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(54) **LOW-ALLOY STEEL, SEAMLESS STEEL PIPE FOR OIL WELL, AND PROCESS FOR PRODUCING SEAMLESS STEEL PIPE**

STAHL MIT GERINGEM LEGIERUNGSANTEIL, NAHTLOSES STAHLROHR FÜR EIN ÖLBOHRLOCH UND VERFAHREN ZUR HERSTELLUNG DES NAHTLOSEN STAHLROHRS

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Description

TECHNICAL FIELD

[0001] The present invention relates to a low alloy steel, and relates in particular to a low alloy steel suitable for use in a highly corrosive deep oil wells containing hydrogen sulfide at high pressure, a seamless steel oil country tubular goods, and a method for producing a seamless steel pipe.

BACKGROUND ART

[0002] Steel utilized in harsh, high temperature environments such as oil wells must possess better performance in terms of strength, toughness and sour resistance. In deeper wells, the steel must possess even higher strength and even better stress corrosion cracking resistance.

[0003] In steel products, the hardness becomes higher as the material strength increases, which in turn raises the dislocation density so the hydrogen content in the steel product increases making it become brittle with stress. Strengthening the steel product therefore usually causes poor resistance to sulfide stress corrosion cracking. In particular, when a steel member is produced at a desired yield strength in a steel product whose "yield strength/tensile strength" ratio (hereinafter called "yield ratio") is low, then the tensile strength and hardness tend to become higher, so the sulfide stress corrosion cracking resistance drastically deteriorates. So when raising the strength of a steel product, increasing the yield ratio is essential for keeping the hardness low.

[0004] Obtaining a high yield ratio of steel is preferably achieved by making the steel product a uniform tempered martensitic structure. Making the prior austenite grain finer is also effective.

[0005] Patent documents 1 and 2 for example disclose an invention for improving the sulfide stress corrosion cracking resistance in seamless steel pipes by suppressing precipitation of $M_{23}C_6$ type carbide at grain boundary by adjusting the balance of carbide-forming elements such as V, Nb, Ti, Cr and Mo. Patent document 3 discloses a method for improving the sulfide stress corrosion cracking resistance by making the grains finer. Patent document 4 discloses an invention for improving the toughness of seamless steel oil country tubular goods by utilizing a specified chemical composition containing from 0.0003 to 0.005% of B. Patent document 5 discloses a steel material having a high level of toughness suited for use in producing steel pipes to be used under severe conditions in oil well environments and a method of producing them.

[0006]

[Patent document 1] JP 3449311 B
[Patent document 2] JP 2000-17389 A
[Patent document 3] JP H9-111343 A
[Patent document 4] WO 2005/073421 A1
[Patent document 5] EP1413639 A1

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0007] The above-described documents 1-4 described sour resistance of low alloy steel used in hydrogen sulfide environments of about 1 atm. However, the study by the present inventors found that the sour resistance mechanism in low alloy steel in a hydrogen sulfide environment at low pressures of about 1 atm is different from that in hydrogen sulfide environments at higher pressures.

[0008] The present inventors tested sulfide stress corrosion cracking resistance in various kinds of low alloy steel by four-point bending and obtained the following findings. The low alloy steel used in this test contains by mass %, Mn of 0.5 to 1.3%, Cr of 0.2 to 1.1% and Mo of 0 to 0.7%.

[0009]

(1) Corrosion rate increases at 2 atm or more, and becomes especially high at 5 to 10 atm hydrogen sulfide, but decreases at 15 atm hydrogen sulfide.

(2) Sulfide stress corrosion cracking has been assumed to occur in hydrogen sulfide at a partial pressure around 1 atm in the past. However, the present investigation clearly shows that it tends to occur in hydrogen sulfide at a partial pressure of 2 atm or more and particularly 5 to 10 atm. Conversely, when the hydrogen sulfide partial pressure becomes as high as 15 atm then hardly any sulfide stress corrosion cracking occurs.

[0010] Based on the above findings, the present inventors realized that in low alloy steel usable in a hydrogen sulfide environment of 2 atm or more and particularly at 5 to 10 atm, the corrosion rate in high-pressure hydrogen sulfide environments can be lowered by increasing the chromium (Cr) content to 1.0% or more.

