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

(11) EP 2 889 390 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
01.07.2015 Bulletin 2015/27

(21) Application number: **13830674.1**

(22) Date of filing: **24.04.2013**

(51) Int Cl.:
C22C 38/00 *(2006.01)* ***C21D 8/02*** *(2006.01)*
C21D 9/08 *(2006.01)* ***C22C 38/58*** *(2006.01)*

(86) International application number:
PCT/JP2013/062004

(87) International publication number:
WO 2014/030392 (27.02.2014 Gazette 2014/09)

(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
Designated Extension States:
BA ME

(30) Priority: **24.08.2012 JP 2012184802**

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(54) HIGHLY STRONG, HIGHLY TOUGH AND HIGHLY CORROSION-RESISTANT MARTENSITIC STAINLESS STEEL

(57) It is an object of the present invention to provide a high performance-stainless steel exhibiting a corrosion resistance even under a very severe corrosion environment at temperatures of equal to or higher than 180 °C, for example, 220 °C while maintaining a strength and a toughness by improving a corrosion resistance of a conventional martensitic stainless steel with high strength.

The present invention provides a martensitic stainless steel containing, in mass %, C: 0.005 % to 0.05 %, Si: equal to or less than 1.0 %, Mn: equal to or less than 2.0 %, Cr: 16 to 18 %, Ni: 2.5 to 6.5 %, Mo: 1.5 to 3.5 %, W: equal to or less than 3.5 %, Cu: equal to or less than 3.5 %, V: 0.01 to 0.08 %, Sol.Al: 0.005 to 0.10 %, N: equal to or less than 0.05 %, and Ta: 0.01 to 0.06 %, and the balance Fe with inevitable impurities.

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a martensitic stainless steel having a high strength, a high toughness, and a high corrosion resistance, particularly relates to martensitic stainless steel with a high strength, high toughness, and high corrosion resistance suitable for use in an environment containing a high temperature humid carbon dioxide gas in drilling for and transporting petroleum and natural gas, and to a method of producing the same.

BACKGROUND ART

[0002] Cases where petroleum and natural gas produced in recent years contain a large amount of a humid carbon dioxide gas have been increasing, and a martensitic stainless steel of 13 % Cr series stainless steel has been used in place of a conventional carbon steel as a material of a steel pipe or the like used in drilling for and transporting such petroleum and natural gas.

[0003] However, although the conventional martensitic stainless steel is excellent in a corrosion resistance against a humid carbon dioxide gas (hereinafter, referred to as "corrosion resistance") up to 180 °C, the corrosion resistance is not sufficient at temperatures of higher than 180 °C. Further, a steel pipe or the like used in drilling for or transporting petroleum or natural gas is placed under a high temperature and a high pressure environment, and therefore, it is also preferable that the steel pipe has a high strength as well as an excellent toughness.

[0004] Therefore, a stainless steel exhibiting a corrosion resistance at a temperature of equal to or higher than 180 °C, for example, 220 °C while maintaining a strength and a toughness has been desired.

[0005] Patent Literatures 1 to 7 disclose such stainless steels exhibiting corrosion resistances at temperatures of equal to or higher than about 180 °C. A basic concept of the stainless steels disclosed in the literatures is that a corrosion resistance is maintained under an environment of a high temperature and humid dioxide gas by increasing an amount of Cr.

[0006] Patent Literatures 1 and 2 disclose high strength-stainless steel pipes for an oil well having C, Si, Mn, Cr, Ni, Mo, W, Cu, V, and N in specific compositions. Patent Literature 1 produced a stainless steel having a strength up to 792 MPa in a yield stress, and investigated a toughness or the like thereof. In Patent Literature 2, no description is found concerning a strength, and only a toughness was investigated. An investigation concerning a higher strength stainless steel was not carried out in either of Patent Literatures 1 and 2.

