(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 562 284 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
03.06.2020 Bulletin 2020/23

(21) Application number: **11772096.1**

(22) Date of filing: **15.04.2011**

(51) Int Cl.:
C22C 38/00 *(2006.01)* ***C22C 38/58*** *(2006.01)*
C21D 1/25 *(2006.01)* ***C21D 6/00*** *(2006.01)*
C21D 9/08 *(2006.01)* ***C21D 9/50*** *(2006.01)*
C22C 38/46 *(2006.01)* ***C22C 38/44*** *(2006.01)*
C22C 38/06 *(2006.01)* ***C22C 38/02*** *(2006.01)*
C22C 38/04 *(2006.01)*

(86) International application number:
PCT/JP2011/059891

(87) International publication number:
WO 2011/132765 (27.10.2011 Gazette 2011/43)

(54) **Cr-CONTAINING STEEL PIPE FOR LINE PIPE AND HAVING EXCELLENT INTERGRANULAR STRESS CORROSION CRACKING RESISTANCE AT WELDING-HEAT-AFFECTED PORTION**

CR-HALTIGES STAHLROHR FÜR EIN LEITUNGSROHR MIT HERVORRAGENDER BRUCHFESTIGKEIT DER DURCH SCHWEISSUNGSHITZE BETROFFENEN TEILE BEI INTERGRANULARER STRESSKORROSION

TUYAU D'ACIER CONTENANT DU CHROME POUR UNE CANALISATION AYANT UNE EXCELLENTE RÉSISTANCE À LA FISSURATION PAR CORROSION INTERGRANULAIRE SOUS CONTRAINTE DANS LA PARTIE AFFECTÉE PAR LA CHALEUR DE SOUDAGE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **19.04.2010 JP 2010095860**

(43) Date of publication of application:
27.02.2013 Bulletin 2013/09

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Description

[Technical Field]

[0001] The present invention relates to a Cr-containing steel pipe suitable for a steel pipe for linepipe used in a pipeline for transporting crude oil or natural gas produced in an oil well or a gas well, and more particularly to an improvement of corrosion resistance in an extremely harsh corrosion environment and an improvement of resistance to intergranular stress corrosion cracking, IGSCC, in a welded heat affected zone.

[Background Art]

[0002] From a viewpoint of skyrocketing crude oil prices and the drying up of oil resources expected in near future, there has been recently observed the vigorous development of deep layer oil wells or gas wells having a large depth which has not been noticed because of the deepness of the well or highly corrosive oil wells and gas wells whose development has been abandoned once. Such oil wells or gas wells are deep in depth in general, are in the high-temperature atmosphere, and contain carbon dioxide gas (CO_2), chloride ion (Cl^-) and the like thus being a harsh corrosion environment. Further, there has been also observed the vigorous development of oil wells and gas wells where the drilling environment is harsh such as a bottom of the ocean. As a pipeline for transporting crude oil or natural gas produced in such oil wells and gas wells, from a viewpoint of the acquisition of high-strength, high-toughness and excellent corrosion resistance and the reduction of a pipeline laying cost, there has been a demand for the use of a steel pipe which also has excellent weldability.

[0003] To satisfy such a demand, for example, patent document 1 discloses a martensitic stainless steel pipe which is suitable for a linepipe, can prevent intergranular stress corrosion cracking (abbreviated as IGSCC) generated in a welded heat affected zone without applying a post weld heat treatment, and has an excellent resistance to intergranular stress corrosion cracking in the welded heat affected zone. The martensitic stainless steel pipe disclosed in patent document 1 has the composition which contains by mass% less than 0.0100% C, less than 0.0100% N, 10 to 14% Cr, 3 to 8% Ni, 0.05 to 1.0% Si, 0.1 to 2.0% Mn, 0.03% or less P, 0.010% or less S, and 0.001 to 0.10% Al and, further, contains one kind or two or more kinds selected from a group consisting of 4% or less Cu, 4% or less Co, 4% or less Mo, and 4% or less W, and one kind or two or more kinds selected from a group consisting of 0.15% or less Ti, 0.10% or less Nb, 0.10% or less V, 0.10% or less Zr, 0.20% or less Hf, and 0.20% or less Ta such that Csol satisfies less than 0.0050%. In the technique disclosed in patent document 1, by setting Csol which is an effective content of dissolved carbon effectively acting on the formation of Cr carbide to less than 0.0050%, the formation of Cr carbide on prior-austenite grain boundaries can be prevented, and the formation of Cr depleted zones which cause intergranular stress corrosion cracking in the welded heat affected zone can be prevented so that it is possible to suppress the intergranular stress corrosion cracking generated in a welded heat affected zone without applying a post weld heat treatment.

[0004] Further, patent document 2 discloses a stainless steel pipe with high strength for linepipe excellent in corrosion resistance. The stainless steel pipe with high strength described in patent document 2 has the composition which contains by mass% 0.001 to 0.015% C, 0.001 to 0.015% N, 15 to 18% Cr, 0.5% or more and less than 5.5% Ni, 0.5 to 3.5% Mo, 0.02 to 0.2% V, 0.01 to 0.5% Si, 0.1 to 1.8% Mn, 0.03% or less P, 0.005% or less S, 0.001 to 0.015% N, and 0.006% or less O such that both the relationship of $Cr + 0.65Ni + 0.6Mo + 0.55Cu - 20C \geq 18.5$, the relationship of $Cr + Mo + 0.3Si - 43.5C - 0.4Mn - Ni - 0.3Cu - 9N \geq 11.5$, and the relationship of $C + N \leq 0.025$ are simultaneously satisfied. In the technique disclosed in patent document 2, while the steel pipe contains a proper amount of ferrite phase so as to maintain the ferrite-martensite dual phase microstructure, the composition also contains Cr such that the content of Cr is adjusted to high level of 15 to 18%. Accordingly, it is possible to provide a steel pipe which is excellent in hot workability and low temperature toughness, has a sufficient strength for a linepipe, and is excellent in corrosion resistance even under high-temperature (200°C) corrosion environment containing a carbon dioxide gas and chloride ions.

Patent document 3 discloses a martensitic stainless steel welded steel pipe excellent in corrosion resistance, particularly stress corrosion cracking resistance. More specifically, Patent document 3 relates to a welded steel pipe used for pipelines, especially trunk lines, for transporting fluids that are prone to corrosion of metals such as oil and natural gas, having an outer diameter of more than 20 inches and a wall thickness of more than 0.5 inches.

[Prior art literature]

[Patent document]

[0005]

[Patent document 1] JP-A-2005-336601 (WO2005/073419 A1)

[Patent document 2] JP-A-2005-336599
[Patent document 3] JP-A-2001-115238

[Summary of Invention]

[Technical Problem]

[0006] However, under the harsh corrosion environment, even with the technique disclosed in patent document 1, there still remains a drawback that the intergranular stress corrosion cracking generated in a welded heat affected zone cannot be completely suppressed, and a current situation is that intergranular stress corrosion cracking generated in the welded heat affected zone is prevented by performing the post weld heat treatment. Further, a steel pipe manufactured by the technique disclosed in patent document 2 does not take the resistance to intergranular stress corrosion cracking into consideration at all. Rather, in spite of the increase of the content of Cr, from a viewpoint of resistance to intergranular stress corrosion cracking, the resistance of the steel pipe manufactured by the technique disclosed in patent document 2 is lowered compared to the steel pipe disclosed in patent document 1 which has less content of Cr compared to the steel pipe disclosed in patent document 2. Accordingly, the steel pipe disclosed in patent document 2 also has a drawback that intergranular stress corrosion cracking generated in the welded heat affected zone cannot be completely suppressed.