[0011] In the seamless steel oil country tubular goods described in the foregoing patent document 4, boron (B) is added to improve hardenability for the purpose of boosting resistance to sulfide stress corrosion cracking. However, in cases where producing seamless steel oil country tubular goods by in-line quenching as described in the invention in patent document 4, converting the austenite grain into fine grains is difficult. In this case, when B is present in a high Cr content alloy, the $M_{23}C_6$ type carbide in the alloy precipitates and coarsens in the prior austenite grain boundary during heat treatment after quenching, and consequently the sulfide stress corrosion cracking resistance deteriorates. The present invention provides both hardenability and toughness in steel without adding boron (B).

[0012] In-line quenching" refers to quick quenching (hereinafter called "in-line quenching") after supplemental in-line heating of seamless pipe obtained for example by the Mannesmann pipe production method. However, heat treatments such as tempering, annealing and normalizing conducted after quenching may be carried out off-line as needed.

[0013] Compared to quenching after reheating in a separate process, in-line quenching has lower production costs and is superior in terms of reaching the quenching temperature compared to so-called direct quenching, where the pipe is quenched right after being produced. However, the above in-line quenching, tends to coarsen the $M_{23}C_6$ type carbide in grain boundaries in the low alloy steel. This coarse carbide in grain boundaries becomes more noticeable in steel production methods where the steel contains boron (B).

[0014] The present invention was rendered on the basis of that knowledge. An object of this invention is to provide a low-alloy steel with hardenability and toughness as well as increased resistance to sulfide stress corrosion by increasing the chromium (Cr) content and not utilizing a boron (B) additive normally used in the conventional art, and a seamless steel oil country tubular goods utilizing that low-alloy steel, and a method for producing seamless steel pipe. Though obtaining a yield strength (YS) of 654 to 793 MPa (95 to 115 ksi) in the low alloy steel is a goal of the present invention, this figure need not always be satisfied.

[0015] The low alloy steel of the present invention is also usable in environments at 2 atm or more, and can also be used at a hydrogen sulfide environment of 5 to 10 atm where sulfide stress corrosion cracking is most likely to occur. Needless to say, this steel can also be used in hydrogen sulfide environments at a lower pressure or a higher pressure.

MEANS FOR SOLVING THE PROBLEMS

[0016] The present invention resolves the aforementioned problems. A description of the low alloy steel is shown in the following (A), a seamless steel oil country tubular goods is shown in (B), and a method for producing the seamless steel pipe is shown in (C).

[0017]

(A) A low alloy steel having a tempered martensitic structure with a martensite ratio of 90% or greater and consisting of by mass %, C : 0.10 to 0.18%, Si : 0.05 to 1.0%, Mn : 0.05 to 1.5%, Cr : 1.1 to 2.0%, Mo : 0.05 to 2.0%, sol. Al : 0.10 % or less and Ti : 0.002 to 0.05%, and optionally one or more elements selected from 0.03 to 0.2% V, 0.002 to 0.04% Nb,
0.0003 to 0.005% Ca, 0.0003 to 0.005% Mg and 0.0003 to 0.005% REM, and with a Ceq value obtained by the following formula (1) of 0.65 or more, with the balance being Fe and impurities, wherein in the impurities, P is 0.025% or less, S is 0.010% or less, N is 0.007% or less, and B is less than 0.0003%, and the number per unit area of $M_{23}C_6$ type precipitates (M: a metal element) whose grain diameter is 1 μm or more is 0.1/mm^2 or less.

$$Ceq = C + (Mn/6) + (Cr + Mo + V)/5 \quad (1)$$

where C, Mn, Cr, Mo and V in the formula (1) denote the content of respective elements (mass %).

[0018] (B) A seamless steel oil country tubular goods characterized in utilizing the low alloy steel described in (A)

[0019]

(C) A method for producing a seamless steel pipe comprising the following steps:

(a) hot piecing a steel billet possessing the chemical composition described in (A) and a value Ceq obtained by the following formula (1) of 0.65 or more;
(b) elongation rolling; producing a pipe at a final rolling temperature of 800 to 1100°C;

(c) supplementary heating the resultant steel pipe in-line in a temperature range from the Ar_3 transition point to 1000˚C;
(d) quenching the pipe from a temperature of the Ar_3 transition point or higher; and then
(e) tempering the pipe at the temperature of the Ac_1 transition point or lower.

$$Ceq = C + (Mn/6) + (Cr + Mo + V)/5 \quad \text{formula (1)}$$

where C, Mn, Cr, Mo and V in the formula (1) indicate the content of the respective elements (mass %).