[0007] In Patent Literatures 3 to 7, although there were examples investigating high strength steels which are equivalent to or higher than those of Patent Literatures 1 and 2, investigations concerning toughness thereof were not carried out. Generally, a stainless steel pipe is deteriorated in a toughness thereof by making a strength thereof higher. Therefore, it seems that the toughness of the stainless steels disclosed in the literatures cannot withstand completely drilling for or transportation of petroleum or natural gas.

PRIOR ART LITERATURES

Patent Literatures

[0008]

Patent Literature 1: Japanese Unexamined Patent Application Publication No. 2008-81793
Patent Literature 2: Japanese Unexamined Patent Application Publication No. 2010-209402
Patent Literature 3: Japanese Patent No. 2814528
Patent Literature 4: Japanese Patent No. 4577457
Patent Literature 5: Japanese Patent No. 4761008
Patent Literature 6: Japanese Patent No. 4911266
Patent Literature 7: WO2009/119048

SUMMARY OF INVENTION

Problems to be solved by the Invention

[0009] Furthermore, an environment encountered by a steel pipe, particularly, an oil well pipe has been severer and severer, and there is a necessity for a steel pipe having a high strength of equal to or higher than 758 MPa, exhibiting an excellent corrosion resistance against a humid dioxide gas at temperatures of equal to or higher than 180 °C, and also being excellent in a toughness. Hence, it is an object of the present invention to provide a high performance-stainless steel exhibiting a corrosion resistance even under a very severe corrosion environment at temperatures of equal to or higher than 180 °C, for example, 220 °C while maintaining a strength and a toughness thereof.

[0010] Here, an aimed performance is set as follows in view of a performance requested for a steel pipe for drilling for or transportation of petroleum or natural gas including a carbon dioxide gas. Further, as the steel pipe, although a main object of the present invention is an oil well pipe, also a steel pipe for a line pipe for transportation for which a similar performance is requested can be an object.

[0011] strength: equal to or higher than 758 MPa and equal to or lower than 965 MPa in an 0.2 % proof stress.
toughness: an absorbed energy in a Charpy full size test at -20 °C is equal to or higher than 100 J.
corrosion resistance: a corrosion rate is 0.5 mm/year or less under an environment of a 20 % NaCl aqueous solution, 220 °C, and 10 atmospheric pressure-CO_2.

Means for Solving the Problems

[0012] The present inventors have acquired the following knowledge as a result of carrying out an intensive research in order to solve the problem described above.

[0013] Although an increase of Cr and Mo which are ferrite forming elements is effective for enhancing a corrosion resistance of a martensitic stainless steel, on the other hand, the increase of the elements forms more δ-ferrite phase, and a hot workability as well as a strength and a toughness of the steel may be deteriorated. Although an increase of Ni which is an austenite forming element is effective for controlling formation of the δ-ferrite phase, a tempering temperature in production may be restricted. Hence, according to the present invention, Cr, Mo, and Ni are brought into optimum ranges described later, thereby, the formation of the δ-ferrite is restrained.

[0014] Further, when a large amount of the austenite forming elements is contained and the tempering temperature is high, there is a case where a small amount of austenite is precipitated, which hampers enhancement of strength of a stainless steel, and therefore, also formation of the austenite phase needs to be controlled. Particularly, a tendency of accelerating the austenite formation by an increase of Ni is strong, and an amount of Ni is restricted.

[0015] Generally, when a strength of the steel is made higher, a toughness thereof is deteriorated. The present inventors have found a synergistic effect that a martensitic stainless steel containing a pertinent amount of V in the stainless steel, and further containing simultaneously a pertinent amount of Ta as an indispensable component is easy to disperse a precipitate of a fine carbide into a matrix of the stainless steel after a heat treatment as compared with a case of individually adding V or Ta or a case of simultaneously adding V and Nb, and the enhancement of strength while maintaining a toughness is facilitated. Also, the present inventors have found that its effect is more significant by further adding Nb in addition to V and Ta.