[0007] Accordingly, it is an object of the present invention to overcome the above-mentioned drawbacks of the related art and to provide a Cr-containing steel pipe for linepipe having desired high-strength and being excellent in toughness, corrosion resistance and resistance to sulfide stress corrosion cracking and also being excellent in resistance to intergranular stress corrosion cracking in a welded heat affected zone. A steel pipe which the present invention aims at is an X-65 to X-80 class steel pipe (steel pipe having yield strength (YS) of 448 to 651MPa). Here, "excellent in toughness" means a case where absorbed energy E_{-40}(J) at -40°C in a Charpy impact test is 50J or more. Further, "excellent in corrosion resistance" means a case where a corrosion rate (mm/year) (hereinafter abbreviated as mm/y) in 200 g/liter of an NaCl aqueous solution at a temperature of 150°C in which a carbon dioxide gas at 3.0MPa is saturated is 0.10mm/y or less. Here, "steel pipe" includes a seamless steel pipe and a welded steel pipe in its definition.

[Solution to Problem]

[0008] The inventors of the present invention, to achieve the above-mentioned object, have extensively studied various factors which affect resistance to intergranular stress corrosion cracking in a welded heat affected zone under a corrosion environment containing carbon dioxide gas or chloride ion with respect to a ferrite-martensite stainless steel pipe containing 16 to 17% of Cr.

[0009] As a result, the inventors of the present invention have found out that, in such ferrite-martensitic stainless steel, intergranular stress corrosion cracking occurs through a process that coarse ferrite grains are formed in a welded heat affected zone during a heating cycle at the time of welding, Cr carbide precipitates in grain boundaries of coarse ferrite grains during a cooling cycle which follows the heating cycle, and Cr depleted zones are formed in the grain boundaries along with such precipitation. Based on such finding, the inventors of the present invention have arrived at an idea that, in this kind of steel, by generating the transformation from ferrite (α) to austenite (γ) at least from grain boundaries before Cr carbide precipitates in grain boundaries of coarse ferrite grains so that most grain boundaries are occupied by austenite, the precipitation of Cr carbide in the grain boundaries can be prevented so that the occurrence of intergranular stress corrosion cracking can be prevented by suppressing the formation of Cr depleted zones. Then, as the result of further studies, the inventors of the present invention have found out that, to generate the transformation from ferrite (α) to austenite (γ) from grain boundaries before Cr carbide precipitates in grain boundaries, it is necessary to properly set a composition range such that the composition range satisfies the following formula (1).

$$11.5 \leq Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N \leq 13.3 \quad \ldots (1)$$

[0010] According to the studies made by the inventors of the present invention, it is also found out that, when the steel adopts the composition where {Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N} becomes equal to or less than 13.3, carbide (Cr carbide) hardly precipitates in grain boundaries so that Cr depleted zones are also hardly formed whereby intergranular stress corrosion cracking can be prevented. This is because when the steel has the composition where a rate of ferrite forming elements is low such that {Cr+Mo+0.4M+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N} is equal to or less than 13.3, in performing girth welding such as at the time of installing a pipeline, the microstructure of a coarse ferrite phase is formed in a region which is exposed to high temperature exceeding 1200°C around a melting point at the time of heating, while the transformation from α to γ is generated so that a γ phase is generated in grain boundaries or in grains at the time of cooling. In such a case, a solubility product of carbide in the γ phase is larger than a solubility product in

the α phase so that carbide (Cr carbide) hardly precipitates in grain boundaries whereby Cr depleted zones are also hardly formed thus preventing intergranular stress corrosion cracking. It is needless to say that most or all γ phase is transformed into a martensite phase by cooling which follows thereafter.

[0011] On the other hand, when the steel has the composition where a rate of ferrite forming elements is high such that {Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N} exceeds 13.3, the microstructure of a coarse ferrite phase arrives at a room temperature as it is without generating the transformation from α to γ at the time of cooling which follows thereafter and hence, Cr carbide precipitates on grain boundaries so that Cr depleted zones are formed whereby intergranular stress corrosion cracking is liable to occur.

[0012] Next, the result of an experiment based on which the present invention is made is explained. From various kinds of steel pipes where contents of respective compositions are changed from each other, specimen having a size: a thickness of 4mm, a width of 15mm and a length of 115mm respectively are sampled, and a welding heat cycle was applied to a center portion of the specimen under conditions shown in Fig. 1. A specimen for microstructural observation was sampled from the specimen after a welding heat cycle was given, the specimen for microstructural observation was polished, and corroded, and the microstructure of the specimen for microstructural observation after the welding heat cycle was given was observed. Then, the presence or non-presence of a transformed product (martensite phase and/or austenite phase) in prior α grain boundaries and a length of the prior α grain boundaries which are occupied by the transformed product (martensite phase and/or austenite phase) were measured, and an occupancy ratio relative to the whole length of the prior α grain boundaries was calculated.

[0013] Further, a specimen having a thickness of 2mm, a width of 15mm and a length of 75mm was cut out from a center portion of the obtained specimen to which a welding heat cycle was already given, and a U bend stress corrosion cracking test was carried out on the specimen. In the U bend stress corrosion cracking test, as shown in Fig. 2, the specimen was bent in a U shape with an inner radius of 8mm and was subjected to a corrosion test where the specimen was immersed in a corrosive solution. A 50g/l NaCl solution having a solution temperature of 100°C, a CO_2 pressure of 0.1MPa and pH of 2.0 was used as the corrosive solution. A test period was 168 hours.

[0014] After the test was finished, a cross section of the specimen was observed using an optical microscope with a magnification ratio of 100 times, and the presence and non-presence of cracks was observed. Fig. 3 shows the relationship between a prior α grain boundary occupancy ratio and {Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N} by determining a case where there was cracking as " × " and a case where there was no cracking as "O". Fig. 3 shows that when {Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N} in the formula (1) exceeds 13.3, a rate of a length occupied by a martensite phase and/or an austenite phase relative to the whole length of the prior ferrite (α) grain boundaries becomes less than 50% so that intergranular stress corrosion cracking occurred.

[0015] The present invention has been completed as the result of the further studies based on the above-mentioned findings and is directed to a Cr-containing steel pipe for line pipe excellent in resistance to intergranular stress corrosion cracking in a welded heat affected zone which has the composition which contains ,by mass% 0.001 to 0.015% C, 0.05 to 0.50% Si, 0.10 to 2.0% Mn, 0.020% or less P, 0.010% or less S, 0.001 to 0.10% Al, 15.0 to 18.0% Cr, 2.0 to 6.0% Ni, 1.8 to 3.0% Mo, 0.001 to 0.20% V, and 0.015% or less N so as to satisfy a following formula (1), optionally one kind or two kinds selected from a group consisting of, by mass%, 0.01 to 3.5% Cu and 0.01 to 3.5% W, optionally further one kind or two or more kinds selected from a group consisting of, by mass%, 0.01 to 0.20% Ti, 0.01 to 0.20% Nb, and 0.01 to 0.20% Zr, and optionally further one kind or two kinds selected from a group consisting of, by mass%, 0.0005 to 0.0100% Ca and 0.0005 to 0.0100% REM, and Fe and inevitable impurities as a balance, wherein a welded heat affected zone has a microstructure where 50% or more of prior-ferrite grain boundaries is occupied by a martensite phase and/or an austenite phase in a ratio to the whole length of prior-ferrite grain boundaries, and wherein formula (1) is:

$$11.5 \leq Cr + Mo + 0.4W + 0.3Si - 43.5C - 0.4Mn - Ni - 0.3Cu - 9N \leq 13.3, \quad (1)$$

in which formula (1) Cr, Mo, W, Si, C, Mn, Ni, Cu, N indicate contents of respective elements in mass%.

[Advantageous Effects of Invention]

[0016] According to the present invention, a Cr-containing steel pipe for linepipe excellent in resistance to intergranular stress corrosion cracking in a welded heat affected zone which requires no post weld heat treatment can be manufactured at a low cost so that the present invention exhibits remarkable advantageous effects industrially. Further, the present invention also has an advantageous effect that the steel pipe structure such as a pipeline can be constructed without performing post weld heat treatment so that a construction period can be shortened whereby a construction cost can be remarkably reduced.

[Brief Description of Drawings]

[0017]

[Fig. 1]
An explanatory view schematically showing a simulated welding thermal cycle used in an embodiment.
[Fig. 2]
An explanatory view schematically showing a bending state of a test specimen for U-bend test used in an embodiment.
[Fig. 3]
A view showing the relationship between a ratio of a length occupied by a martensite phase and/or an austenite phase with respect to the whole length of prior ferrite grain boundaries and formula (1) and the presence or non-presence of the generation of intergranular stress corrosion cracking(hereinafter abbreviated as IGSCC).

