lower limit according to the present invention, the volume percentage of ferrite phase was 0% and there was a deterioration in resistance to IGSCC in HAZ in the case of corrosive solution ② which was more intensely corrosive.

[Table 1-1]

[0073]

Table 1-1

Steel No.	Chemical Composition (mass%)															P_1	P_2	Note
	C	Si	Mn	P	S	Al	Cr	Ni	Mo	Cu	W	V	Ti,Nb,Zr	Ca, REM	N			
A	0.009	0.20	0.55	0.014	0.001	0.015	14.8	4.5	2.0	-	-	0.021	-	-	0.011	11.65	0.75	Inventive Example
B	0.006	0.15	0.45	0.012	0.001	0.021	14.5	4.2	1.8	-	-	0.021	-	-	0.009	11.62	0.63	Inventive Example
C	0.008	0.34	0.53	0.011	0.002	0.028	14.4	4.4	2.2	-	-	0.031	-	-	0.009	11.66	0.54	Inventive Example
D	0.010	0.20	0.68	0.013	0.002	0.017	14.2	4.6	3.2	1.04	-	- 0.015	-	-	0.009	11.76	0.34	Inventive Example
E	0.010	0.21	1.21	0.009	0.002	0.030	14.0	4.4	2.8	-	1.06	0.032	-	-	0.010	11.88	0.12	Inventive Example
F	0.010	0.19	1.30	0.014	0.002	0.018	13.5	3.2	2.1	1.21	1.53	0.028	-	-	0.011	11.65	0.10	Example
G	0.009	0.35	0.54	0.008	0.001	0.029	14.8	4.3	2.0	-	-	0.024	Ti/0.085	-	0.012	11.89	0.51	Inventive Example
H	0.009	0.42	0.19	0.016	0.002	0.026	14.0	4.6	2.6	-	-	0.031	Nb/ 0.048	-	0.008	11.59	0.41 .	Inventive Example
I	0.009	0.41	0.42	0.012	0.002	0.022	14.5	4.5	2.0	1.02	1.03	0.045	Zr/0.045	-	0.011	11.57	0.68	Inventive Example
J	0.010	0.16	0.54	0.012	0.001	0.015	14.2	4.2	2.3	-	-	0.020	-	Ca/ 0.0023	0.012	11.59	0.51	Inventive Example
K	0.009	0.20	0.49	0.011	0.001	0.027	13.5	3.1	1.9	-	-	0.016	-	REM/ 0.0044	0.009	11.69	0.06	Example
L	0.012	0.21	0.89	0.014	0.002	0.020	13.4	2.4	2.5	3.2	-	0.045	-	Ca/ 0.0046	0.012	11.62	0.08	Example
M	0.006	0.19	0.61	0.008	0.002	0.015	14.7	4.6	2.0	-	1.15	0.023	Ti/0.098	Ca/ 0.0034	0.012	12.00	0.35	Inventive Example
N	0.010	0.21	0.53	0.013	0.001	0.020	14.8	3.4	2.1	-	-	0.041	-	-	0.011	12.82	-0.42	Comparative Example

(continued)

Steel No.	Chemical Composition (mass%)														P_1	P_2	Note
	C	Si	Mn	P	S	Al	Cr	Ni	Mo	Cu	W	V	Ti,Nb,Zr	Ca, REM	N			
O	0.009	0.32	0.40	0.011	0.001	0.030	14.0	3.1	2.0	-	-	0.020	-	-	0.010	12.35	-0.35	Comparative Example

[Table 1-2]

[0074]