[0016] Based on the knowledge described above, the present inventors have completed a novel martensitic stainless steel having a high toughness and a high strength and being excellent in a corrosion resistance under an environment at temperatures of equal to or higher than 180 °C and its production method, which martensitic stainless was not realized in the conventional martensitic stainless steel. The martensitic stainless steel has been attained by making the steel contain certain amounts of V and Ta, or V, Ta, and Nb, adjusting a heat treatment condition in a certain range in order to stably acquire a strength of equal to or higher than 758 MPa in a constant range, and making the carbide precipitate to disperse uniformly in the matrix in consideration of a restriction of a metallographic structure described above.

[0017] That is, the present invention provides a martensitic stainless steel having a high strength of equal to or higher than 758 MPa which can be used under a humid carbon dioxide gas environment at temperatures of equal to or higher than 180 °C while maintaining a toughness thereof, by improving a corrosion resistance of the conventional high strength-martensitic stainless steel by limiting an alloy composition and a production condition in certain ranges.

[0018] That is, the present invention is as follows.

(1) A martensitic stainless steel containing, in mass %, C: 0.005 % to 0.05 %, Si: equal to or less than 1.0 %, Mn: equal to or less than 2.0 %, Cr: 16 to 18 %, Ni: 2.5 to 6.5 %, Mo: 1.5 to 3.5 %, W: equal to or less than 3.5 %, Cu: equal to or less than 3.5 %, V: 0.01 to 0.08 %, Sol.Al: 0.005 to 0.10 %, N: equal to or less than 0.05 %, and Ta: 0.01 to 0.06 %, and the balance Fe with inevitable impurities.
(2) The martensitic stainless steel described in (1) above, further containing, in mass %, Nb: equal to or less than 0.1 %.
(3) The martensitic stainless steel described in (1) or (2) above, in which a 0.2 % proof stress thereof is equal to or higher than 758 MPa and equal to or lower than 965 MPa, an absorbed energy thereof in a Charpy full size test at -20 °C is equal to or higher than 100 J, and a corrosion rate thereof under an environment of a 20 % NaCl aqueous solution, 220 °C, and 10 atmospheric pressure-CO_2 is equal to or lower than 0.5 mm/year.
(4) A martensitic stainless steel pipe for an oil well, a gas well, or a line pipe comprising the martensitic stainless steel described in any one of (1) to (3) above.
(5) A method of producing a martensitic stainless steel including the steps of: subjecting the martensitic stainless

steel having a composition as described in (1) or (2) above to hot working,

thereafter forming austenite in the stainless steel at a temperature of equal to or higher than 800 °C and equal to or lower than 980 °C and successively quenching and cooling the steel at a temperature of equal to or lower than 100 °C, followed by tempering the steel at a temperature of equal to or higher than 500 °C and equal to or lower than 700 °C.

Effects of the Invention

[0019] According to the present invention, martensitic stainless steel with a high strength, high toughness, and high corrosion resistance which is excellent in a toughness, and in which a corrosion resistance is good against carbon dioxide gas corrosion under an environment at a temperature of equal to or higher than 180 °C, can be obtained by specifying an alloy composition and a production condition.

DESCRIPTION OF EMBODIMENTS

[0020] A description will be given of the reason of adding alloy elements in a martensitic stainless steel of the present invention, the reason of limiting amounts thereof, and the reason of limiting production conditions as follows. Incidentally, a content of each alloy element in the steel is a value based on a mass in which a total of the steel is 100 % unless specified otherwise.

(1) content composition range

<C: 0.005 to 0.05 %>

[0021] C is a strong austenite forming element, and an element which is indispensable also for achieving a high strength in a stainless steel. However, when tempering is carried out in producing the steel, C is bonded with Cr and is precipitated as a carbide thereof, which deteriorates a corrosion resistance and a toughness of the steel. When a content of C is less than 0.005 %, a sufficient strength is not achieved, and when the content of C exceeds 0.05 %, the deterioration becomes significant, and therefore, the content is set at 0.005 to 0.05 %.

