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(54) **LOW ALLOY STEEL**

(57) A low alloy steel subjected to post weld heat treatment, containing, by mass percent, of C: 0.01 to 0.15%, Si: 3% or less, Mn: 3% or less, and Al: 0.08% or less, one or more kinds of elements selected from Ti, V and Nb: the range satisfying Formula (1), and the balance being Fe and impurities, wherein in the impurities, N: 0.01% or less, P: 0.05% or less, S: 0.03% or less, and O: 0.03% or less:

$$0.1 \times [C(\%)] \leq [Ti(\%)] + [V(\%)] + 0.5 \times [Nb(\%)] \leq 0.2 \quad \dots (1)$$

where, the symbol of element in the formula represents the content (mass%) of each element.

In the alloy steel, a HAZ subjected to PWHT, especially short-time PWHT, has excellent hydrogen embrittlement resistance in wet hydrogen sulfide environments or the like.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a low alloy steel. More particularly, it relates to a low alloy steel in which a weld heat affected zone that has been subjected to postweld heat treatment has excellent resistance to embrittlement attributable to hydrogen, such as stress corrosion cracking in wet hydrogen sulfide environments.

BACKGROUND ART

[0002] In the development of submarine oilfields, a steel pipe called a riser, flowline, or trunkline is used for transmission of crude oil or natural gas between an oil well or gas well located at the bottom of the sea and a platform on the sea or between the platform and a refinery station on the land. On the other hand, with the worldwide exhaustion of fossil fuels, oil fields containing much hydrogen sulfide having corrosiveness have been developed actively. A steel pipe for transmitting crude oil or natural gas exploited from oil fields containing such a corrosive gas is sometimes broken by embrittlement attributable to hydrogen formed from a corrosion reaction called hydrogen induced cracking (hereinafter, referred to as "HIC") and sulfide stress cracking (hereinafter, referred to as "SSC"). Many steels developed from the viewpoint of improving the HIC resistance and SSC resistance have traditionally been proposed.

[0003] For example, Patent Document 1 (JP5-255746A) proposes a steel provided with excellent HIC resistance by defining the heat history and heat treatment conditions at the production time without substantially containing Ni, Cu and Ca. Also, Patent Document 2 (JP6-336639A) proposes a steel provided with HIC resistance and SSC resistance by essentially adding Cr, Ni and Cu. Further, Patent Document 3 (JP2002-60894A) proposes a steel in which the HIC resistance and SSC resistance are enhanced by defining the specific ranges of amounts of C, Ti, N, V and O.

[0004] When a structure is assembled by using any of these steels, for example, when a steel pipe consisting of any of these steels is laid, welding work is generally performed. Unfortunately, for example, as described in non-Patent Document 1, it is widely known that the SSC susceptibility is increased by the increase in hardness. When a steel undergoes heating due to welding, a hardened portion is produced in a so-called weld heat affected zone (hereinafter, referred to as a "HAZ"). As a result, however much the HIC resistance and SSC resistance of the steel itself are enhanced, practically sufficient performance of a welded structure cannot be achieved in many cases.

[0005] Therefore, in recent years, as described in Patent Document 4 (JP2010-24504A), there has also been proposed a high-strength steel in which, by reducing the amounts of C and Mn and by containing 0.5% or more of Mo, the hardening of weld heat affected zone is restrained, and both of HIC resistance and SSC resistance of base metal and HAZ are achieved.

[0006] As a method for reducing the hardness of weld heat affected zone, postweld heat treatment (hereinafter, referred to as "PWHT") is widely used for a Cr-Mo steel or martensitic stainless steel used for pressure vessels and the like in large amounts. For example, Patent Document 5 (JP2007-321228A) proposes a low alloy steel containing 0.5% or more of Cr assuming that PWHT of one hour per one-inch wall thickness.