[Description of Embodiment]

[0018] Firstly, the reason for limiting the composition of a steel pipe according to the present invention is explained. Hereinafter, unless otherwise specified, "mass%" is simply indicated as "%".

C: 0.001 to 0.015%

[0019] C is an element which contributes to the increase of strength of a steel pipe, and in the present invention, the steel pipe is required to contain 0.001% or more C.

[0020] On the other hand, when the steel pipe contains a large content of C exceeding 0.015%, toughness of the steel pipe in a welded heat affected zone is deteriorated. When the steel pipe contains a large content of C, particularly, it becomes difficult to prevent intergranular stress corrosion cracking in a welded heat affected zone. Accordingly, the content of C is limited to a value which falls within a range from 0.001 to 0.015%. The content of C is preferably limited to a value which falls within a range from 0.002 to 0.010%.

Si: 0.05 to 0.50%

[0021] Si acts as a deoxidizing agent and is an element for increasing strength of a steel pipe by solid solution and, in the present invention, the steel pipe is required to contain 0.05% or more Si. However, when the steel pipe contains a large content of Si exceeding 0.50%, toughness of a base material and a welded heat affected zone is deteriorated. Accordingly, the content of Si is limited to a value which falls within a range from 0.05 to 0.50%. The content of Si is preferably limited to a value which falls within a range from 0.10 to 0.40%.

Mn: 0.10 to 2.0%

[0022] Mn contributes to the increase of strength of a steel pipe by solid solution, and is also an austenite forming element so that Mn enhances toughness of a base material and a welded heat affected zone by suppressing the generation of ferrite. To acquire such effects, the steel pipe is required to contain 0.10% or more Mn. However, even when the content of Mn exceeds 2.0%, the effect is saturated so that an effect corresponding to the content of Mn cannot be expected. Accordingly, the content of Mn is limited to a value which falls within a range from 0.10 to 2.0%. Here, the content of Mn is preferably limited to a value which falls within a range from 0.20 to 0.90%.

P: 0.020% or less

[0023] P is an element which deteriorates corrosion resistance such as CO_2 corrosion resistance and resistance to sulfide stress corrosion cracking and hence, in the present invention, it is desirable that the content of P is set as small as possible. However, the excessive reduction of P pushes up a manufacturing cost. Accordingly, as a range of the content of P which enables the industrial manufacture of a steel pipe at a relatively low cost and does not cause the deterioration of corrosion resistance, the content of P is limited to 0.020% or less. The content of P is preferably set to 0.015% or less.

S: 0.010% or less

[0024] S is an element which remarkably deteriorates hot workability in a pipe manufacturing process and hence, it is desirable that the content of S is set as small as possible. However, a steel pipe can be manufactured through usual

steps by decreasing the content of S to 0.010% or less and hence, the content of S is limited to 0.010% or less. Here, the content of S is preferably set to 0.004% or less.

Al: 0.001 to 0.10%

[0025] Al is an element having a strong deoxidization function. To allow Al to exhibit such a strong deoxidization action, the steel pipe is required to contain 0.001% or more Al. However, when the content of Al exceeds 0.10%, Al exerts an adverse effect on toughness of the steel pipe. Accordingly, the content of Al is limited to 0.10% or less. The content of Al is preferably set to 0.05% or less.

Cr: 15.0 to 18.0%

[0026] Cr is an element which enhances corrosion resistance such as CO_2 corrosion resistance and resistance to sulfide stress corrosion cracking by forming a protective surface film. In the present invention, a steel pipe is required to contain 15% or more Cr particularly for the purpose of enhancing corrosion resistance under harsh corrosion environment. On the other hand, when the content of Cr exceeds 18%, the hot workability is deteriorated. Accordingly, the content of Cr is limited to a value which falls within a range from 15.0 to 18.0%.

Ni: 2.0 to 6.0%

[0027] Ni is an element which has a function of hardening a protective film, enhances corrosion resistance such as CO_2 corrosion resistance and resistance to sulfide stress corrosion cracking, and contributes to the increase of strength of a steel pipe. To acquire such effects, the steel pipe is required to contain 2.0% or more Ni. However, the content of Ni exceeding 6.0% lowers hot workability and brings about the lowering of strength. Accordingly, the content of Ni is limited to a value which falls within a range from 2.0 to 6.0%. The content of Ni is preferably limited to a value which falls within a range from 3.0 to 5.0%.

Mo: 1.8 to 3.0%

[0028] Mo is an element which has a function of increasing resistance to pitting corrosion generated by Cl^- (chloride ions) and is effectively used for enhancing corrosion resistance. To acquire such effects, the steel pipe is required to contain 1.5% or more Mo. On the other hand, when the content of Mo exceeds 3.5%, hot workability is lowered and a manufacturing cost is pushed up. Accordingly, the content of Mo is limited to a value which falls within a range from 1.8 to 3.0%.

V: 0.001 to 0.20%

[0029] V is an element which contributes to the increase of strength and has a function of enhancing resistance to stress corrosion cracking. Although these effects appear in an outstanding manner when the content of V is set to 0.001% or more, toughness of a steel pipe is lowered when the content of V exceeds 0.20%. Accordingly, the content of V is limited to a value which falls within a range from 0.001 to 0.20%. The content of V is preferably limited to a value which falls within a range from 0.010 to 0.10%.

N: 0.015% or less

[0030] N is an element which has a function of enhancing pitting corrosion resistance. However, N is an element having a function of remarkably lowering weldability and hence, in the present invention, it is desirable to set the content of N as small as possible. However, excessive reduction of N pushes up a manufacturing cost. Accordingly, as a range of the content of N which enables the industrial manufacture of a steel pipe at a relatively low cost and does not cause the deterioration of weldablity, the content of N is set to 0.015% as an upper limit.

[0031] While the above-mentioned compositions are basic compositions, in addition to the basic composition, as selective elements, the steel pipe may selectively contain one kind or two kinds selected from a group consisting of: 0.01 to 3.5% Cu and 0.01 to 3.5% W and/or one kind or two or more kinds selected from a group consisting of 0.01 to 0.20% Ti, 0.01 to 0.20% Nb, and 0.01 to 0.20% Zr and/or one kind or two kinds selected from a group consisting of 0.0005 to 0.0100% Ca and 0.0005 to 0.0100% REM when necessary.

One kind or two kinds selected from a group consisting of 0.01 to 3.5% Cu and 0.01 to 3.5% W

[0032] Both Cu and W are elements which enhance CO_2 corrosion resistance, and a steel pipe may selectively contain Cu, W when necessary.

[0033] Cu is an element which enhances CO_2 corrosion resistance and also contributes to the increase of strength of a steel pipe. The content of Cu is preferably set to 0.01% or more for acquiring such effects. However, even when the content of Cu exceeds 3.5%, the effects are saturated, and an effect corresponding to the content of Cu cannot be expected so that it becomes economically disadvantageous. Accordingly, when the steel pipe contains Cu, the content of Cu is preferably limited to a value which falls within a range from 0.01 to 3.5%. Here, the content of Cu is more preferably limited to a value which falls within a range from 0.30 to 2.0%.

[0034] W is an element which enhances CO_2 corrosion resistance, and enhances resistance to stress corrosion cracking and, further, resistance to sulfide stress corrosion cracking and pitting corrosion resistance. The content of W is preferably set to 0.01% or more for acquiring such effects. However, even when the content of W exceeds 3.5%, the effects are saturated, and an effect corresponding to the content of W cannot be expected so that it becomes economically disadvantageous. Accordingly, when a steel pipe contains W, the content of W is preferably limited to a value which falls within a range from 0.01 to 3.5%. The content of W is more preferably limited to a value which falls within a range from 0.30 to 2.0%.