<Si: equal to or less than 1.0 %>

[0022] Although Si is an element which is necessary as a deoxidizer, Si is also a strong ferrite forming element. In the martensitic stainless steel of the present invention, it is necessary to control ferrite for achieving a high strength and a high toughness. When Si is included in the stainless steel in an amount of exceeding 1.0 %, it is difficult to control ferrite, and therefore, an upper limit of the content is set at 1.0 %, preferably 0.5 %, further preferably 0.3 %.

<Mn: equal to or less than 2.0 %>

[0023] Mn is effective as a deoxidizer and a desulfurizing agent. However, Mn reduces a corrosion resistance of the stainless steel, and therefore, an upper limit of the content is set at 2.0 %, preferably 0.5 %, further preferably 0.3 %.

<Cr: 16 to 18 %>

[0024] Cr is a basic element constituting the martensitic stainless steel, and is an important element which manifests a corrosion resistance. In a case where the corrosion resistance is taken into consideration under a severe environment at temperatures of equal to or higher than 180 °C, when the content is less than 16 %, a sufficient corrosion resistance is not achieved, when the content exceeds 18 %, its effect is saturated, and a problem is posed in view of economy, and therefore, the content is set at 16 to 18 %.

<Ni: 2.5 to 6.5 %>

[0025] Ni is an element which enhances a corrosion resistance of a stainless steel and is extremely effective for stabilizing austenite. However, when the content thereof is less than 2.5 %, its effect is not sufficiently achieved and on the other hand, when the content is increased, a transformation temperature (Ac1 point) of martensite is lowered, restricting a tempering temperature in producing the martensitic stainless steel of the present invention. Furthermore, when the content of Ni is increased, there is a case where austenite is precipitated, which hampers enhancement of strength of the stainless steel. Hence, the content of Ni is set at 2.5 to 6.5 %.

<Mo: 1.5 to 3.5 %>

[0026] Mo is an element which is particularly effective for enhancing a corrosion resistance of the stainless steel. However, when the content thereof is less than 1.5 %, its effect is not exhibited, and when the content exceeds 3.5 %, it is difficult to control ferrite, and therefore, the content is set at 1.5 to 3.5 %.

<W, Cu: equal to or less than 3.5 %>

[0027] All of these are elements which are effective for enhancing the strength and the corrosion resistance of the stainless steel. In a case of adding W and/or Cu, when each amount exceeds 3.5 %, a hot workability of the steel is deteriorated, and therefore, an upper limit thereof is set at 3.5 %.

<V: 0.01 to 0.08 %>

[0028] V is a strong carbide forming element and contributes to increase the strength of the steel by making a crystal grain of carbide fine by uniformly precipitating the fine carbide within a matrix grain of the stainless steel and preventing the fine carbide from being precipitated preferentially on a grain boundary. The carbide is precipitated finely and uniformly in this way, and therefore, an increase in the strength is achieved without lowering the toughness of the steel. When the content of V is less than 0.01 %, the effect of increasing the strength is not exhibited, when the content exceeds 0.08 %, the effect is saturated, and therefore, the content is set at 0.01 to 0.08 %, preferably 0.02 to 0.04 %.

<Sol.Al: 0.005 to 0.10 %>

[0029] Acid soluble Al (Sol.Al) is added for deoxidizing the stainless steel in a refining step and for enhancing the toughness of the steel by making a y grain fine through precipitation of AlN. When the content thereof is less than 0.005 %, a toughness enhancing effect is not achieved, on the contrary, when the content exceeds 0.10 %, the toughness may be reduced, and therefore, the content is set at 0.005 to 0.10 %.

<N: equal to or less than 0.05 %>

[0030] N is an element which is harmful in enhancing the corrosion resistance of the stainless steel, and is also an austenite forming element. When N is contained in an amount of exceeding 0.05 %, N is precipitated as a nitride in tempering when the martensitic stainless steel of the present invention is produced, and the corrosion resistance and the toughness of the steel are deteriorated, and therefore, an upper limit of the content is set at 0.05 %, preferably 0.02 %.