LIST OF PRIOR ART DOCUMENT(S)

[0007]

[Patent Document 1] JP5-255746A

[Patent Document 2] JP6-336639A

[Patent Document 3] JP2002-60894A

[Patent Document 4] JP2010-24504A

[Patent Document 5] JP2007-321228A

[0008] [Non-Patent Document 1] Masanori Kowaka, Corrosion damage and anticorrosion engineering of metal, August 25, 1983, issued by Agne Corporation, p.198

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009] According to the invention described in Patent Document 4, it is described that the hardening of weld heat affected zone is restrained, and both of HIC resistance and SSC resistance of base metal and HAZ can be achieved. However, since Mo is an expensive element, there has been desired a method for improving hydrogen embrittlement

resistance of HAZ without requiring much cost.

[0010] As described in Patent Document 5, PWHT brings about a certain effect. However, since importance is attached to efficiency in laying line pipes so that welding work is performed, for example, on a ship on the sea, it is generally desirable that PWHT be eliminated, or, even if being performed, the PWHT be performed for a very short period of time.

[0011] An objective of the present invention is to provide a low alloy steel in which a HAZ subjected to PWHT, especially short-time PWHT, has excellent hydrogen embrittlement resistance in wet hydrogen sulfide environments or the like.

MEANS FOR SOLVING THE PROBLEMS

[0012] To enhance the hydrogen embrittlement resistance of HAZ of a steel subjected to PWHT, the present inventors first examined hydrogen embrittlement of as-welded HAZ to clarify necessary conditions. As a result, it is considered that the hydrogen embrittlement of HAZ is produced by the mechanism described below.

[0013] In the case where a steel is exposed to a corrosive environment containing hydrogen sulfide, hydrogen intrudes into the steel on account of corrosion reaction. This hydrogen can move freely in the crystal lattice of the steel. This hydrogen is so-called diffusible hydrogen. The intruding diffusible hydrogen accumulates in a dislocation or a vacancy, which is one kind of defects in the crystal lattice, and further, at the lattice strain of interface between a carbide such as cementite and a matrix to embrittle the steel. In particular, the HAZ is heated to a high temperature by the heat history of welding, being cooled rapidly, and becomes an as-quenched martensite or bainite structure. Therefore, in the HAZ, the dislocations and vacancies in which hydrogen is trapped exist densely as compared with a thermally refined base metal, and cementite also disperses. For this reason, it is considered that the HAZ is highly susceptible to hydrogen embrittlement as compared with the base metal.

[0014] In the case where PWHT is performed, the density of dislocations or vacancies is reduced, and softening advances, and on the other hand, cementite precipitates. Therefore, especially in the case where sufficient softening does not occur due to short-time PWHT, it is considered that the reduction effect of hydrogen embrittlement susceptibility is not high because of a trade-off with the precipitation of cementite.

[0015] Accordingly, in order to enhance the hydrogen embrittlement resistance of HAZ to which PWHT has been applied, the present inventors attempted to optimize the alloying elements. As a result, it was found that, in order to enhance the hydrogen embrittlement susceptibility of HAZ to which PWHT has been applied, it is effective to contain one or more kinds of any of Ti, V and Nb. The reason for this is considered to be as follows.

[0016] Each of the elements of Ti, V and Nb has a high affinity for carbon as compared with iron, and therefore forms fine MX-type carbides in the process of PWHT. The MX-type carbides have a high consistency with a parent phase as compared with cementite, so that the lattice strain of interface with the matrix is small, and the amount of occlusion of diffusible hydrogen in the carbides is large. Therefore, it is considered that, when hydrogen intrudes due to corrosion reaction, the accumulation site of diffusible hydrogen is dispersed, whereby remarkable hydrogen accumulation and formation of embrittlement starting point due to this accumulation are restrained, and embrittlement is resultantly alleviated.

[0017] It was verified that a proper amount of Ti, V and Nb must be contained as the amount of C increases, that is, as the hardenability of HAZ at the cooling time of welding is higher, as the density of dislocations or vacancies is higher, and as the driving force of precipitation of cementite at the application time of PWHT is higher. Specifically, it was verified that one or more kinds selected from Ti, V and Nb must be contained in the range satisfying Formula (1):

$$0.1 \times [C(\%)] \leq [Ti(\%)] + [V(\%)] + 0.5 \times [Nb(\%)] \leq 0.2 \quad \dots (1)$$

where, the symbol of element in the formula represents the content (mass%) of each element.