Table 1-2

steel No.	Chemical Composition (mass%)															P_1	P_2	Note
	C	Si	Mn	P	S	Al	Cr	Ni	Mo	Cu	W	V	Ti,Nb,Zr	Ca,REM	N			
P	0.010	0.15	0.40	0.013	0.002	0.020	14.0	3.0	2.1	-	0.65	0.026	Nb/0.035	-	0.010	12.72	-0.72	Comparative Example
Q	0.012	0.15	1.23	0.017	0.002	0.034	13.6	2.6	2.1	-	-	0.027	-	-	0.012	12.02	-0.22	Comparative Example
R	0.010	0.25	1.27	0.013	0.002	0.031	14.2	4.2	2.0	-	-	0.022	-	-	0.012	11.02	1.08	Comparative Example
S	0.010	0.26	1.23	0.009	0.001	0.033	13.6	3.2	2.1	1.5	-	0.019	-	-	0.012	11.09	0.71	Comparative Example
T	0.025	0.20	0.58	0.012	0.001	0.020	14.8	3.8	2.2	-	-	0.022	-	-	0.011	11.84	0.56	Comparative Example
U	0.009	0.20	0.45	0.012	0.001	0.022	14.8	3.7	1.2	-	-	0.021	-	-	0.011	11. 69	0.71	Comparative Example
V	0.0068	0.24	0.61	0.017	0.002	0.018	12.6	6.1	2.3	-	-	0.051	Ti/0.072	Ca/ 0.0022	0.0078	8.26	3.04	Comparative Example (Steel F in Patent Literature 1)
W	0.0083	0.49	1.18	0.019	0.002	0.029 ’	12.9	6.5	2.1	-	-	0.051	Ti/0.065, Nb/0. 031, - Zr/ 0.026	Ca/ 0.0010	0.0082 .	7.74	3.71	Comparative Example (Steel K in Patent Literature 1)
X	0.0085	0.13	0.46	0.015	0.001	0.031	- 12.5	5.6	2.6	-	-	0.064	Ti/0.059, Nb/ 0.021, Zr/ 0.026	Ca/ 0.0018	0.0062	- 8.93	2.32	Comparative Example (Steel M in Patent Literature 1)

[Table 2]

[0075]

Table 2

Pipe No.	Steel steel No.	Cooling after Hot Rolling		Quenching			Tempering	Note
		Cooling Method	Cooling Rate (°C/s)	Quenching Temperature (°C)	Holding Time (min)	Cooling Rate (°C/s)	Tempering Temperature (°C)	
1	A	Air-cooling	3.3	900	20	3.3	600	Inventive Example
2	A	Air-cooling	3.3	900	20	3.3	620	Inventive Example
3	A	Air-cooling	3.3	900	20	3.3	640	Inventive Example
4	B	Air-cooling	3.3	900	20	3.3	600	Inventive Example
5	B	Air-cooling	3.3	900	20	3.3	620	Inventive Example
6	B	Air-cooling	3.3	900	20	3.3	640	Inventive Example
7	C	Air-cooling	3.3	900	20	3.3	600	Inventive Example
8	C	Air-cooling	3:3	900	20	3.3	620	Inventive Example
9	C	Air-cooling	3.3	900	20	3.3	640	Inventive Example
10	D	Air-cooling	3.3	900	20	3.3	620	Inventive Example
11	E	Air-cooling	3.3	900	20	3.3	620	Inventive Example
12	F	Air-cooling	3.3	930	20	3.3	620	Example
13	G	Air-cooling	3.3	900	20	3.3	620	Inventive Example
14	H	Air-cooling	3.3	900	20	3.3	620	Inventive Example
15	I	Air-cooling	3.3	900	20	3.3	620	Inventive Example
16	J	Air-cooling	3.3	900	20	50	620	Inventive Example
17	K	Air-cooling	3.3	930	20	50	650	Example
18	L	Air-coolinq	3.3	930	20	3.3	650	Example
19	M	Air-coolina	3.3	900	20	3.3	620	Inventive Example

(continued)