<Ta: 0.01 to 0.06 %>

[0031] Ta is a strong carbide forming element and contributes to increase the strength of the steel by uniformly precipitating a fine carbide of Ta within a matrix grain of the stainless steel. The fine carbide is uniformly precipitated, and therefore, an increase in the strength can be achieved without reducing the toughness of the steel. Further, by adding a certain amount of Ta along with V described above, higher strength and toughness can be achieved than those in a case of adding either one of Ta and V. When the content of Ta is less than 0.01 %, an effect of enhancing the strength is not exhibited, when the content exceeds 0.06 %, its effect is generally saturated, and the addition is not preferable also in view of cost. Therefore, the content is set at 0.01 to 0.06 %.

<Nb: equal to or less than 0.1 %>

[0032] According to the present invention, Nb may be included other than the basic components described above. Nb is a strong carbide forming element and increases the strength of the stainless steel by making the crystal grain fine through precipitation of the fine carbide of Nb. When the content thereof exceeds 0.1 %, its effect is saturated, and therefore, the content is set equal to or less than 0.1 %, preferably equal to or less than 0.05 %.

<balance>

[0033] Further, in the martensitic stainless steel of the present invention, the balance other than the components explained above consists of Fe and inevitable impurities. Among inevitable impurities represented by P, S, and O, when an amount of P is equal to or less than 0.04 % and that of S is equal to or less than 0.01 %, no hindrance is configured in producing a seamless steel pipe or an electric resistance welded steel pipe with a hot-rolled steel plate as a material thereof which is considered to embody the present invention. However, all of the impurities are elements deteriorating the hot workability of the steel, and the smaller the contents, the more preferable it is. Also, concerning inevitable impurities of O and the like, the lower the content, the more preferable it is.

<properties of martensitic stainless steel>

[0034] A martensitic stainless steel of 758 MPa or higher which can be used in a humid carbon dioxide gas environment at temperatures of equal to or higher than 180 °C while maintaining the toughness can be obtained by improving the corrosion resistance of the conventional high strength-martensitic stainless steel by adjusting the stainless steel used in the present invention to have the composition component range described above.

[0035] Specifically, a 0.2 % proof stress of the martensitic stainless steel of the present invention is equal to or higher than 758 MPa and equal to or lower than 965 MPa, an absorbed energy thereof in a Charpy full size test at -20 °C is equal to or higher than 100 J, preferably, equal to or higher than 200 J, a corrosion rate thereof under an environment of a 20 % NaCl aqueous solution, 220 °C, and 10 atmospheric pressure-CO_2 is equal to or lower than 0.5 mm/year, preferably, equal to or lower than 0.3 mm/year. Incidentally, when the 0.2 % proof stress exceeds 965 MPa, in a case where a small amount of hydrogen is included in the stainless steel by corrosion or the like, a crack is liable to be brought about in the steel.

[0036] According to the present invention, a pertinent strength, a high toughness, and a high corrosion resistance which can withstand the use in a severe environment are achieved by executing prescribed production conditions with a composition of the stainless steel as the metal composition described above.

(2) production steps of martensitic stainless steel

[0037] The martensitic stainless steel of the present invention can be produced by the following production method.

[0038] The martensitic stainless steel with the component composition adjusted to the range described above is melted by a converter or an electric furnace and is made into a bloom, a slab or a billet by an ordinary ingot casting method followed by blooming or slabbing or a continuous casting method. The bloom, slab or billet is subjected to hot working, and is provided with a prescribed shape of a seamless steel pipe or a steel plate as needed (in the martensitic stainless steel under this state, a strength, a toughness and the like aimed by the present invention are not achieved). The hot-worked steel is heated at a temperature of equal to or higher than 800 °C, and equal to or lower than 980 °C to form austenite, successively quenched and cooled to a temperature of equal to or lower than 100 °C, and successively tempered at a temperature of equal to or higher than 500 °C and equal to or lower than 700 °C. A description will be given of heating temperatures in quenching and tempering operations as follows.