EFFECT OF THE INVENTION

[0020] The low-alloy steel of the present invention improves resistance to sulfide stress corrosion cracking and provides hardenability and toughness. The low-alloy steel of the present invention is effective when used hydrogen sulfide environments at 2 atm or more, and especially under the 5 to 10 atm environment most vulnerable to sulfide stress corrosion cracking.

BEST MODE FOR CARRYING OUT THE INVENTION

[0021] The low-alloy steel of the present invention as already described lowers the corrosion rate of sulfide stress corrosion cracking by containing a higher chromium (Cr) content, as well as providing hardenability and toughness without a boron (B) additive, and providing improved resistance to sulfide stress corrosion cracking. The reason for limiting each component is described next.

[0022] C: 0.10 to 0.18%
Carbon (or C) is an element that enhances the strength of the steel. When the C (carbon) content is less than 0.1%, then tempering at low temperature is needed to obtain the desired strength. This tempering consequently lowers the resistance to sulfide stress corrosion cracking. The lowered resistance can be compensated by raising the tempering temperature and improving the softening resistance to tempering, but it needs to add much amount of expensive elements. When the content of C exceeds 0.18% however the yield ratio deteriorates. Attempting to achieve the desired strength while maintaining this excessive C content, increases the hardness and lowers the resistance to sulfide stress corrosion cracking. In view of these circumstances, the C content was set from 0.10 to 0.18%. The lower C content limit is preferably 0.14%.

[0023] Si: 0.05 to 1.0%
Silicon (or Si) is an element possessing a deoxidizing effect. This element also enhances the hardenability of steel and improves strength. To obtain this effect, the Si content must be 0.05% or more. However, when the content exceeds 1.0%, resistance to sulfide stress corrosion cracking is lowered. Therefore, the Si content was therefore set from 0.05 to 1.0%. The lower Si content limit is preferably 0.1%. The upper limit is preferably 0.6%.

[0024] Mn: 0.05 to 1.5%
Manganese (or Mn) is an element possessing a deoxidizing effect. This element also enhances the hardenability of steel and improves strength. To obtain this effect, the Mn content must be 0.05% or more. However, when the content exceeds 1.5%, resistance to sulfide stress corrosion cracking deteriorates. The content of Mn therefore was set from 0.05 to 1.5%.

[0025] Cr: 1.1 to 2.0%
Chromium (or Cr) is an effective element for enhancing the hardenability of steel and improving the resistance to sulfide stress corrosion cracking. To obtain this effect, the Cr content must be 1.1% or more. Conversely, a content in excess of 2.0% causes lower resistance to sulfide stress corrosion cracking resistance. The Cr content was therefore set from 1.1 to 2.0%. The lower Cr content limit is preferably 1.2%. The upper Cr content limit is preferably 1.8%.

[0026] Mo: 0.05 to 2.0%
Molybdenum (or Mo) is an effective element that enhances the hardenability of steel and provides high strength. This element also possesses the effect of enhancing resistance to sulfide stress corrosion cracking. To obtain these effects, the Mo content must be 0.05% or more. However, when the Mo content exceeds 2.0%, a coarse carbide forms at the prior austenite grain boundary, and resistance to sulfide stress corrosion cracking deteriorates. The Mo content is therefore set from 0.05 to 2.0%. The preferable Mo content range is 0.1 to 0.8%

[0027] sol. Al: 0.10% or less
Aluminum (or Al) is an element having deoxidizing effect. This element is also effective for enhancing the toughness and workability of the steel. However, when the content exceeds 0.10%, generation of flaw becomes noticeable. The Al content was therefore set to 0.10% or less. The Al content may be the impurity level but 0.005% or more is preferable.

The Al content upper limit is preferably 0.05%. The Al content in the present invention denotes the content of acid-soluble Al (so called sol. Al).

[0028] Ti: 0.002 to 0.05%

Titanium (or Ti) is an effective element to fix N in steel as nitride and improve the hardenability of the steel. To obtain this effect, the Ti content must be 0.002% or more. However, when the Ti content exceeds 0.05%, a coarse nitride forms and sulfide stress cracking tends to occur. The Ti content was set from 0.002 to 0.05%. The lower limit is preferably 0.005% and the upper limit is preferably 0.025%.

[0029] One of the low alloy steels of the present invention has a chemical composition containing each element described above, and the balance being Fe and impurities. The low alloy steel of the present invention may further comprise either one or both of 0.03 to 0.2% V and 0.002 to 0.04% Nb in addition to the above-described elements, in order to form fine precipitates such as carbides.