Pipe No.	Steel steel No.	Cooling after Hot Rolling		Quenching			Tempering	Note
		Cooling Method	Cooling Rate (°C/s)	Quenching Temperature (°C)	Holding Time (min)	Cooling Rate (°C/s)	Tempering Temperature (°C)	
20	N	Air-coolina	3.3	930	20	3.3	650	Comparative Example
21	O	Air-cooling	3.3	930	20	3.3	650	Comparative Example
22	P	Air-cooling	3.3	930	20	3.3	650	Comparative Example
23	Q	Air-coolina	3.3	930	20	3.3	- 650	Comparative Example
24	R	Air-coolina	3.3	900	20	3.3	620	Comparative Example
25	S	Air-coolina	3.3	930	20	3.3	620	Comparative Example
26	T	Air-coolina	3.3	900	20	3.3	620	Comparative Example
27	U	Air-cooling	3.3	900	20	3.3	650	Comparative Example
28	V	Air-cooling	3.3	900	20	3.3	620	Comparative Example (Steel F in Patent Literature 1)
29	W	Air-cooling	3.3	900	20	3.3	620	Comparative Example (Steel K in Patent Literature 1)
30	X	Air-cooling	3.3	900	20	3.3	620	Comparative Example (Steel M in Patent Literature 1)

[Table 3-1]

[0076]

Table 3-1

Pipe No.	Steel No.	P1	P2	Hot Workability	Phase Percentage of Base steel (%)*			Tensile Property		Toughness	CO_2 Corrosion Resistance		Resistance to SSC	Resistance to IGSCC in HAZ			Note
					M	F	γ	YS (MPa)	TS (MPa)	vE-40 (J/cm^2)	corrosion Rate (mm/y)	with or without Pitting	with or without Crack	Grain Boundary Occupancy Ratio**)	with or without Crack ①	with or without Crack ②	
1	A	11.65	0.75	○	64	18	18	631	761	123	0.05	○	○	100	○	○	Inventive Example
2	A	11.65	0.75	○	61	17	22	573	738	140	0.06	○	○	100	○	○	Inventive Example
3	A	11.65	0.75	○	56	18	26	504	700	211	0.07	○	○	92	○	○	Inventive Example
4	B	11.91	0.44	○	71	12	17	604	765	168	0.05	○	○	97	○	○	Inventive Example
5	B	11.91	0.44	○	66	12	22	564	735	172	0.06	○	○	85	○	○	Inventive Example
6	B	11.91	0.44	○	62	13	25	514	703	225	0.08	○	○	100	○	○	Inventive Example
7	C	11.66	0.54	○	67	18	15	593	740	154	0.05	○	○	100	○	○	Inventive Example
8	C	11.66	0.54	○	62	17	21	553	729	165	0.07	○	○	95	○	○	Inventive Example
9	C	11.66	0.54	○	59	17	24	517	718	183	0.08	○	○	100	○	○	Inventive Example
10	D	11.76	0.34	○	63	22	15	596	785	231	0.03	○	○	100	○	○	Inventive Example
11	E	11. 88	0.12	○	64	20	16	611	839	172	0.05	○	○	92	○	○	Inventive Example
12	F	11. 65	0.10	○	60	28	12	600	773	99	0.07	○	○	100	○	○	Example

(continued)

Pipe No.	Steel No.	P1	P2	Hot Workability	Phase Percentage of Base steel (%)*			Tensile Property		Toughness	CO_2 Corrosion Resistance		Resistance to SSC	Resistance to IGSCC in HAZ			Note
					M	F	γ	YS (MPa)	TS (MPa)	vE-40 (J/cm^2)	corrosion Rate (mm/y)	with or without Pitting	with or without Crack	Grain Boundary Occupancy Ratio**)	with or without Crack ①	with or without Crack ②	
13	G	11.89	0.51	○	65	21	14	617	823	127	0.06	○	○	100	○	○	Inventive Example
14	H	11.59	0.41	○	53	25	22	589	773	160	0.06	○	○	100	○	○	Inventive Example
15	I	11.57	0.68	○	67	17	16	573	769	154	0.05	○	○	98	○	○	Inventive Example
16	J	11.59	0.51	○	56	26	18	637	857	137	0.05	○	○	99	○	○	Inventive Example
17	K	11.69	0.06	○	70	16	14	599	807	118	0.09	○	○	96	○	○	Example
18	L	11.62	0.08	○	64	26	10	594	764	74	0.09	○	○	100	○	○	Example
	*) F: ferrite, M: martensite, y: austenite																
	**) the percentage of prior-ferrite grain boundaries occupied by martensite phase or austenite phase with-respect																
	to the total length of the prior-ferrite grain boundaries																
	Resistance to IGSCC O NaCl: 50 g/liter, 100°C, CO_2 pressure: 0.1 MPa, pH: 2.0.																
	Resistance to IGSCC ② NaCl: 200 g/liter, 100°C, CO_2 pressure: 0.1 MPa, pH: 2.0																