One kind or two or more kinds selected from a group consisting of 0.01 to 0.20% Ti, 0.01 to 0.20% Nb, 0.01 to 0.20% Zr

[0035] All of Ti, Nb, Zr are elements which have strong carbide forming tendency compared to Cr, and have a function of suppressing the precipitation of Cr carbide in grain boundaries at the time of cooling. The steel pipe of the present invention may selectively contain one kind or two or more kinds selected from Ti, Nb, Zr when necessary. To acquire the above-mentioned advantageous effects, it is preferable that the steel pipe of the present invention contains 0.01% or more Ti, 0.01% or more Nb and 0.01% or more Zr respectively. However, the content of Ti exceeds 0.20%, the content of Nb exceeds 0.20% or the content of Zr exceeds 0.20%, weldability and toughness are lowered. Accordingly, when the steel pipe of the present invention contains these elements, the content of Ti is preferably limited to a value which falls within a range from 0.01 to 0.20%, the content of Nb is preferably limited to a value which falls within a range from 0.01 to 0.20%, and the content of Zr is preferably limited to a value which falls within a range from 0.01 to 0.20%. Here, it is more preferable that the steel pipe of the present invention contains 0.02 to 0.10% Ti, 0.02 to 0.10% Nb and 0.02 to 0.10% Zr respectively.

One kind or two kinds selected from a group consisting of: 0.0005 to 0.0100% Ca and 0.0005 to 0.0100% REM

[0036] Both Ca and REM are elements which enhance hot workability and manufacture stability at the time of continuous casting through a morphology control of inclusion and the composition of the steel pipe of the present invention may selectively contain these elements when necessary. To acquire such advantageous effects, it is preferable that the steel pipe of the present invention contains 0.0005% or more Ca and 0.0005% or more REM respectively. However, the content of Ca exceeding 0.0100% or the content of REM exceeding 0.0100% brings about the increase of an content of inclusion so that cleanness of steel is lowered. Accordingly, when the steel pipe of the present invention contains these elements, the content of Ca is preferably limited to a value which falls within a range from 0.0005 to 0.0100%, and the content of REM is preferably limited to a value which falls within a range from 0.0005 to 0.0100%. Here, it is more preferable that the content of Ca is limited to a value which falls within a range from 0.0010 to 0.0030% and the content of REM is limited to a value which falls within a range from 0.0010% to 0.0050%.

[0037] In the present invention, the contents of the respective compositions are adjusted such that the next formula (1) is satisfied within the above-mentioned composition range.

$$11.5 \leq Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N \leq 13.3 \quad \ldots (1)$$

(Here, Cr, Mo, W, Si, C, Mn, Ni, Cu, N: contents of respective elements(mass%))

[0038] The center value {Cr+Mo+0.4W+0.3Si-43.5C-0.4Mn-Ni-0.3Cu-9N} in the formula (1) is an index used for evaluating hot workability and, further, resistance to intergranular stress corrosion cracking. In the present invention, the contents of the respective elements are adjusted within the ranges described above such that the center value in the formula (1) falls within a range of 11. 5 to 13.3 which satisfies the formula (1). When the center value in the formula (1) is less than 11. 5, hot workability becomes insufficient so that hot workability necessary and sufficient for the manufacture

of a seamless steel pipe cannot be secured whereby the manufacture of the seamless steel pipe becomes difficult. On the other hand, when the center value in the formula (1) is exceeds 13.3, as described above, the resistance to intergranular stress corrosion cracking is lowered. From the above, the contents of the respective elements are adjusted such that the contents of the respective elements fall within the above-mentioned ranges and satisfy the formula (1).

[0039] The balance other than the above-mentioned compositions is constituted of Fe and inevitable impurities. As the inevitable impurities, the steel pipe may contain 0.010% or less O.

[0040] The steel pipe of the present invention has the above-mentioned composition and, further, has the microstructure formed of 10 to 50% of ferrite phase by volume and 30% or less of austenite phase by volume, and a martensite phase as a base phase. The martensite phase also includes a tempered martensite phase in its definition. It is preferable that the steel pipe of the present invention contains 25% or more of martensite phase by volume to ensure desired strength. The ferrite phase is the microstructure which is soft and enhances workability, and it is desirable that the steel pipe of the present invention contains 10% or more of ferrite phase by volume from a viewpoint of enhancing workability. On the other hand, when the steel pipe of the present invention contains a ferrite phase exceeding 50% by volume, the steel pipe of the present invention cannot ensure desired high strength (X-65,YS: 448MPa or more). Further, although the austenite phase is the microstructure which enhances toughness, when the content of austenite phase exceeds 30%, it is difficult for the steel pipe of the present invention to ensure strength.

[0041] The austenite phase may take a case where the whole austenite phase is not transformed into a martensite phase at the time of quenching and the austenite phase remains partially or a case where a part of a martensite phase or a ferrite phase is subjected to reverse transformation at the time of tempering and the transformed austenite phase remains even after cooling.

[0042] In the steel pipe of the present invention having the above-mentioned composition and the above-mentioned microstructure, when a welded portion is formed, in the composition range of the steel of the present invention, a ferrite single phase temperature region appears at a temperature of 1300°C or more. Accordingly, it is desirable that a welded heat affected zone which is heated to the ferrite single phase temperature region of 1300°C or more at the time of welding and is cooled has the microstructure where 50% or more of prior-ferrite grain boundaries is occupied by a martensite phase and/or an austenite phase in a ratio to the whole length of the prior-ferrite grain boundaries. As a result, the precipitation of Cr carbide in grain boundaries of the coarse prior ferrite grains can be avoided so that the intergranular stress corrosion cracking is suppressed whereby the resistance to intergranular stress corrosion cracking of the welded heat affected zone can be improved.

[0043] Next, the preferred method of manufacturing the steel pipe of the present invention is explained by taking a seamless steel pipe as an example.

[0044] Firstly, it is preferable that molten steel having the above-mentioned composition is made by a conventional steel making method such as a converter, an electric furnace or a vacuum melting furnace, and a billet is formed from the molten steel by a conventional method such as a continuous casting method and a slabing mill method for rolling an ingot. Then, the billet is heated and is subjected to hot rolling through a conventional manufacturing step such as a Mannesmann-plug mill method or a Mannesmann-mandrel mill method, and is formed into a pipe shape thus manufacturing a seamless steel pipe having a desired size. The seamless steel pipe after pipe manufacturing is preferably subjected to accelerated cooling where the seamless steel pipe is cooled to a room temperature at a cooling rate above an air-cooling rate, preferably, at an average cooling rate of 0.5°C/s or more from 800 to 500°C. Due to such accelerated cooling, provided that the steel pipe has the composition within the composition range of the present invention, the steel pipe can have the microstructure where a martensite phase is a base phase as described above. When the cooling rate is less than 0.5°C/s, the steel pipe cannot have the microstructure where a martensite phase is a base phase . Here, the microstructure where a martensite phase is a base phase means the microstructure where the martensite phase has the largest volume ratio or has a volume ratio which is substantially equal to a volume ratio of another microstructure which has the largest volume ratio.

[0045] In place of the above-mentioned accelerated cooling after rolling, reheating, quenching and tempering may be performed. Such quenching may preferably be done in such a way that the seamless pipe is reheated to a temperature of 800°C or more, held at the temperature for 10min or more, and cooled to a temperature of 100°C or less at a cooling rate above an air-cooling rate or at an average cooling rate of 0.5°C/s or more from 800 to 500°C. When the reheating temperature is less than 800°C, the seamless pipe cannot ensure the desired microstructure where a martensite phase is a base phase.

[0046] Tempering may preferably be done in such a way that, after quenching, the seamless pipe is heated to a temperature of 500°C or more and 700°C or less, and more preferably, to a temperature of 580°C or more and 680°C or less, held at the same temperature for a predetermined time, and cooled by air. Due to such tempering, the seamless pipe can acquire all of desired high strength, desired high toughness and desired excellent corrosion resistance.

[0047] Although the explanation has been made heretofore by taking the seamless pipe as an example, the present invention is not limited to the seamless pipe. Using a steel sheet having the above-mentioned composition, an electric resistance seam welded steel pipe or a UOE steel pipe is manufactured through conventional steps for linepipe. It is

also preferable that the electric resistance seam welded steel pipe or the UOE steel pipe be formed into a steel pipe having the above-mentioned microstructure by applying the above-mentioned quenching-tempering treatment to a steel sheet or steel plate).