[0030] V: 0.03 to 0.2%

Vanadium (V) is an element that enhances strength of low alloy steel by precipitation as fine carbide during tempering. To obtain this effect, a V content of 0.03% or more is preferable. However, the toughness might decline when the V content exceeds 0.2%. The content is therefore preferably set to 0.03 to 0.2% when adding V.

[0031] Nb: 0.002 to 0.04%

Nobium (Nb), which forms carbonitride in high temperature regions and prevents crystal grains from coarsening, is an effective element for improving resistance to sulfide stress corrosion cracking. To obtain these effects, the Nb content is preferably 0.002% or more. Conversely however, when the content exceeds 0.04%, the carbonitride becomes too coarse, which causes sulfide stress cracking easily. The Nb additive content is therefore preferably 0.002 to 0.04%. The upper limit is preferably 0.02%.

[0032] To improve resistance to sulfide stress corrosion cracking, the low alloy steel of the present invention may further contain at least one selected from 0.0003 to 0.005% Ca, 0.0003 to 0.005% Mg and 0.0003 to 0.005% REM in addition to each of the above-described elements.

[0033] Ca: 0.0003 to 0.005%

Mg: 0.0003 to 0.005%

REM: 0.0003 to 0.005%

Ca, Mg, and REM all react with S in steel to form sulfide which improves the shape of inclusions to improve the sulfide stress corrosion cracking resistance. To obtain these effects, one or more selected from Ca, Mg and REM (rare earth metals such as, Ce, La, Y and the like) may be added. However, the above-described effects become noticeable when the contents of these elements are each 0.0003% or more. On the other hand, when any element exceeds a content of 0.005%, the amount of inclusions in the steel increase, and steel purity decreases so that sulfide stress cracking tends to occur. Therefore, when adding these elements, their respective contents are preferably 0.0003 to 0.005%.

[0034] In the low alloy steel of the present invention, P, S, N and B in the impurities must be restricted within the following range.

[0035] P: 0.025% or less

Phosphorus (or P) is an element present in steel as an impurity. This element lowers toughness, and when the content exceeds 0.025%, a drop in the sulfide stress corrosion cracking resistance becomes more noticeable. In view of this the P was set to 0.025% or less. The P content is preferably 0.020% or less, and more preferably is 0.015% or less.

[0036] S: 0.010% or less

Sulfur (or S) is an element present in steel as an impurity. When the S content exceeds 0.010%, the degradation in sulfide stress corrosion cracking resistance becomes noticeable. The S content was therefore set to 0.010% or less. The S content is preferably 0.005% or less.

[0037] N: 0.007% or less

Nitrogen (or N) is an element present in steel as an impurity. It forms nitrides by bonding with Al, Ti or Nb. When N is present in large quantities, coarsening of AlN or TiN takes place. The N content was therefore limited to 0.007% or less.

[0038] B: less than 0.0003%

Boron (or B) is an element present in steel as an impurity. When there is an increased Cr content in the alloy, then B causes the $M_{23}C_6$ type boundary carbides in alloy to become coarse, which lowers the toughness and causes lower sulfide stress corrosion cracking resistance. The B content was therefore limited to less than 0.0003%.

[0039] Ceq: 0.65 or more

Hardenability might prove poor even if the steel is of the above-described chemical composition, so in the low alloy steel of the present invention the chemical composition must be adjusted to achieve a Ceq of 0.65 or more as expressed by the following formula (1).

$$Ceq = C + (Mn/6) + (Cr + Mo + V)/5 \quad \text{formula (1)}$$

where C, Mn, Cr, Mo and V in the formula (1) indicate the content of respective elements (mass %).

[0040] Although C is an effective element for improving hardenability, when the C content is increased, the hardness rises and the YR deteriorates. Therefore, in the present invention the Ceq obtained from the relational expression (1) for elements that improve hardenability other than C (Mn, Cr, Mo and V) is used as an index to ensure hardenability. In cases where the Ceq obtained from the above formula (1) is less than 0.65, the hardenability will be insufficient, especially in thick-walled products, and resistance to sulfide stress corrosion cracking will deteriorate. So the Ceq in the present invention was therefore adjusted to 0.65 or more.

[0041] Since $M_{23}C_6$ type precipitate with a grain diameter of 1μm or more lowers toughness and sour resistance, in the low alloy steel of the present invention the number per unit area must therefore be 0.1/mm^2 or less.