[Table 3-2]

[0077]

Table 3-2

Pipe No.	Steel No.	P1	P2	Hot Workability	Phase Percentage of Base steel (9)*)			Tensile Property		Toughness	Resistance to CO_2 Corrosion		Resistance to SSC	Resistance to IGSCC in HAZ			Note
					M	F	γ	YS (MPa)	TS (MPa)	vE-40 (J/cm^2)	Corrosion Rate (mm/y)	with or without Pitting	with or without Crack	Grain Boundary Occupancy Ratio ")	with or without Crack ①	with or without Crack ②	
19	M	12.00	0.35	○	55	27	18	606	789	205	0.06	○	○	99	○	○	Example
20	N	12.82	-0.42	○	65	20	15	561	739	131	0.07	○	○	59	×	×	Comparative Example
21	O	12.35	-0.35	○	65	20	15	594	787	118	0.07	○	○	69	×	×	Comparative Example
22	P	12.72	-0.72	○	63	25	12	583	801	111	0.07	○	○	71	×	×	Comparative Example
23	Q	12.02	-0.22	○	77	16	7	590	600	75	0.09	○	○	84	×	×	Comparative Example
24	R	11.02	1.08	×	56	26	18	592	799	119	0.09	○	○	100	○	○	Comparative Example
25	S	11.09	0.71	×	61	27	12	616	795	100	0.09	○	○	100	○	○	Comparative Example
26	T	11.84	0.56	○	55	31	14	598	790	32	0.06	○	○	87	○	○	Comparative Example
27	U	11.69	0.71	○	56	27	17	580	774	117	0.07	×	×	97	○	○	Comparative Example
28	V	8.26	3.04	○	83	0	17	608	770	204	0.048	○	○	-	○	×	Comparative Example (Steel F in Patent Literature 1)

(continued)

Pipe No.	Steel No.	P1	P2	Hot Workability	Phase Percentage of Base steel (9)*)			Tensile Property		Toughness	Resistance to CO_2 Corrosion		Resistance to SSC	Resistance to IGSCC in HAZ			Note
					M	F	γ	YS (MPa)	TS (MPa)	vE-40 (J/cm^2)	Corrosion Rate (mm/y)	with or without Pitting	with or without Crack	Grain Boundary Occupancy Ratio ")	with or without Crack ①	with or without Crack ②	
29	W	7.74	3.71	○	86	0	14	619	814	219	0.060	○	○	-	○	×	Comparative Example (Steel K in Patent Literature 1)
30	X	8.93	2.32	○	88	0	12	639	664	250	0.092	○	○	-	○	×	Comparative Example (Steel M in Patent Literature 1)
	*) F: ferrite, M: martensite, y: austenite																
	**) the percentage of prior-ferrite grain boundaries occupied by martensite phase or austenite phase with respect																
	**) the																
	Resistance to IGSCC ① NaCl: 50 g/liter, 100°C, CO_2 pressure: 0.1 MPa, pH: 2.0 0.1 MPa, pH: 2.0																
	Resistance to IGSCC ② NaCl : 200 g/liter, 100°C, CO_2 pressure :																