[0048] Further, the welded structure (steel pipe structure) can be formed by joining the steel pipes of the present invention by welding. The joining of the steel pipes of the present invention by welding also includes a case where the steel pipes of the present invention and other kind of steel pipes are joined to each other by welding. In the welded structure which is formed by joining the steel pipes of the present invention by welding, at the time of welding, a welded heat affected zone which is preferably heated to a ferrite single phase temperature region of 1300°C or more and is cooled includes a welded heat affected zone having the microstructure where 50% or more of prior-ferrite grain boundaries is occupied by a martensite phase and/or an austenite phase in a ratio to the whole length of prior-ferrite grain boundaries. Accordingly, intergranular stress corrosion cracking can be suppressed so that resistance to intergranular stress corrosion cracking in the welded heat affected zone can be improved without performing the post weld heat treatment.

[0049] The present invention is further explained hereinafter based on examples.

[Examples]

[0050] Molten steel having the composition shown in Table 1 was made by a vacuum melting furnace and was subjected to degassing, and thereafter, a steel ingot having 100kgf was produced by casting. The steel ingot was formed into a steel pipe having a predetermined size by hot forging. The steel pipe was heated and formed into a pipe by hot working using a model seamless mill (a miniaturized seamless mill for experimental use) thus producing a seamless steel pipe (outer diameter: 65mmϕ, wall thickness: 5.5mm).

[0051] For the obtained seamless steel pipe, the presence or non-presence of cracking on inner and outer surfaces of the seamless steel pipe was investigated by visually eyes, and hot workability was evaluated as follows. When cracking having a length of 5mm or more is recognized on an end surface on the pipe longitudinal direction, it is evaluated that cracking is present and the evaluation "×" is given, while it is evaluated that cracking is not present in other cases and the evaluation "○" is given.

[0052] Then, test materials (steel pipes) were sampled from the obtained seamless steel pipe, and quenching and tempering were applied to the test materials (steel pipes) under conditions shown in Table 2.

[0053] Specimens were sampled from the test materials (steel pipes) to which the quenching and tempering were applied, and the microstructural observation, a tensile test, an impact test, a corrosion test, a sulfide stress corrosion cracking test, a U bend stress corrosion cracking test were carried out on the specimens. Testing methods are as follows.

(1) Microstructural observation

[0054] Specimens for microstructural observation were sampled from the obtained test materials (steel pipes) . The specimens for microstructural observation were polished and corroded, and thereafter, the specimens for microstructural observation were observed and were imaged using an optical microscope (magnification ratio: 1000 times), the microstructure of the specimen for microstructural observation was identified, and microstructure fractions of respective phases in a base metal were obtained using an image analyzer. Here, an amout of residual austenite was measured using an X-ray diffraction method.

(2) Tensile test

[0055] Arc-shaped pieces for a tensile test specified in the API standards were sampled from the obtained test materials (steel pipes) such that the pipe axial direction becomes the tensile direction, a tensile test was carried out on the arc-shaped pieces for a tensile test thus obtaining tensile properties (yield strength YS, tensile strength TS), and strength of the base metal was evaluated.

(3) Impact test

[0056] V-notched specimens (thickness: 5.0mm) were sampled from the obtained test materials (steel pipes) in accordance with the provision of JIS Z 2242, and a Charpy impact test was carried out on the V-notched specimens, absorption energy vE_{-40} (J) at -40°C was obtained and the toughness of the base metal was evaluated.

(4) Corrosion test

[0057] Corrosion specimens each having a thickness of 3mm, a width of 25mm and a length of 50mm were sampled from the obtained test materials (steel pipes) by machining, the corrosion test was carried out on the corrosion specimens,

and the corrosion resistance(CO_2 corrosion resistance, pitting corrosion resistance) was evaluated. In the corrosion test, 200 g/liter of an NaCl aqueous solution at a temperature of 150°C in which a carbon dioxide gas at 3.0MPa is saturated was held in an autoclave, the corrosion specimens were immersed in the aqueous solution for 30 days. After the corrosion test was finished, a weight of each specimen was measured and a corrosion rate was calculated based on a change in weight (reduction of weight) before and after the corrosion test. Further, after the corrosion test, the presence or non-presence of pitting corrosion on a surface of the specimen was observed using a laupe with a magnification rate of 10 times. The evaluation "×" is given when the pitting corrosion occurs and the evaluation "○" is given when there is no pitting corrosion.

(5) Sulfide stress corrosion cracking (SSC) test

[0058] Four-point bending test specimens (size: thickness of 4mm, width of 15mm and length of 115mm) were sampled from the obtained test materials (steel pipes), and a four-point bending test in accordance with EFC (European Federation of Corrosion) No.17 was carried out on the specimens, and the resistance to sulfide stress corrosion cracking was evaluated. 50g/liter of NaCl+$NaHCO_3$ solution (pH: 4.5) was used as a test solution, the test was carried out while flowing a 10vol% H_2S+90vol% CO_2 mixture gas, and the presence or non-presence of breaking was investigated. An applied stress was set to YS (yield strength) of a base material, and a test period was set to 720 hours (abbreviated as h hereinafter). The evaluation "X" is given to the specimen which was broken and the evaluation "○" is given to the specimen which was not broken.

(6) U bend stress corrosion cracking test

[0059] Test specimen raw materials (size: thickness of 4mm, width of 15mm and length of 115mm) were sampled from the obtained test materials (steel pipes), and a welding heat cycle was given to a center portion of the test material under conditions shown in Fig. 1. Specimens for microstructural observation were sampled from the specimens after the welding heat cycle was given under conditions shown in Fig. 1, and were polished and corroded, and the microstructures of the specimens after the welding heat cycle was given were observed. The presence or non-presence of a product by transformation (martensite phase and/or austenite phase) from the prior α grain boundaries was investigated, and a length of prior α grain boundaries occupied by the product by transformation (the martensite phase and/or the austenite phase) was measured, and an occupancy ratio of the length of prior α grain boundaries relative to the whole length of the prior α grain boundaries was calculated.

[0060] Further, a specimen having a thickness of 2mm, a width of 15mm and a length of 75mm was cut out from the center portion of the obtained specimen raw material to which the welding heat cycle was given and the U bend stress corrosion cracking test was carried out on the specimen. In the U bend stress corrosion cracking test, the specimen was bent in a U shape with an inner diameter of 8mm, and the specimen was immersed in a corrosive solution.

[0061] 50 g/liter of NaCl solution which is under a condition where solution temperature is 100°C, a CO_2 pressure is 0.1MPa and pH is 2.0 was used as the corrosive solution. A test period was 168 hours.

[0062] After the test was finished, a cross section of the specimen was observed by an optical microscope with a magnification ratio of 100 times, and the presence or non-presence of cracking was investigated, and resistance to intergranular stress corrosion cracking was evaluated. The evaluation "×" is given when there is cracking and the evaluation "○" is given when there is no cracking.

[0063] The result of the test is shown in Table 3.

[0064] All present invention examples have excellent hot workability, high strength of YS: 448MPa (65ksi)or more, high-toughness of vE_{-40}: 50 J or more and high corrosion resistance of a corrosion rate: 0.12mm/y or less, no sulfide stress corrosion cracking, no intergranular stress corrosion cracking in a welded heat affected zone which is heated to 1300°C or more, and exhibit excellent resistance to intergranular stress corrosion cracking in the welded heat affected zone. In comparison examples which do not fall within the range of the present invention, hot workability is lowered, toughness is lowered, corrosion resistance is lowered, resistance to sulfide stress corrosion cracking is lowered, or resistance to intergranular stress corrosion cracking in the welded heat affected zone is lowered.

[0065] Steel pipes (steel pipe No. 27 to 31) manufactured by using steels No. F, G, M, N and O (Steels No. U, V, W, X and Y) relating to the inventions disclosed in JP-A-2005-336599 (patent document 2) satisfy the range of the present invention with respect to the composition ranges of individual elements as shown in Table 1. However, in all these steel pipes, the formula (1) defined by the present invention exceeds 13.3 and hence, as shown in Table 3, a ratio of a length occupied by a martensite phase and/or an austenite phase relative to the whole length of the prior-ferrite grain boundaries (an occupancy ratio (%) of prior α-grain boundaries) becomes less than 50% so that intergranular stress corrosion cracking occurred.