[0018] The present invention has been made based on the above-described findings, and the gist thereof is low alloy steels described in the following items [1] to [6].

[1] A low alloy steel subjected to post weld heat treatment, containing, by mass percent, of

C: 0.01 to 0.15%,

Si: 3% or less,

Mn: 3% or less, and

Al: 0.08% or less,

one or more kinds of elements selected from Ti, V and Nb: the range satisfying Formula (1), and

the balance being Fe and impurities,

wherein in the impurities,

N: 0.01% or less,

P: 0.05% or less,
S: 0.03% or less, and
O: 0.03% or less:

$$0.1 \times [C(\%)] \leq [Ti(\%)] + [V(\%)] + 0.5 \times [Nb(\%)] \leq 0.2 \quad \dots (1)$$

where, the symbol of element in the formula represents the content (mass%) of each element.

[2] The low alloy steel described in item [1], wherein the low alloy steel contains, by mass percent, Cr and/or Mo: 1.5% or less in total in lieu of a part of Fe.

[3] The low alloy steel described in item [1] or [2], wherein the low alloy steel contains, by mass percent, Ni and/or Cu: 0.8% or less in total in lieu of a part of Fe.

[4] The low alloy steel described in any one of items [1] to [3], wherein the low alloy steel contains, by mass percent, Ca and/or Mg: 0.05% or less in total in lieu of a part of Fe.

[5] The low alloy steel described in any one of items [1] to [4], wherein the low alloy steel contains, by mass percent, B: the range satisfying Formula (2) in lieu of a part of Fe:

$$[B(\%)] < 0.1 \times [C(\%)] \quad \dots (2)$$

where, the symbol of element in the formula represents the content (mass%) of each element.

[6] The low alloy steel described in any one of items [1] to [5], wherein post weld heat treatment is performed under the condition satisfying Formula (3):

$$8000 \leq T \times \{20 + \log(t/3600)\} \leq 15000 \quad \dots (3)$$

where, T is treatment temperature (°C) of postweld heat treatment, and t is treatment time (sec) of postweld heat treatment.

ADVANTAGEOUS EFFECT(S) OF THE INVENTION

[0019] According to the present invention, there can be provided a low alloy steel in which a HAZ subjected to PWHT, especially short-time PWHT, has excellent hydrogen embrittlement resistance in wet hydrogen sulfide environments or the like.

MODE FOR CARRYING OUT THE INVENTION

[0020] Hereunder, the range of chemical composition of the low alloy steel in accordance with the present invention and the reason for restricting the chemical composition are explained. In the following explanation, "%" representing the content of each element means "mass%".

C: 0.01 to 0.15%

[0021] C (carbon) is an element effective in enhancing the hardenability of steel and increasing the strength thereof. In order to achieve these effects, 0.01% or more of C must be contained. However, if the content of C exceeds 0.15%, when PWHT is performed, a large amount of cementite is precipitated, and the hydrogen embrittlement susceptibility of HAZ is enhanced. Therefore, the C content is set to 0.01 to 0.15%. The lower limit of the C content is preferably 0.03%. The C content is preferably 0.12% or less.

Si: 3% or less

[0022] Si (silicon) is an element effective for deoxidation, but brings about a decrease in toughness if being contained excessively. Therefore, the Si content is set to 3% or less. The Si content is preferably 2% or less. The lower limit of the Si content is not particularly defined; however, even if the Si content is decreased, the deoxidizing effect decreases, the cleanliness of steel is deteriorated, and an excessive decrease in the Si content leads to an increase in production cost. Therefore, the Si content is preferably 0.01% or more.