Claims

1. A method of making a Cr containing steel pipe for linepipe, which steel pipe has a chemical composition consisting of, by mass%, C: 0.001% to 0.010%, Si: 0.05% to 0.50%, Mn: 0.10% to 2.0%, P: 0.020% or less, S: 0.010% or less, Al: 0.001% to 0.10%, Cr: more than 14% and less than 15%, Ni: 2.0% to 5.0%, Mo: 1.5% to 3.5%, V: 0.001% to 0.20%, N: 0.015% or less, optionally at least one selected from Cu: 0.01% to 3.5%, W: 0.01% to 3.5%, Ti: 0.01% to 0.20%, Nb: 0.01% to 0.20%, Zr: 0.01% to 0.20%, Ca: 0.0005% to 0.0100% and REM: 0.0005% to 0.0100%, and the balance being Fe and inevitable impurities, under the condition that P_1 defined by equation (1) below is 11.5 to 13.3 and that P_2 defined by equation (2) below is 0 or more, and in which method a microstructure in a welded heat affected zone, which when welding is performed is subjected to heating up to a temperature range for forming ferrite single phase of 1300°C or higher and to cooling, is formed by said welding such that 50% or more of prior-ferrite grain boundaries, in a ratio with respect to the total length of the prior-ferrite grain boundaries, is occupied by martensite phase,

$$P_1 = Cr + Mo + 0.4\,W + 0.3\,Si - 43.5\,C - 0.4\,Mn - Ni - 0.3\,Cu - 9\,N \quad (1),$$

$$P_2 = (0.5\,Cr + 5.0) - P_1 \quad (2),$$

where Cr, Mo, W, Si, C, Mn, Ni, Cu, N: the contents in mass% of the chemical elements represented respectively by the corresponding atomic symbols.

Patentansprüche

1. Verfahren zum Herstellen eines Cr-haltigen Stahlrohrs für Leitungsrohr, wobei das Stahlrohr eine chemische Zusammensetzung hat, die in Masse-% aus 0,001 % bis 0,010 % C, 0,05 % bis 0,50 % Si, 0,10 % bis 2,0 % Mn, 0,020 % oder weniger P, 0,010 % oder weniger S, 0,001 % bis 0,10 % Al, mehr als 14 % und weniger als 15 % Cr, 2,0 % bis 5,0 % Ni, 1,5 % bis 3,5 % Mo, 0,001 % bis 0,20 % V, 0,015 % oder weniger N, optional wenigstens ein Element ausgewählt aus 0,01 % bis 3,5 % Cu, 0,01 % bis 3,5 % W, 0,01 % bis 0,20 % Ti, 0,01 % bis 0,20 % Nb, 0,01 % bis 0,20 % Zr, 0,0005 % bis 0,0100 % Ca, sowie 0,0005 % bis 0,0100 % REM besteht, wobei der Rest Fe und unvermeidbare Verunreinigungen sind, unter der Bedingung, dass Pi, definiert durch Gleichung (1) unten, 11,5 bis 13,3 beträgt und dass P2, definiert durch Gleichung (2) unten, 0 oder mehr beträgt, und
wobei bei diesem Verfahren ein Mikrogefüge in einer geschweißten Wärmeeinflusszone, die, wenn Schweißen durchgeführt wird, Erwärmung bis auf einen Temperaturbereich zum Ausbilden einer ferritischen Einzelphase von 1300 °C oder darüber und Abkühlen unterzogen wird, durch das Schweißen so ausgebildet wird, dass 50 % oder mehr der ehemaligen Ferrit-Korngrenzen in einem Verhältnis in Bezug auf die Gesamtlänge der ehemaligen Ferrit-Korngrenzen von martensitischer Phase eingenommen wird,

$$Pi = Cr + Mo + 0{,}4\,W + 0{,}3\,Si - 43{,}5\,C - 0{,}4\,Mn - Ni - 0{,}3\,Cu - 9\,N \quad (1),$$

$$P_2 = (0{,}5\,Cr + 5{,}0) - Pi \quad (2),$$

wobei Cr, Mo, W, Si, C, Mn, Ni, Cu, N die Gehalte in Masse-% der chemischen Elemente sind, die jeweils durch die entsprechenden Elementsymbole dargestellt werden.