[0042] The low alloy steel of the present invention, having mainly tempered martensitic structure, has a high yield ratio and excellent resistance to sulfide stress corrosion cracking, although the steel has a coarse-grained structure such that an austenite crystal grain number defined in JIS G 0551 is No. 7 or less. Hence, using a steel ingot with the above-described chemical composition as the raw material offers a high degree of freedom when selecting production methods for low alloy steel. The production method for the low alloy steel of the present invention is described using a method for producing seamless steel pipe as an example.

[0043] A steel pipe may be produced by piercing and elongation rolling, for example, by Mannesmann mandrel mill pipe production method, and fed without cooling to a heat treatment facility in the later step of a finishing mill while maintaining the temperature at the Ar_3 transition point or higher, subjected to quenching, and then tempered at 600 to 750˚C. This steel pipe will possess a high yield ratio even if an energy-saving, in-line pipe production / heat treatment process was selected and will also have the desired strength and high resistance to sulfide stress corrosion cracking.

[0044] A steel pipe may alternatively be produced by hot finishing; temporarily cooled to room temperature; reheated in a quenching furnace and soaking in a temperature range of 900 to 1000˚C, then water-quenched, and thereafter, tempered at 600 to 750˚C. The process i.e. an offline pipe production process has an effect of forming tempered martensite structure and further an effect of prior-austenite grain refinement. Accordingly, the steel pipe produced by the above process has much higher yield ratio, therefore, the steel pipe with higher strength and high sulfide stress corrosion cracking resistance can be obtained.

[0045] However, the following production method is most desirable. The reason for this is that pipe kept at a high temperature from the pipe making through quenching processes, easily retains elements such as V and Mo in a solid solution state, and high-temperature tempering is advantageous for improving sulfide stress corrosion cracking resistance because these elements precipitate as fine carbide which increases the strength of the steel pipe.

[0046] The production method for the seamless steel pipe of the present invention is characterized by a final rolling temperature for elongation rolling, and that heat treatment is performed after rolling is completed. Each of these features is described next.

(1) Final rolling temperature for elongation rolling

[0047] This temperature is set to 800 to 1100˚C. When the temperature is lower than 800˚C, then deformation resistance of steel pipe becomes too large, posing the problem of tool abrasion. On the other hand, when the temperature is higher than 1100˚C, then the crystal grains become too coarse, and degrade the sulfide stress corrosion cracking. Additionally, the piercing process prior to elongation rolling may be a conventional method such as the Mannesmann piercing method.

(2) Supplementary heating treatment

[0048] After completing the elongation rolling, the steel is charged in-line, or namely loaded in a supplementary heating furnace provided in a continuous steel pipe production line, and subjected to supplementary heating in a temperature range from the Ar_3 point to 1000˚C. The purpose of this supplementary heating is to reduce temperature variations in the longitudinal direction of the steel pipe in order to make the structure uniform.

[0049] When the supplementary heating temperature is lower than the Ar_3 point, generation of ferrite starts, and no uniform quenched structure can be obtained. On the other hand, when higher than 1000˚C, the crystal grain growth is accelerated, which worsens the sulfide stress corrosion cracking resistance due to coarser grains. The time of the supplementary heating is set to the time required to make the entire wall thickness of the pipe a uniform temperature. This time required may be about 5 to 10 minutes. Additionally, when the final rolling temperature for elongation rolling is in a temperature range from the Ar_3 point to 1000˚C, then the supplementary heating process may be omitted, but supplementary heating is preferable because it decreases temperature variations in the longitudinal direction and along the wall thickness of the pipe.

(3) Quenching and tempering

[0050] The above-described processes serve to quench the steel pipe in a temperature range from the Ar_3 point to 1000˚C. Quenching is conducted at a cooling rate sufficient for the entire wall thickness of the pipe to become a martensitic structure. Ordinarily, quenching may consist of water cooling. Tempering is conducted at a lower temperature than the Ac_1 point. Preferably tempering is conducted at 600 to 700˚C. The tempering time differs depending on wall thickness of the pipe, and may be about 20 to 60 minutes.

[0051] The above process renders a low alloy steel with excellent properties and made of tempered martensite.

Examples

[0052] A billet of low alloy steel with the chemical composition shown in Table 1 was produced, and was formed into a seamless steel pipe of 273.1 mm in outer diameter and 16.5 mm in wall thickness by Mannesmann mandrel pipe production method. The temperature of this steel pipe was not lower than the Ar_3 point during forming. The pipe was immediately charged in a supplementary heating furnace, soaked at 950˚C for 10 minutes, then water quenched, further subjected to tempering heat treatment, by which the yield strength (YS) in the longitudinal direction of steel pipe was adjusted to about 758 MPa (110 ksi) in an arcwise tensile test specified by API.