[0066] This advantageous effect of the present invention on resistance to intergranular stress corrosion cracking of the welded heat affected zone cannot be expected from JP-A-2005-336599 (patent document 2) at all.

[Table 1]

steel No.	chemical component (mass%)															note
	C	Si	Mn	P	S	Al	Cr	Ni	Mo	V	N	Cu,W	Ti,Nb, Zr	Ca, REM	formula (1)*	
A	0.010	0.25	0.41	0.013	0.001	0.020	16.0	4.6	2.0	0.020	0.011	-	-	-	12.78	present invention example
B	0.004	0.27	0.45	0.011	0.002	0.012	15.6	4.2	2.0	0.012	0.009	-	-	-	13.05	present invention example
C	0.012	0.31	0.45	0.009	0.001	0.026	17.3	5.4	1.9	0.026	0.012	-	-	-	13.08	present invention example
D	0.012	0.21	0.35	0.011	0.002	0.060	16.0	4.6	2.0	0.060	0.009	Cu:0.97	-	-	12.43	present invention example
E	0.010	0.35	0.75	0.013	0.001	0.026	16.0	4.6	1.9	0.026	0.010	W:1.34	-	-	13.12	present invention example
F	0.009	0.25	0.43	0.012	0.001	0.028	15.8	4.5	2.1	0.028	0.010	Cu: 1.63,W: 0.51	-	-	12.54	present invention example
G	0.011	0.28	0.5	0.01	0.002	0.012	16.5	5.4	2.7	0.012	0.010	-	Ti: 0.125	-	13.12	present invention example
H	0.011	0.24	0.58	0.008	0.002	0.025	16.0	4.2	2.0	0.025	0.011	-	Nb: 0.035	-	13.06	present invention example
I	0.010	0.25	0.45	0.006	0.001	0.031	15.3	5.0	2.1	0.031	0.010	-	Zr: 0.043	-	11.77	present invention example
J	0.010	0.30	0.55	0.011	0.002	0.034	16.4	5.3	2.0	0.034	0.011	Cu:1.53	Ti: 0.087	-	11.98	present invention example
K	0.011	0.13	0.49	0.012	0.001	0.025	16.3	4.5	1.9	0.025	0.010	-	-	Ca: 0.0018	12.97	present invention example
L	0.008	0.24	0.62	0.01	0.002	0.035	16.0	4.4	2.0	0.035	0.011	W:0.54	-	REM: 0,0046	13.19	present invention example
M	0.010	0.25	0.55	0.009	0.001	0.021	16.3	4.2	2.1	0.021	0.010	-	-	-	13.53	comparison example
N	0.011	0.16	0.42	0.012	0.001	0.025	16.4	4.1	2.6	0.025	0.011	-	Ti: 0.087	-	14.20	comparison example

(continued)

steel No.	chemical component (mass%)														note
	C	Si	Mn	P	S	Al	Cr	Ni	Mo	V	N	Cu,W	Ti,Nb, Zr	Ca, REM	formula (1)*	
O	0.011	0.16	0.39	0.011	0.002	0.019	16.4	4.1	2.5	0,019	0,008	Cu: 1.04,W: 1.02	-	-	14.26	comparison example
P	0.012	0.24	0.32	0.009	0.001	0.034	16.0	5.6	1.6	0.034	0.011	Cu:0.58	-	-	11.15	comparison example
Q	0.010	0.40	0.54	0.008	0.002	0.014	15.5	4.9	1.8	0.014	0.012	Cu:1.78	-	-	1.1,23	comparison example
R	0.006	0.15	0.45	0.012	0.001	0.021	14.5	4.2	1.8	0.021	0.009	-	-	-	11.62	comparison example
S	0.010	0.34	0.46	0.015	0.001	0.034	16.5	4.1	1.2	0.034	0.011	-	-	-	12.98	comparison example
T	0.021	0.24	0.44	0.014	0.002	0.024	16.2	4.0	1.8	0.025	0.014	-	-	-	12.86	comparison example
U	0.012	0.25	0.36	0.01	0.001	0.001	16.9	4.6	2.1	0.046	0.008	Cu:1.17	-	-	13.45	comparison example (**) steel No. F)
V	0.009	0.24	0.39	0.02	0.001	0.002	16.8	4.1	1.9	0.051	0.006	Cu:1.26	Nb: 0.068	Ca: 0.002	13.62	comparison example (**) steel No. G)
W	0.008	0.23	0.39	0.01	0.001	0.001	16.2	4.2	2.3	0.062	0.005	-	-	-	13.82	comparison example (**) steel No. M)
X	0.006	0.29	0.33	0.01	0.001	0.001	16.4	4.1	2.2	0.050	0.008	Cu:0.75	-	-	13.87	comparison example (**) steel No. N)
Y	0.012	0.26	0.30	0.02	0.001	0.001	16.5	4.3	2.3	0.043	0.011	Cu:1.01	Ti: 0.071	-	13.60	comparison example (**) steel No. O)

*) center value of formula (1): = Cr + Mo + 0.4W + 0.3Si - 43.5C - 0.4Mn - Ni - 0.3Cu-9N **) invention example of JP-A-2005336599

[Table 2]

steel pipe No.	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	present invention example
2	A	air cooling	3.3	900	20	3.3	620	present invention example
3	A	air cooling	3.3	900	20	3.3	640	present invention example
4	B	air cooling	3.3	890	20	3.3	600	present invention example
5	B	air cooling	3.3	890	20	3.3	620	present invention example
6	B	air cooling	3.3	890	20	3.3	640	present invention example
7	C	air cooling	3.3	910	20	3.3	600	present invention example
8	C	air cooling	3.3	910	20	3.3	620	present invention example
9	C	air cooling	3.3	910	20	3.3	640	present invention example
10	D	air cooling	3.3	850	20	3.3	600	present invention example
11	E	air cooling	3.3	870	20	3.3	620	present invention example
12	F	air cooling	3.3	900	20	50	620	present invention example
13	G	air cooling	3.3	900	20	3.3	630	present invention example
14	H	air cooling	3.3	900	20	3.3	620	present invention example

(continued)

steel pipe No.	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)	
15	I	air cooling	3.3	870	20	3.3	620	present invention example
16	J	air cooling	3.3	890	20	3.3	630	present invention example
17	K	air cooling	3.3	900	20	3.3	630	present invention example
18	L	air cooling	3.3	900	20	50	620	present invention example
19	M	air cooling	3.3	900	20	3.3	620	comparison example
20	N	air cooling	3.3	900	20	3.3	620	comparison example
21	O	air cooling	3.3	900	20	3.3	620	comparison example
22	P	air cooling	3.3	900	20	3.3	620	comparison example
23	Q	air cooling	3.3	900	20	3,3	620	comparison example
24	R	air cooling	3.3	900	20	3.3	620	comparison example
25	S	air cooling	3.3	900	20	3.3	620	comparison example
26	T	air cooling	3.3	900	20	3.3	620	comparison example
27	U	air cooling	3.3	870	20	3.3	610	comparison example(**) steel No.F)
28	V	air cooling	3.3	930	20	3.3	610	comparison example(**) steel No.G)
29	W	air cooling	3.3	890	20	3.3	610	comparison example(**) steel No.M)
30	X	air cooling	3.3	890	20	3.3	610	comparison example(**) steel No.N)

(continued)

steel pipe No.	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)	
31	Y	air cooling	3.3	890	20	3.3	610	comparison example(**) steel No.O)
**) invention example of JP-A-2005-336599								