<a. heating temperature: equal to or higher than 800 °C and equal to or lower than 980 °C>

[0039] When the heating temperature is less than 800 °C, austenite is not formed in the stainless steel, an effect of quenching is not achieved, and therefore, a lower limit of the heating temperature is set at 800 °C. On the other hand, when the heating temperature exceeds 980 °C, a crystal grain is coarsened to deteriorate a toughness, and therefore, an upper limit of the heating temperature is set at 980 °C.

<b. tempering temperature: equal to or higher than 500 °C and equal to or lower than 700 °C>

[0040] A tempering treatment is generally a treatment which is carried out for providing a toughness to a steel. According to the present invention, in addition to the provision of the toughness, this is a step indispensable for enhancing strength of a stainless steel by uniformly dispersing and precipitating fine carbides of V and Ta. However, when a tempering temperature exceeds 700 °C, a 0.2 % proof stress of equal to or higher than 758 MPa is not achieved, and therefore, an upper limit of the tempering temperature is set at 700 °C. Also, when the tempering temperature is lower than 500 °C, the precipitation of the carbide is not sufficient, the aimed 0.2 % proof stress and the aimed toughness are not achieved, and therefore, a lower limit of the tempering temperature is set at 500 °C.

EXAMPLES

[0041] A description will be given of specific embodiments of the present invention as follows. The present inventors produced martensitic stainless steels by melting invented steels N1 to N8 and comparative steels C1 to C5 having chemical compositions shown in Table 1 described below as test steels (martensitic stainless steels), producing steel plates having a thickness of 12 mm by hot rolling, thereafter, carrying out heat treatments (quenching and tempering treatments) shown in Table 2 described below. Incidentally, the steel plates were cooled down to room temperature by water after the quenching heat treatment, thereafter, subjected to a tempering heat treatment.

[0042] Tests of mechanical properties (strength and toughness), and a corrosion resistance were carried out under the following conditions concerning the martensitic stainless steels. Incidentally, the comparative steels C1 and C5 are steels which do not include Ta. Further, the comparative steel C2 is a steel in which a content of V does not reach the lower limit of the present invention, the comparative steel C3 is a steel in which contents of Cr and Mo do not reach the lower limits of the present invention, and the comparative steel C4 is a steel in which a content of Ta exceeds the upper limit value of the present invention.

strength: a 0.2 proof stress at ordinary temperature
toughness: an absorbed energy (J) in a Charpy full size test at -20 °C
corrosion resistance: a corrosion rate over 2 weeks under an environment of a 20 % NaCl aqueous solution, 220 °C, 10 atmospheric pressure-CO_2.

[0043] Table 3 described below shows a test result of the mechanical properties and the corrosion resistance.

[0044] [Table 1]