Revendications

1. Procédé de fabrication d'un tube en acier contenant du Cr pour canalisation, lequel tube en acier a une composition chimique constituée, en % massique, de C : 0,001 % à 0,010 %, Si : 0,05 % à 0,50 %, Mn: 0,10 % à 2,0 %, P : 0,020 % ou moins, S : 0,010 % ou moins, Al : 0,001 % à 0,10 %, Cr : plus de 14 % et moins de 15 %, Ni : 2,0 % à 5,0 %, Mo: 1,5 % à 3,5 %, V: 0,001 % à 0,20 %, N : 0,015 % ou moins, éventuellement au moins

un élément choisi parmi Cu : 0,01 % à 3,5 %, W : 0,01 % à 3,5 %, Ti : 0,01 % à 0,20 %, Nb : 0,01 % à 0,20 %, Zr : 0,01 % à 0,20 %, Ca : 0,0005 à 0,0100 % et terres rares : 0,0005 % à 0,0100 %, le reste étant du Fe et des impuretés inévitables, à la condition que P_1 défini par l'équation (1) ci-dessous aille de 11,5 à 13,3 et que P_2 défini par l'équation (2) ci-dessous soit supérieur ou égal à 0, et

dans lequel procédé, une microstructure dans une zone affectée thermiquement, qui lorsqu'un soudage est réalisé est soumise à un chauffage jusqu'à une plage de température de formation d'une phase unique de ferrite supérieure ou égale à 1300 °C et à un refroidissement, est formée par ledit soudage de telle manière que 50 % ou plus des joints de grain de ferrite antérieurs, rapportés à la longueur totale des joints de grain de ferrite antérieurs, sont occupés par une phase martensite,

$$P_1 = Cr + Mo + 0{,}4W + 0{,}3Si - 43{,}5C - 0{,}4Mn - Ni - 0{,}3Cu - 9N \quad (1)$$

$$P_2 = (0{,}5Cr + 5{,}0) - P_1 \quad (2)$$

où Cr, Mo, W, Si, C, Mn, Ni, Cu, N : teneurs, en % massique, des éléments chimiques représentés respectivement par les symboles atomiques correspondants.

FIG. 1

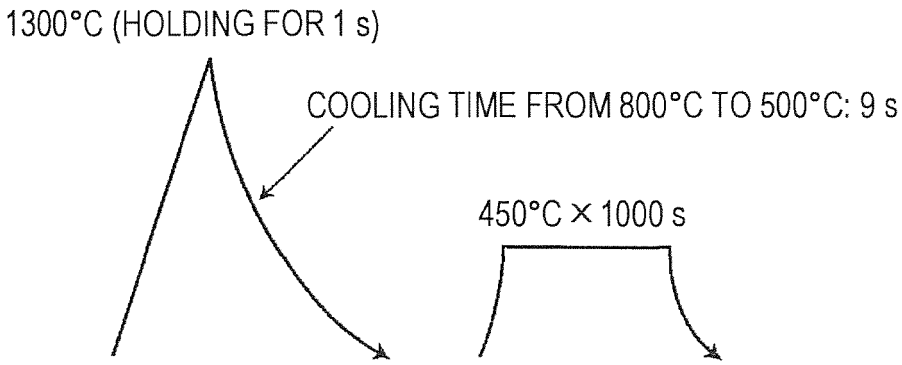
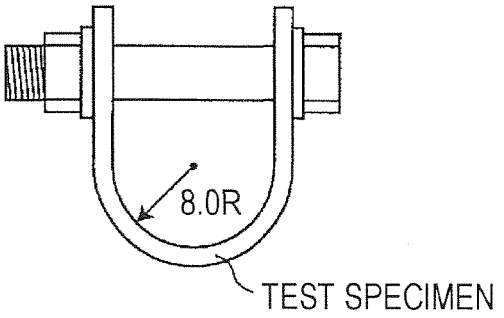

1300°C (HOLDING FOR 1 s)
COOLING TIME FROM 800°C TO 500°C: 9 s
450°C × 1000 s

FIG. 2


8.0R
TEST SPECIMEN

REFERENCES CITED IN THE DESCRIPTION

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