Mn: 3% or less

[0023] Like Si, Mn (manganese) is an element effective for deoxidation, and also is an element contributing to the enhancement of hardenability of steel and to the increase in strength thereof. However, if Mn is contained excessively, remarkable hardening of HAZ is caused, and the hydrogen embrittlement susceptibility is enhanced. Therefore, the Mn content is set to 3% or less. The lower limit of the Mn content is not particularly defined; however, in order to achieve the strength increasing effect of Mn, 0.2% or more of Mn is preferably contained. The lower limit thereof is further preferably 0.4%, and the preferable upper limit thereof is 2.8%.

Al: 0.08% or less

[0024] Al (aluminum) is an element effective for deoxidation, but if being contained excessively, the effect is saturated, and also the toughness is decreased. Therefore, the Al content is set to 0.08% or less. The Al content is preferably 0.06% or less. The lower limit of the Al content is not particularly defined; however, an excessive decrease in the Al content does not sufficiently achieve the deoxidizing effect, deteriorates the cleanliness of steel, and also increases the production cost. Therefore, 0.001% or more of Al is preferably contained. The Al content in the present invention means the content of acid soluble Al (so-called "sol.Al").

[0025] One or more kinds selected from Ti (titanium), V (vanadium) and Nb (niobium): in the range satisfying Formula (1):

$$0.1 \times [C(\%)] \leq [Ti(\%)] + [V(\%)] + 0.5 \times [Nb(\%)] \leq 0.2 \quad \dots (1)$$

where, the symbol of element in the formula represents the content (mass%) of each element.

[0026] These elements form fine MX-type carbides in the process of PWHT, and enhance the hydrogen embrittlement resistance. In order to achieve this effect, "[Ti(%)] + [V(%)] + 0.5 x [Nb(%)]" must be 0.1 x [C(%)] or more. However, if the content of these elements is excessively high, the carbides are coarsened, and rather the hydrogen embrittlement susceptibility is enhanced and the toughness is decreased. Therefore, "[Ti(%)] + [V(%)] + 0.5 x [Nb(%)]" must be 0.2% or less. The upper limit thereof is preferably 0.18%, further preferably 0.15%.

[0027] The low alloy steel in accordance with the present invention contains the above-described elements, and the balance consists of Fe and impurities. The "impurities" mean components that are mixed on account of various factors including raw materials such as ore or scrap when a steel material is produced on an industrial scale. Of the impurities, concerning the elements described below, the content thereof must be restricted stringently.

N: 0.01% or less

[0028] N (nitrogen) exists in the steel as an impurity. Nitrogen produces embrittlement when fine carbo-nitrides are formed, and decreases the toughness even when being dissolved. Therefore, the N content must be restricted to 0.01% or less. The N content is preferably 0.008% or less. The lower limit of the N content is not particularly defined; however, an excessive decrease in the N content leads to a remarkable increase in production cost. Therefore, the lower limit of the N content is preferably 0.0001%.

P: 0.05% or less

[0029] P (phosphorus) exists in the steel as an impurity. Phosphorus segregates at grain boundaries in HAZ, and decreases the toughness. Therefore, the P content is restricted to 0.05% or less. The lower limit of the P content is not particularly defined; however, an excessive decrease in the P content leads to a remarkable increase in production cost. Therefore, the lower limit of the P content is preferably 0.001%.

S: 0.03% or less

[0030] Like P, S (sulfur) exists in the steel as an impurity. Sulfur forms sulfides in a steel material, and since the interface with a matrix acts as an accumulation site of hydrogen, S enhances the hydrogen embrittlement susceptibility, and also decreases the HAZ toughness. Therefore, the S content is restricted to 0.03% or less, more severely than P. The lower limit of the S content is not particularly defined; however, an excessive decrease in the S content leads to a remarkable increase in production cost. Therefore, the lower limit of the S content is preferably 0.0001%.

O: 0.03% or less

[0031] O (oxygen) exists in the steel as an impurity. If much O is contained, large amounts of oxides are formed, and the workability and ductility are deteriorated. Therefore, the O content must be set to 0.03% or less. The O content is preferably 0.025% or less. The lower limit of the O content need not particularly be defined; however, an excessive decrease in the O content leads to a remarkable increase in production cost. Therefore, the O content is preferably 0.0005% or more.