Table 1 chemical composition (mass %) of test steels

Steel No.	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	W	N	Sol. Al	V	Nb	Ta	Reference
N1	0.022	0.21	0.22	0.014	0.001	4.05	17.12	2.61	1.00	0.00	0.012	0.041	0.032	0.000	0.015	Invented steel
N2	0.024	0.20	0.22	0.014	0.001	4.03	16.97	2.58	1.50	0.00	0.012	0.038	0.031	0.000	0.016	Invented steel
N3	0.021	0.21	0.21	0.013	0.001	4.06	17.19	2.65	0.01	0.00	0.015	0.035	0.033	0.000	0.031	Invented steel
N4	0.016	0.22	0.21	0.012	0.001	4.64	17.25	3.15	0.01	0.00	0.014	0.021	0.034	0.000	0.034	Invented steel
N5	0.018	0.22	0.21	0.011	0.001	4.04	17.24	2.62	0.01	0.49	0.016	0.025	0.033	0.000	0.033	Invented steel
N6	0.019	0.22	0.22	0.012	0.001	4.55	16.57	2.61	0.01	0.98	0.015	0.024	0.034	0.000	0.034	Invented steel
N7	0.022	0.20	0.24	0.011	0.001	5.55	17.67	1.53	3.10	3.03	0.013	0.037	0.028	0.040	0.018	Invented steel
N8	0.020	0.20	0.22	0.012	0.001	4.48	17.11	2.55	0.01	0.00	0.013	0.039	0.065	0.000	0.030	Invented steel
C1	0.021	0.22	0.24	0.013	0.001	4.03	17.18	2.64	0.01	0.00	0.012	0.038	0.033	0.000	0.000	comparative steel
C2	0.023	0.21	1.98	0.013	0.001	3.01	17.22	2.65	0.01	0.00	0.014	0.037	0.003	0.000	0.033	Comparative steel
C3	0.021	0.21	0.22	0.014	0.001	3.52	15.53	1.34	0.01	0.00	0.014	0.033	0.033	0.000	0.025	Comparative steel
C4	0.023	0.21	0.21	0.013	0.001	4.05	17.17	2.64	0.01	0.00	0.015	0.032	0.032	0.000	0.073	Comparative steel
C5	0.022	0.20	0.21	0.012	0.001	4.11	16.89	2.55	0.01	0.00	0.012	0.035	0.033	0.027	0.000	Comparative steel

[0045] [Table 2]

Table 2 heat treatment condition (°C) of test steels

Steel No.	Quenching	Tempering	Reference
N1	920	600	Invented steel
N2A	940	600	Invented steel
N2B	930	575	Invented steel
N3	920	575	Invented steel
N4	910	590	Invented steel
N5	920	600	Invented steel
N6A	920	600	Invented steel
N6B	930	575	Invented steel
N7	900	600	Invented steel
N8	920	580	Invented steel
C1	920	600	Comparative steel
C2	920	585	Comparative steel
C3	910	580	Comparative steel
C4	900	555	Comparative steel
C5	900	560	Comparative steel

[0046] [Table 3]

Table 3 test result

Steel No.	0.2% proof stress MPa	Absorbed energy J at -20 °C	Corrosion resistance (corrosion rate) mm/year	General evaluation	Reference
N1	827	275	0.12	Good	Invented steel
N2A	869	272	0.06	Good	Invented steel
N2B	902	268	0.09	Good	Invented steel
N3	762	276	0.47	Good	Invented steel
N4	773	123	0.05	Good	Invented steel
N5	780	182	0.15	Good	Invented steel
N6A	778	109	0.22	Good	Invented steel
N6B	798	105	0.21	Good	Invented steel
N7	949	210	0.02	Good	Invented steel
N8	820	255	0.11	Good	Invented steel

(continued)

Steel No.	0.2% proof stress MPa	Absorbed energy J at -20 °C	Corrosion resistance (corrosion rate) mm/year	General evaluation	Reference
C1	***710***	288	***0.53***	No Good	Comparative steel
C2	***638***	***98***	***0.55***	No Good	Comparative steel
C3	775	279	***0.82***	No Good	Comparative steel
C4	***974***	170	0.45	No Good	Comparative steel
C5	***998***	133	0.42	No Good	Comparative steel
*Concerning corrosion resistance, a corrosion rate per year was calculated from a corrosion rate over 2 weeks					

[0047] Concerning all of the invented steels of "N1, N2A, N2B, N3, N4, N5, N6A, N6B, N7, N8", the 0.2 % proof stress, and the absorbed energy in the Charpy full size test fell in target ranges. Also, the corrosion resistance achieved the target value.

[0048] On the other hand, in comparative steels, C1 and C5 are steels which do not include Ta, C2 is a steel in which the V content does not reach the lower limit of the present invention, C3 is a steel in which Cr and Mo contents do not reach the lower limits of the present invention, and C4 is a steel in which the Ta content exceeds the upper limit value of the present invention.