[0053] The corrosion test in a high-pressure hydrogen sulfide environment of 10 atm was conducted by the following method. The steel pipe was formed along the longitudinal direction and heat treated as described above. A stress corrosion test piece 2 mm thick, 10 mm wide and 75 mm long was sampled from each test material. By applying a specific amount of strain to the test piece by 4-point bending in accordance with the method specified in ASTM-G39, a stress of 90% of the above-described yield stress was applied. After the test piece in this state was put in an autoclave together with the test tools, a 5% degassed saline solution was poured into the autoclave leaving a vapor phase portion. Hydrogen sulfide gas at 10 atm was charged under pressurization, and this hydrogen sulfide gas at high pressure was saturated in the liquid phase by stirring the liquid phase. After the autoclave was sealed, it was kept at 25˚C for 720 hours while stirring the liquid, and then decompressed to remove the test piece.

[0054] After testing, the test piece was observed by the naked eye for the presence of sulfide stress corrosion cracking (SSC). In Table 1, "x" in "SSC resistance" signifies the generation of SSC, and "o" signifies no generation of SSC.

[0055] The number per unit area of $M_{23}C_6$ type precipitates (M: a metal element) whose grain diameter was 1 μm or more was measured as follows. Ten pieces of extraction replica specimen for observation of carbide (view area of one replica specimen: 3 mm^2) were sampled from arbitrary positions on the steel pipe produced through pipe making, quenching and tempering as described above. These pieces were observed at each prior y grain boundary by TEM, for grain sizes of grain boundary carbide that were 1 μm or more in diameter. Whether these grains were the $M_{23}C_6$ type or not was determined from the diffraction pattern of the carbide. If the $M_{23}C_6$ type, then the number was counted, and was divided by the total area of observation views as the number per unit area

[0056] In Table 1, "o" in "number of $M_{23}C_6$" indicates that the number per unit area of $M_{23}C_6$ type precipitates (M: a metal element) whose grain diameter was 1 μm or more was 0.1/mm^2 or less. The "×" indicates the number was more than 0.1/mm^2.

[0057] Whether a uniform martensitic structure was obtained or not was determined by the following method. A billet of low alloy steel having a chemical composition shown in Table 1 was produced. This billet was formed into a seamless steel pipe of 273.1 mm in outer diameter and 16.5 mm in wall thickness by Mannesmann mandrel pipe production method. During this forming the temperature of this steel pipe was not lower than the Ar_3 point, and was immediately charged in a supplementary heating furnace, soaked at 950˚C for 10 minutes, then water quenched to produce an as-quenched steel pipe. The average cooling rate from 800 to 500˚C upon water quenching was about 10˚C per second in the center part of the wall thickness in the center of steel pipe longitudinal direction. The hardness in the center part of wall thickness of this as-quenched steel pipe was measured by a Rockwell hardness test. The quenched structure was judged as satisfactory when the value was higher than a predicted Rockwell C hardness value of [(C%x58) + 27] which corresponds to a 90% martensite rate. The quenched structure was judged unsatisfactory if below the predicted Rockwell C hardness value.

[0058] [Table 1]

Table 1

No.	Chemical composition (mass %, balance: Fe and impurities)														Ceq	Y.S. (MPa)	Quenched structure	Number of $M_{23}C_6$	SSC resistance
	C	Si	Mn	Cr	Mo	Sol-Al	Ti	V	Ca	B	P	S	N	Nb					
1	0.16	0.28	1.09	1.19	0.50	0.035	0.008	0.04	0.0013	-	0.012	0.0018	0.0053	-	0.69	771	Satisfactory	○	○
2	0.16	0.28	1.12	1.42	0.31	0.033	0.008	0.06	0.0025	-	0.013	0.0021	0.0062	-	0.70	754	Satisfactory	○	○
3	0.17	0.28	1.11	1.40	0.30	0.036	0.011	0.04	0.0017	0.0002	0.012	0.0016	0.0050	-	0.70	753	Satisfactory	○	○
4	0.17	0.27	1.11	1.47	1.50	0.038	0.011	0.01	0.0016	0.0001	0.014	0.0018	0.0063	-	0.95	715	Satisfactory	○	○
5	0.17	0.29	0.60	1.41	0.69	0.037	0.004	-	0.0018	-	0.017	0.0016	0.0064	0.03	0.69	775	Satisfactory	○	○
7	0.16	0.28	1.18	1.01*	0.30	0.033	0.008	0.06	0.0022	-	0.012	0.0021	0.0055	-	0.63*	761	Unsatisfactory	○	×
8	0.16	0.28	1.12	0.01*	0.70	0.036	0.015	0.02	0.0014	-	0.012	0.0019	0.0050	-	0.49*	761	Unsatisfactory	○	×
9	0.16	0.29	1.21	0.30*	0.51	0.035	0.015	0.04	0.0014	0.0014*	0.012	0.0018	0.0054	-	0.53*	757	Satisfactory	×	×
10	0.36*	0.19	0.62	0.99	0.70	0.037	0.011	0.02	0.0016	-	0.011	0.0020	0.0054	-	0.80	762	Satisfactory	○	×
* indicates a figure outside the range specified by the invention																			