[Table 3]

steel pipe No.	steel No.	hot workability	microstructure of base material* fraction (volume %)			tensile property		toughness	CO_2 corrosion resistance		SSC resistance	resistance to intergranular stress corrosion cracking		note
			M	F	γ	YS (MPa)	TS (MPa)	vE_{-40} (J)	corrosion rate (mm/y)	presence or non-presence of pitting corrosion	presence or non-presence of cracking	occupancy ratio of prior α-grain boundaries (%)**	presence or non-presence of cracking	
1	A	○	66	19	15	584	738	95	0,08	○	○	88	○	present invention example
2	A	○	59	21	20	543	706	121	0.09	○	-	87	-	present invention example
3	A	○	57	18	25	501	661	132	0.1	○	-	90	-	present invention example
4	B	○	62	27	11	592	728	86	0.04	○	○	60	○	present invention example
5	B	○	58	29	13	556	691	108	0.05	○	-	71	-	present invention example
6	B	○	51	27	22	521	668	123	0.06	○	-	75	-	present invention example
7	C	○	51	32	17	602	728	98	0.08	○	○	65	○	present invention example
8	C	○	47	31	22	561	691	119	0.08	○	-	62	-	present invention example

(continued)

steel pipe No.	steel No.	hot workability	microstructure of base material*			tensile property		toughness	CO_2 corrosion resistance		SSC resistance	resistance to intergranular stress corrosion cracking		note
			fraction (volume %)											
			M	F	γ	YS (MPa)	TS (MPa)	vE_{-40} (J)	corrosion rate (mm/y)	presence or non-presence of pitting corrosion	presence or non-presence of cracking	occupancy ratio of prior α-grain boundaries (%)**	presence or non-presence of cracking	
9	C	○	40	33	27	511	666	134	0.1	○	-	68	-	present invention example
10	D	○	39	29	32	606	739	85	0.07	○	○	97	○	present invention example
11	E	○	56	31	13	580	700	96	0.06	○	○	66	○	present invention example
12	F	○	50	33	17	614	744	91	0.05	○	○	86	○	present invention example
13	G	○	47	39	14	574	710	114	0.08	○	○	77	○	present invention example
14	H	○	55	20	25	580	705	95	0.08	○	○	66	○	present invention example
15	I	○	54	18	28	577	716	117	0.08	○	○	100	○	present invention example
16	J	○	49	31	20	580	742	108	0.07	○	○	100	○	present invention example

(continued)

steel pipe No.	steel No.	hot workability	microstructure of base material*			tensile property		toughness	CO_2 corrosion resistance		SSC resistance	resistance to intergranular stress corrosion cracking		note
			fraction (volume %)											
			M	F	γ	YS (MPa)	TS (MPa)	vE_{-40} (J)	corrosion rate (mm/y)	presence or non-presence of pitting corrosion	presence or non-presence of cracking	occupancy ratio of prior α-grain boundaries (%)**	presence or non-presence of cracking	
17	K	○	41	39	20	583	727	74	0.09	○	○	65	○	present invention example
18	L	○	34	38	28	600	767	71	0.07	○	○	61	○	present invention example

*) F: ferrite, M: martensite, B: bainite, P: pearlite, γ: austenite

**) ratio (%) of a length of prior α-grain boundaries occupied by a martensite phase and/or an austenite phase relative to the whole length of the prior-ferrite (α) grain boundaries

[Table 3 (continuance)]

steel pipe No.	steel No.	hot workability	microstructure of base material*			tensile property		toughness	CO_2 corrosion resistance		SSC resistance	resistance to intergranular stress corrosion cracking		note
			fraction (volume %)											
			M	F	γ	YS (MPa)	TS (MPa)	VE_{-40} (J)	corrosion rate (mm/y)	presence or non-presence of pitting corrosion	presence or non-presence of cracking	occupancy ratio of prior α-grain boundaries (%)**	of cracking	
19	M	○	39	37	24	586	709	88	0.10	○	○	48	×	comparison example
20	N	○	57	31	12	588	747	113	0.08	○	○	17	×	comparison example
21	○	○	47	46	7	590	736	73	0.07	○	○	22	×	comparison example
22	P	×	49	19	32	596	724	47	0.05	○	○	100	○	comparison example
23	Q	×	54	16	30	592	747	46	0.06	○	○	100	○	comparison example
24	R	○	51	14	35	601	768	94	0.21	×	×	100	○	comparison example
25	S	○	55	29	16	592	755	107	0.10	○	×	78	○	comparison example
26	T	○	46	31	23	611	754	85	0.20	×	×	80	○	comparison example
27	U	○	35	35	30	478	611	105	0.08	○	○	43	×	comparison example(**) steel No. F)
28	V	○	51	20	29	575	668	92	0.07	○	○	41	×	comparison example(**) steel No. G)
29	W	○	46	17	37	530	655	85	0.08	○	○	38	×	comparison example(**) steel No. M)

(continued)

steel pipe No.	steel No.	hot workability	microstructure of base material*			tensile property		toughness	CO_2 corrosion resistance		SSC resistance	resistance to intergranular stress corrosion cracking		note
			fraction (volume %)											
			M	F	γ	YS (MPa)	TS (MPa)	VE_{-40} (J)	corrosio n rate (mm/y)	presence or non-presence of pitting corrosion	presence or non-presence of cracking	occupancy ratio of prior α-grain boundaries (%)**	of cracking	
30	X	○	49	18	33	528	648	87	0.07	○	○	38	×	comparison example(**) steel No. N)
31	Y	○	48	19	33	536	629	89	0.06	○	○	42	×	comparison example(**) steel No. O)

*) F: ferrite, M: martensite, B: bainite, P: pearlite, γ: austenite
**) ratio (%) of a length of prior α-grain boundaries occupied by a martensite phase and/or an austenite phase relative to the whole length of the prior-ferrite (α) grain boundaries
**) invention example of JP-A-2005-336599

Claims

1. A Cr-containing steel pipe for line pipe having the composition which contains, by mass%, 0.001 to 0.015% C, 0.05 to 0.50% Si, 0.10 to 2.0% Mn, 0.020% or less P, 0.010% or less S, 0.001 to 0.10% Al, 15.0 to 18.0% Cr, 2.0 to 6.0% Ni, 1.8 to 3.0% Mo, 0.001 to 0.20% V, and 0.015% or less N so as to satisfy the following formula (1), optionally one kind or two kinds selected from a group consisting of, by mass%, 0.01 to 3.5% Cu and 0.01 to 3.5% W, optionally further one kind or two or more kinds selected from a group consisting of, by mass%, 0.01 to 0.20% Ti, 0.01 to 0.20% Nb, and 0.01 to 0.20% Zr, and optionally further one kind or two kinds selected from a group consisting of, by mass%, 0.0005 to 0.0100% Ca and 0.0005 to 0.0100% REM, and Fe and inevitable impurities as a balance, wherein
a welded heat affected zone has a microstructure where 50% or more of prior-ferrite grain boundaries is occupied by a martensite phase and/or an austenite phase in a ratio to the whole length of prior-ferrite grain boundaries, and wherein formula (1) is:

$$11.5 \leq Cr + Mo + 0.4W + 0.3Si - 43.5C - 0.4Mn - Ni - 0.3Cu - 9N \leq 13.3,$$

in which formula (1) Cr, Mo, W, Si, C, Mn, Ni, Cu, N indicate contents of respective elements (mass%).

Patentansprüche

1. Cr-enthaltendes Stahlrohr für ein Leitungsrohr mit einer Zusammensetzung, die ausgedrückt in Massen% enthält:

0,001 bis 0,015 % 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,
15,0 bis 18,0 % Cr,
2,0 bis 6,0 % Ni,
1,8 bis 3,0 % Mo,
0,001 bis 0,20 % V,
und 0,015 % oder weniger N,
sodass die nachfolgende Formel (1) erfüllt ist,
optional mit einer Art oder zwei Arten, ausgedrückt in Massen%, die ausgewählt sind aus der Gruppe bestehend aus: 0,01 bis 3,5 % Cu und 0,01 bis 3,5 % W,
mit optional mit einer weiteren Art oder zwei oder mehr Arten, ausgedrückt in Massen%, die ausgewählt sind aus einer Gruppe bestehend aus: 0,01 bis 0,20 % Ti, 0,01 bis 0,20 % Nb und 0,01 bis 0,20 % Zr,
und optional einer weiteren oder zwei weiteren Arten, ausgedrückt in Massen%, die ausgewählt sind aus der Gruppe: 0,0005 bis 0,0100 % Ca und 0,0005 bis 0,0100 % REM,
wobei der Rest Fe und unvermeidbare Verunreinigungen sind, wobei
eine durch Schweißung beeinflusste Zone eine Mikrostruktur hat, in der 50 % oder mehr von Vor-Ferrit-Korngrenzen durch eine Martensitphase und/oder eine Austenitphase in einem Verhältnis zur gesamten Länge von Vor-Ferrit-Korngrenzen besetzt sind, und wobei die Formel (1) lautet:

$$11,5 \leq Cr + Mo + 0,4W + 0,3Si - 43,5C - 0,4Mn - Ni - 0,3Cu - 9N \leq 13,3,$$

wobei in der Formel (1) Cr, Mo, W, Si, C, Mn, Ni, Cu, N die Anteile jeweiliger Elemente (in Massen%) bezeichnen.