[0032] The low alloy steel in accordance with the present invention may contain the elements described below in lieu of a part of Fe.

Cr and/or Mo: 1.5% or less in total

[0033] At least one of Cr (chromium) and Mo (molybdenum) may be contained because these elements enhance the hardenability and contribute to the improvement in strength. However, if the contents thereof are excessively high, these elements precipitate as carbides to hinder the carbides of Ti and the like and to enhance the hydrogen embrittlement susceptibility. Therefore, if Cr and/or Mo are contained, the contents thereof are set to 1.5% or less in total. The lower limit of the contents of Cr and/or Mo is preferably 0.02%, further preferably 0.05%. The upper limit thereof is preferably 1.2%.

Ni and/or Cu: 0.8% or less in total

[0034] At least one of Ni (nickel) and Cu (copper) may be contained because these elements enhance the hardenability and contribute to the improvement in strength. However, even if these elements are contained excessively, not only the effects are saturated, but also the cost is increased. Therefore, if Ni and/or Cu are contained, the contents thereof are set to 0.8% or less in total. The lower limit of the contents of Ni and/or Cu, if added, is preferably 0.02%, further preferably 0.05%. The upper limit thereof is preferably 0.7%.

Ca and/or Mg: 0.05% or less in total

[0035] At least one of Ca (calcium) and Mg (magnesium) may be contained because these elements improve the hot workability of steel. However, if the contents thereof are excessively high, these elements combine with oxygen to remarkably decrease the cleanliness, so that the hot workability may rather be deteriorated. Therefore, if at least one kind of these elements is contained, the contents thereof are set to 0.05% or less in total. The lower limit of the contents of Ca and/or Mg is preferably 0.0005%, further preferably 0.001%. The upper limit thereof is preferably 0.03%.

[0036]

B: in the range satisfying Formula (2)

$$[B(\%)] < 0.1 \times [C(\%)] \quad \dots (2)$$

where, the symbol of element in the formula represents the content (mass%) of each element.

[0037] B (boron) may be contained because it segregates at the grain boundaries, so that it restrains the precipitation of ferrite from the grain boundaries, thereby enhancing the hardenability indirectly, and contributes to the improvement in strength. However, if B is contained excessively, in the process of PWHT, B precipitates as borides or is replaced with C and dissolves in cementite, further increasing the lattice strain with a matrix, and therefore may decrease the hydrogen embrittlement resistance. Therefore, if B is contained, the content of B is preferably in the range satisfying Formula (2). The lower limit of the B content is preferably 0.0001%, further preferably 0.0005%.

[0038] The conditions of PWHT performed for the low alloy steel in accordance with the present invention are not subject to any special restriction. However, when PWHT is performed under the condition satisfying Formula (3), the low alloy steel in accordance with the present invention achieves excellent effects:

$$8000 \leq T \times \{20 + \log(t/3600)\} \leq 15000 \quad \dots (3)$$

where, T is treatment temperature (°C) of postweld heat treatment, and t is treatment time (sec) of postweld heat treatment.

[0039] If " $T \times \{20 + \log(t/3600)\}$ " is less than 8000, there is a possibility that the hydrogen embrittlement resistance of HAZ of steel material consisting of the low alloy steel in accordance with the present invention cannot be enhanced. On the other hand, if " $T \times \{20 + \log(t/3600)\}$ " exceeds 15000, the coarsening of fine MX-type carbides consisting of Ti or the like advances, so that sufficient hydrogen embrittlement resistance cannot be obtained, and also the strength of steel including the weld zone is decreased remarkably. Therefore, the PWHT performed for the low alloy steel in accordance with the present invention is preferably carried out under the condition satisfying Formula (3).

[0040] In particular, the PWHT is preferably carried out in the temperature range of 500 to 750°C for 30 to 600 seconds. The reason for this is that fine MX-type carbides are formed stably by short-time PWHT, whereby the hydrogen embrittlement resistance is enhanced, and also an extreme increase in cost caused by long-time PWHT in actual work is restrained. In particular, the PWHT time is preferably set to 300 seconds or shorter.