[0059] As shown in Table 1, no sulfide stress corrosion cracking (SSC) occurred in Nos. 1 to 5 satisfying the conditions specified by the present invention. In Nos. 7 to 10 sulfide stress corrosion cracking (SSC) occurred and the conditions specified by the present invention were not satisfied.

INDUSTRIAL APPLICABILITY

[0060] The low-alloy steel of the present invention improves resistance to sulfide stress corrosion cracking and provides hardenability and toughness. The low-alloy steel of the present invention is effective when used in hydrogen sulfide environments at 2 atm or more, and especially under the 5 to 10 atm environment most vulnerable to sulfide stress corrosion cracking.

Claims

1. A low alloy steel having a tempered martensitic structure with a martensite ratio of 90% or greater, and consisting of, by mass %, C : 0.10 to 0.18%, Si : 0.05 to 1.0%, Mn : 0.05 to 1.5%, Cr : 1.1 to 2.0%, Mo : 0.05 to 2.0%, sol. Al : 0.10 % or less and Ti : 0.002 to 0.05%, and optionally one or more elements selected from 0.03 to 0.2% V, 0.002 to 0.04% Nb, 0.0003 to 0.005% Ca, 0.0003 to 0.005% Mg and 0.0003 to 0.005% REM, and with a Ceq value obtained by the following formula (1) of 0.65 or more, with the balance being Fe and impurities, wherein in the impurities, P is 0.025% or less, S is 0.010% or less, N is 0.007% or less, and B is less than 0.0003%, and the number per unit area of $M_{23}C_6$ type precipitates (M: a metal element) whose grain diameter is 1 μm or more is 0.1/mm^2 or less.

$$Ceq = C + (Mn/6) + (Cr + Mo + V)/5 \quad \text{formula (1)}$$

where C, Mn, Cr, Mo and V in the formula (1) denote the content of respective elements (mass %).

2. A seamless steel oil country tubular goods using the low alloy steel according to claim 1.

3. A method for producing a seamless steel pipe comprising the following steps:

(a) hot piercing a steel billet possessing the chemical composition claimed in claim 1 and a Ceq value obtained by the following formula (1) of 0.65 or more;
(b) elongation rolling; producing a pipe at a final rolling temperature of 800 to 1100˚C;
(c) supplementary heating the resultant steel pipe in-line in a temperature range from the Ar_3 transition point to 1000˚C;
(d) quenching the pipe from a temperature of the Ar_3 transition point or higher; and then
(e) tempering the pipe at a temperature of the Ac_1 transition point or lower.

$$Ceq = C + (Mn/6) + (Cr + Mo + V)/5 \quad \text{formula (1)}$$

where C, Mn, Cr, Mo and V in the formula (1) denote the content of the respective elements (mass %).

Patentansprüche

1. Ein niedrig legierter Stahl mit einer getemperten martensitischen Struktur mit einem Martensitanteil von 90 % oder höher und bestehend aus in Massenprozent C:0,10 bis 0,18 %, Si:0,05 bis 1,0 %, Mn:0,05 bis 1,5 %, Cr:1,1 bis 2,0 %, Mo: 0,05 bis 2,0 %, sol.Al: 0,10 % oder weniger und Ti: 0,002 bis 0,05 %, und optional ein oder mehrere Elemente ausgewählt aus 0,03 bis 0,2 % V, 0,002 bis 0,04 % Nb, 0,0003 bis 0,005 % Ca, 0,0003 bis 0,005 % Mg und 0,0003 bis 0,005 % REM, und mit einem Ceq-Wert, welcher durch die nachfolgende Formel (1) von 0,65 oder mehr erzielt wird, wobei der Rest Fe und Verunreinigungen sind, wobei in den Verunreinigungen P 0,025 % oder weniger ist, S 0,010 % oder weniger ist, N 0,007 % oder weniger ist und B weniger als 0,0003 % ist, und die Anzahl pro Einheitsbereich von $M_{23}C_6$-artigen Ablagerungen (M: ein Metallelement), deren Korndurchmesser 1μm oder mehr ist, 0,1/mm^2 oder weniger ist.