Revendications

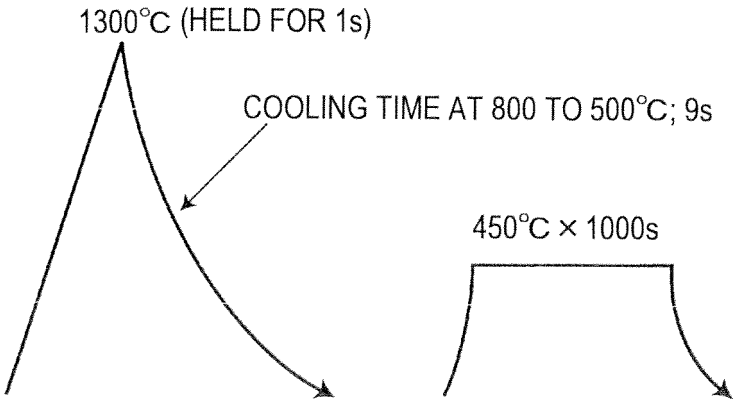
1. Tuyau d'acier contenant du chrome pour de la canalisation ayant la composition qui contient, en % massique, 0,001 à 0,015 % de C, 0,05 à 0,50 % de Si, 0,10 à 2,0 % de Mn, 0,020 % ou moins de P, 0,010 % ou moins de S, 0,001 % à 0,10 % d'Al, 15,0 à 18,0 % de Cr, 2,0 à 6,0 % de Ni, 1,8 à 3,0 % de Mo, 0,001 à 0,20 % de V et 0,015 % ou

moins de N afin de satisfaire à la formule (1) suivante, éventuellement un type ou deux types choisis dans un groupe constitué, en % massique, par 0,01 à 3,5 % de Cu et 0,01 à 3,5 % de W, éventuellement encore un type ou deux types ou plus choisis dans un groupe constitué, en % massique, par 0,01 à 0,20 % de Ti, 0,01 à 0,20 % de Nb et 0,01 à 0,20 % de Zr, et éventuellement encore un type ou deux types choisis dans un groupe constitué, en % massique, par 0,0005 à 0,0100 % de Ca et 0,0005 à 0,0100 % de terres rares, ainsi que du Fe et des impuretés inévitables en complément à cent, dans lequel
une zone soudée affectée thermiquement a une microstructure dans laquelle 50 % ou plus de joints de grains pré-ferritiques sont occupés par une phase martensite et/ou une phase austénite suivant un rapport à la longueur totale des joints de grains pré-ferritiques, et dans lequel la formule (1) est :

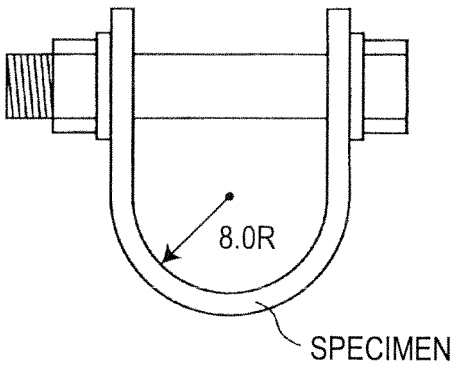
$$11{,}5 \leq Cr + Mo + 0{,}4W + 0{,}3Si - 43{,}5C - 0{,}4Mn - Ni - 0{,}3Cu - 9N \leq 13{,}3$$

formule (1) dans laquelle Cr, Mo, W, Si, C, Mn, Ni, Cu, N indiquent les teneurs des éléments respectifs (% massique).

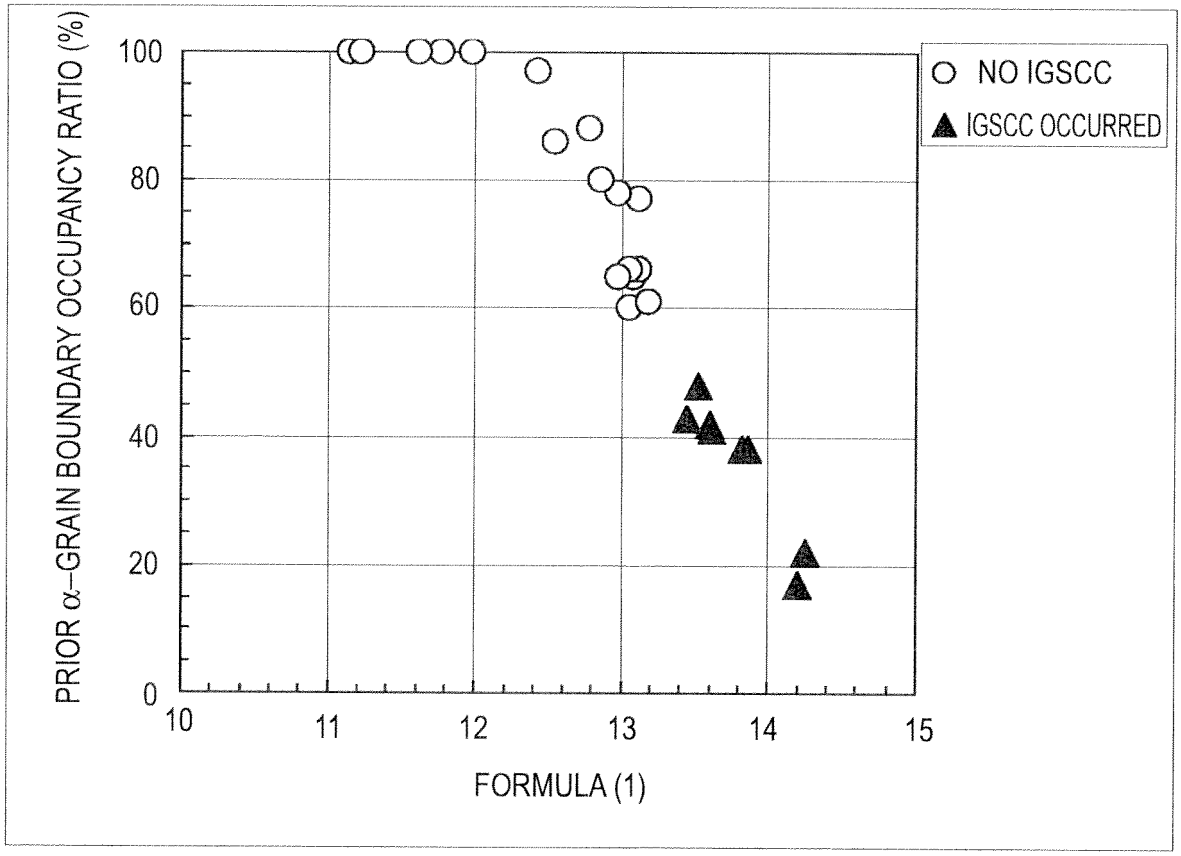
[FIG.1]


1300°C (HELD FOR 1s)
COOLING TIME AT 800 TO 500°C; 9s
450°C × 1000s

[FIG.2]


8.0R
SPECIMEN

[FIG.3]


PRIOR α–GRAIN BOUNDARY OCCUPANCY RATIO (%)
100
80
60
40
20
0
10
11
12
13
14
15
FORMULA (1)
NO IGSCC
IGSCC OCCURRED

REFERENCES CITED IN THE DESCRIPTION

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