[0041] The low alloy steel of the present invention preferably has a yield strength (YS) of 552 MPa or higher. The reason for this is that, for a low alloy steel having a high strength, by PWHT, the strength of steel including the weld zone is decreased remarkably, and the merit of improvement in hydrogen embrittlement resistance brought about by short-time PWHT can be further obtained.

EXAMPLE(S)

[0042] To confirm the effects of the present invention, the experiments described below were conducted. A test material was prepared by machining a 12 mm-thick low alloy steel plate having the chemical composition given in Table 1 into a 12 mm square and a 100 mm length. This test material was subjected to HAZ-simulated thermal cycle in which the test material was heated to a temperature of 1350°C, at which the hardening of HAZ was remarkable, for 3 seconds by high-frequency induction heating, and thereafter was rapidly cooled. By using this test material, the tests described below were conducted.

<Tension test>

[0043] In conformity to JIS Z2241, a round-bar tensile test specimen having a parallel part diameter of 6 mm and a parallel part length of 10 mm was sampled from the obtained test material, and a tension test was conducted at normal temperature.

<SCC resistance test>

[0044] A test specimen having a thickness of 2 mm, a width of 10 mm, and a length of 75 mm was sampled from the obtained test material, and the SCC resistance was evaluated by a four-point bending test in conformity to EFC16 specified by the European Federation of Corrosion. In the test, after a stress corresponding to 50% of 0.2% yield stress, which was derived from the tension test, had been applied to the sampled test specimen by four-point bending, the test specimen was immersed in a 5% common salt + 0.5% acetic acid aqueous solution of normal temperature (24°C), in which 1 atm hydrogen sulfide gas is saturated, for 336 hours, whereby the presence or occurrence of SSC was examined. Test No. in which SSC did not occur was made acceptable, and test No. in which SSC occurred was made unacceptable.

[0045] These test results are given in Table 2.

TABLE 1

Steel No.	Chemical Composition (mass % balance being Fe and impurities)																①	②	Evaluation	
	C	Si	Mn	P	S	B	Al	N	O	Cr	Ni	Mo	Ti	Nb	V	Other			Formula (1)	Formula (2)
A1	0.10	0.25	2.40	0.013	0.001	-	0.021	0.0046	0.003	-	-	-	0.029	-	-	-	0.010	0.0290	satisfaction	-
A2	0.05	0.24	2.41	0.014	0.001	-	0.020	0.0051	0.003	-	-	-	-	0.011	-	-	0.005	0.0055	satisfaction	-
A3	0.11	0.25	2.00	0.012	0.001	-	0.020	0.0046	0.001	-	-	-	-	-	0.020	Ca:0.002	0.011	0.0200	satisfaction	-
A4	0.05	0.28	1.98	0.010	0.001	-	0.027	0.0045	0.002	0.31	-	0.75	-	0.012	0.009	-	0.005	0.0150	satisfaction	-
A5	0.12	0.25	1.29	0.013	0.001	0.0002	0.029	0.0046	0.001	0.50	0.25	0.49	-	0.028	-	Cu:0.02	0.012	0.0140	satisfaction	satisfaction
A6	0.12	0.24	1.83	0.014	0.001	0.0110	0.019	0.0044	0.003	-	-	-	0.010	-	0.018	-	0.012	0.0280	satisfaction	satisfaction
A7	0.09	0.26	1.96	0.014	0.001	0.0085	0.024	0.0060	0.001	0.02	-	-	0.009	0.010	-	-	0.009	0.0140	satisfaction	satisfaction
A8	0.01	0.22	2.03	0.014	0.001	-	0.025	0.0046	0.002	-	0.02	-	-	-	0.180	Mg:0.001	0.001	0.1800	satisfaction	-
B1	0.10	0.22	2.05	0.014	0.001	-	0.020	0.0042	0.001	-	-	-	-*	-*	0.007*	-	0.010	0.0070	dissatisfaction	-
B2	0.06	0.24	2.90	0.013	0.001	-	0.022	0.0050	0.001	-	-	-	-*	0.009*	-*	-	0.006	0.0045	dissatisfaction	-
B3	0.10	0.25	1.78	0.015	0.001	-	0.020	0.0046	0.003	0.02	-	-	-*	0.060*	0.190*	-	0.010	0.2200	dissatisfaction	-
B4	0.10	0.27	1.82	0.014	0.001	0.0170*	0.023	0.0045	0.003	-	-	-	-	0.020	0.010	-	0.010	0.0200	satisfaction	dissatisfaction
B5	0.05	0.26	2.50	0.014	0.001	-	0.020	0.0051	0.002	0.78*	-	0.77*	0.008	-	-	-	0.005	0.0080	satisfaction	-