$$Ceq = C + (Mn/6) + (Cr+Mo+V)/5 \qquad \text{Formel (1)}$$

wobei C, Mn, Cr, Mo und V in der Formel (1) den Gehalt von entsprechenden Elementen (Massenprozente) bezeichnen.

2. Nahtlose Stahlölfeldrohre, welche den niedrig legierten Stahl nach Anspruch 1 verwenden.

3. Verfahren zur Herstellung eines nahtlosen Stahlrohres, umfassend die folgenden Schritte:

(a) Warmlochen eines Stahlblocks, welcher die chemische Zusammensetzung nach Anspruch 1 und einen durch die folgende Formel (1) erhaltenen Ceq-Wert von 0,65 oder mehr besitzt;
(b) Streckrollen; Herstellen eines Rohres bei einer Endrolltemperatur von 800 bis 1100 ˚C;
(c) Nachheizen des resultierenden Stahlrohres hintereinander in einem Temperaturbereich von dem Ar_3-Übergangspunkt auf 1000 ˚C;
(d) Abkühlen des Rohrs von einer Temperatur des Ar_3-Übergangspunkts oder höher; und dann
(e) Tempern des Rohrs bei einer Temperatur des Ac_1-Übergangspunkts oder niedriger.

$$Ceq = C + (Mn/6) + (Cr+Mo+V)/5 \qquad \text{Formel (1)}$$

wobei C, Mn, Cr, Mo und V in der Formel (1) den Gehalt des entsprechenden Elements (Massenprozente) bezeichnen.

Revendications

1. Acier faiblement allié ayant une structure martensitique revenue avec un taux de martensite de 90 % ou plus, et consistant en, en pourcent en masse, C : 0,10 à 0,18 %, Si : 0,05 à 1,0 %, Mn : 0,05 à 1,5 %, Cr : 1,1 à 2,0 %, Mo : 0,05 à 2,0 %, Al sol. : 0,10 % ou moins et Ti : 0,002 à 0,05 %, et éventuellement un ou plusieurs éléments choisis parmi 0,03 à 0,2 % de V, 0,002 à 0,04 % de Nb, 0,0003 à 0,005 % de Ca, 0,0003 à 0,005 % de Mg et 0,0003 à 0,005 % de MTR, et avec une valeur Ceq obtenue par la formule (1) suivante de 0,65 ou plus, le complément étant Fe et des impuretés, où dans les impuretés, P est 0,025 % ou moins, S est 0,010 % ou moins, N est 0,007 % ou moins, et B est moins de 0,0003 %, et le nombre par unité d'aire de précipités de type $M_{23}C_6$ (M : un élément métallique) dont le diamètre de grain est 1 μm ou plus est 0,1/mm^2 ou moins.

$$Ceq = C + (Mn/6) + (Cr + Mo + V)/5 \quad \text{formule (1)}$$

où C, Mn, Cr, Mo et V dans la formule (1) désignent la teneur des éléments respectifs (% en masse).

2. Produits tubulaires pour pays producteurs de pétrole en acier sans soudure utilisant l'acier faiblement allié selon la revendication 1.

3. Procédé pour produire un tube en acier sans soudure comprenant les étapes suivantes :

(a) perçage à chaud d'une billette en acier possédant la composition chimique revendiquée dans la revendication 1 et une valeur Ceq obtenue par la formule (1) suivante de 0,65 ou plus ;
(b) laminage d'allongement ; production d'un tube à une température de laminage finale de 800 à 1 100˚C ;
(c) chauffage supplémentaire du tube en acier résultant en ligne dans une plage de température du point de transition Ar_3 à 1 000˚C ;
(d) trempe du tube depuis une température du point de transition Ar_3 ou plus ; puis
(e) revenu du tube à une température du point de transition Ac_1 ou moins.

$$Ceq = C + (Mn/6) + (Cr + Mo + V)/5 \quad \text{formule (1)}$$

où C, Mn, Cr, Mo et V dans la formule (1) désignent la teneur des éléments respectifs (% en masse).

REFERENCES CITED IN THE DESCRIPTION

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