* indicates it is not satisfy the claimed range.

① indicates the calculated value of " $0.1 \times [C(\%)]$ ".

② indicates the calculated value of " $[Ti(\%)] + [V(\%)] + 0.5 \times [Nb(\%)]$ ".

TABLE 2

No.	Steel No.	Condition of PWHT		③	Property of Formula (3)	Evaluation of SSC Test
		Temperature T(°C)	Time t (sec)			
X1	A1	500	30	8,960	○	No SSC
X2	A1	600	30	10,752	○	No SSC
X3	A1	750	30	13,441	○	No SSC
X4	A1	500	600	9,611	○	No SSC
X5	A1	600	300	11,352	○	No SSC
X6	A2	600	30	10,752	○	No SSC
X7	A3	600	30	10,752	○	No SSC
X8	A4	600	30	10,752	○	No SSC
X9	A5	600	30	10,752	○	No SSC
X10	A6	600	30	10,752	○	No SSC
X11	A7	600	30	10,752	○	No SSC
X12	A8	600	30	10,752	○	No SSC
Y1	A1	not performed		-	×	SSC
Y2	A7	not performed		-	×	SSC
Y3	B1*	600	30	10,752	○	SSC
Y4	B2*	600	30	10,752	○	SSC
Y5	B3*	600	30	10,752	○	SSC
Y6	B4*	600	30	10,752	○	SSC
Y7	B5*	600	30	10,752	○	SSC
* indicates it is not satisfy the claimed range.						
③ indicates the calculated value of " $T \times \{20 + \log(t/3600)\}$ ".						

[0046] As shown in Table 2, in test Nos. X1 to X12, the occurrence of SSC was not recognized in the four-point bending test. Contrarily, in test Nos. Y1 and Y2, although the chemical components met the requirements of the present invention, since PWHT was not performed, MX-type carbides did not precipitate, and SSC occurred. In test Nos. Y3 and Y4, since the addition amounts of Ti, Nb and V, which were constituent elements of MX-type carbides contained in the steel, were small, and the predetermined relationship with C was not satisfied, sufficient amounts of MX-type carbides did not precipitate, and SSC occurred. In test No. Y5, since the addition amounts of Ti, Nb and V were inversely too large, MX-type carbides precipitate coarsely, and SSC occurred. In test No. Y6, although B was added, the addition amount thereof was excessive, so that SSC occurred. Further, in test No. Y7, since Cr and Mo were contained excessively, the carbides thereof were precipitated by PWHT, and MX-type carbides were not formed stably, so that SSC occurred.

INDUSTRIAL APPLICABILITY

[0047] According to the present invention, there can be provided a low alloy steel in which a HAZ subjected to PWHT, especially short-time PWHT, has excellent hydrogen embrittlement resistance in wet hydrogen sulfide environments or the like. This low alloy steel is best suitable as a starting material of a steel pipe for the transmission of crude oil or natural gas.

Claims

1. A low alloy steel subjected to post weld heat treatment, containing, by mass percent, of

C: 0.01 to 0.15%,
 Si: 3% or less,
 Mn: 3% or less, and
 Al: 0.08% or less,

one or more kinds of elements selected from Ti, V and Nb: the range satisfying Formula (1), and the balance being Fe and impurities, wherein in the impurities,

N: 0.01% or less,
 P: 0.05% or less,
 S: 0.03% or less, and
 O: 0.03% or less:

$$0.1 \times [C(\%)] \leq [Ti(\%)] + [V(\%)] + 0.5 \times [Nb(\%)] \leq 0.2 \quad \dots (1)$$

where, the symbol of element in the formula represents the content (mass%) of each element.

2. A low alloy steel subjected to post weld heat treatment, containing, by mass percent, of

C: 0.01 to 0.15%,
 Si: 3% or less,
 Mn: 3% or less, and
 Al: 0.08% or less,

one or more kinds of elements selected from Ti, V and Nb: the range satisfying Formula (1), one or more kinds of elements selected from the elements described in (A) to (D) and the balance being Fe and impurities, wherein in the impurities,

N: 0.01% or less,
 P: 0.05% or less,
 S: 0.03% or less, and
 O: 0.03% or less:

- (A) Cr and/or Mo: 1.5% or less in total
 (B) Ni and/or Cu: 0.8% or less in total
 (C) Ca and/or Mg: 0.05% or less in total
 (D) B: the range satisfying Formula (2):

$$0.1 \times [C(\%)] \leq [Ti(\%)] + [V(\%)] + 0.5 \times [Nb(\%)] \leq 0.2 \quad \dots (1)$$

$$[B(\%)] < 0.1 \times [C(\%)] \quad \dots (2)$$

where, the symbol of element in the formula represents the content (mass%) of each element.

3. The low alloy steel according to claim 1 or 2, wherein post weld heat treatment is performed under the condition satisfying Formula (3):

$$8000 \leq T \times \{20 + \log(t/3600)\} \leq 15000 \quad \dots (3)$$

where, T is treatment temperature (°C) of post weld heat treatment, and t is treatment time (sec) of post weld heat treatment.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/082608

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D9/08(2006.01)i, C21D9/50(2006.01)i, C22C38/14(2006.01)i, C22C38/58(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00, C21D9/08, C21D9/50, C22C38/14, C22C38/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 9-256038 A (Nippon Steel Corp.), 30 September 1997 (30.09.1997), table 3, symbols 1, 2, 8 to 11 (Family: none)	1-3
X	JP 2001-121289 A (NKK Corp.), 08 May 2001 (08.05.2001), claims; paragraph [0031]; table 1, steels A to F (Family: none)	1-3
X	JP 8-309428 A (Sumitomo Metal Industries, Ltd.), 26 November 1996 (26.11.1996), claims; table 3, steel no.a, e (Family: none)	1-3

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
01 March, 2013 (01.03.13)

Date of mailing of the international search report
12 March, 2013 (12.03.13)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/082608

5	C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
10	X	JP 2008-13808 A (JFE Steel Corp.), 24 January 2008 (24.01.2008), claims; paragraph [0056]; table 1-1, steel no.A to D, F, H to J & US 2009/0277544 A1 & EP 2050833 A1 & WO 2008/004453 A1 & KR 10-2009-0016746 A & CN 101484602 A	1-3
15	X A	JP 2008-274405 A (JFE Steel Corp.), 13 November 2008 (13.11.2008), claims; table 1, steel types B to I; paragraph [0067] (Family: none)	2,3 1
20	X A	JP 2007-270194 A (JFE Steel Corp.), 18 October 2007 (18.10.2007), claims; table 1, steel types B to I; paragraph [0049] (Family: none)	2,3 1
25	X A	JP 7-48621 A (Kawasaki Steel Corp.), 21 February 1995 (21.02.1995), claims; table 1, steels (3, 5) according to the invention; paragraph [0022] (Family: none)	2 1,3
30	X A	JP 11-77350 A (NKK Corp.), 23 March 1999 (23.03.1999), claims; table 1, steel types C to F, H, I; paragraph [0041] (Family: none)	2 1,3
35			
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45			
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REFERENCES CITED IN THE DESCRIPTION

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- JP 5255746 A [0003] [0007]
- JP 6336639 A [0003] [0007]
- JP 2002060894 A [0003] [0007]
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