[0049] That is, any of the components are deviated from the ranges of the present invention, and therefore, as for results thereof, the aimed 0.2 % proof stress, toughness or corrosion resistance are not achieved. Particularly, in C2, even when tempering was carried out at a temperature of below 600 °C, the strength of 758 MPa class could not be achieved, and also concerning the toughness and the corrosion resistance, target values could not be achieved. From the above, by a composite addition of V + Ta, an improvement in properties which could not be achieved by single addition of V or Ta was achieved and the synergistic effect by the composite addition was recognized.

INDUSTRIAL APPLICABILITY

[0050] The martensitic stainless steel of the present invention has the corrosion resistance, maintains the toughness despite the high strength equal to or higher than 758 MPa, can be used in the humid carbon dioxide gas environment at temperatures equal to or higher than 180 °C, and can preferably be applied as a steel pipe for drilling for or transporting petroleum or natural gas including the carbon dioxide gas (martensitic stainless steel pipe for an oil well or a gas well or a line pipe).

Claims

1. A martensitic stainless steel containing, in mass %, C: 0.005 % to 0.05 %, Si: equal to or less than 1.0 %, Mn: equal to or less than 2.0 %, Cr: 16 to 18 %, Ni: 2.5 to 6.5 %, Mo: 1.5 to 3.5 %, W: equal to or less than 3.5 %, Cu: equal to or less than 3.5 %, V: 0.01 to 0.08 %, Sol.Al: 0.005 to 0.10 %, N: equal to or less than 0.05 %, and Ta: 0.01 to 0.06 %, and the balance Fe with inevitable impurities.

2. The martensitic stainless steel according to Claim 1, further containing, in mass %, Nb: equal to or less than 0.1 %.

3. The martensitic stainless steel according to Claim 1 or 2, wherein a 0.2 % proof stress thereof is equal to or higher than 758 MPa and equal to or lower than 965 MPa, an absorbed energy thereof in a Charpy full size test at -20 °C is equal to or higher than 100 J, and a corrosion rate thereof under an environment of a 20 % NaCl aqueous solution, 220 °C, 10 atmospheric pressure-CO_2 is equal to or lower than 0.5 mm/year.

4. A martensitic stainless steel pipe for an oil well, a gas well, or a line pipe comprising the martensitic stainless steel according to any one of Claims 1 to 3.

5. A method of producing a martensitic stainless steel comprising the steps of:

subjecting the martensitic stainless steel having a composition as defined in Claim 1 or 2 to hot working, thereafter forming austenite in the steel at a temperature of equal to or higher than 800 °C and equal to or lower than 980 °C and successively quenching and cooling the steel at a temperature of equal to or lower than 100 °C, followed by tempering the steel at a temperature of equal to or higher than 500 °C and equal to or lower than 700 °C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/062004

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D8/02*(2006.01)i, *C21D9/08*(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)
C22C38/00-38/60, C21D8/00-8/10, C21D9/08

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2013
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 A	JP 3-75337 A (Nippon Steel Corp.), 29 March 1991 (29.03.1991), claims (Family: none)	1,2,4,5 3
X A	JP 3-75336 A (Nippon Steel Corp.), 29 March 1991 (29.03.1991), claims (Family: none)	1,2,4,5 3
X A	JP 3-75335 A (Nippon Steel Corp.), 29 March 1991 (29.03.1991), claims (Family: none)	1,2,4,5 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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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 July, 2013 (19.07.13)	30 July, 2013 (30.07.13)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/062004

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/0006945 A1 (MORI Nobuyuki, NAKAMURA Keiichi), 11 January 2007 (11.01.2007), examples & CN 1891846 A	1-5
A	US 5939018 A (Kawasaki Steel Corp.), 17 August 1999 (17.08.1999), examples (Family: none)	1-5

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2008081793 A **[0008]**
- JP 2010209402 A **[0008]**
- JP 2814528 B **[0008]**
- JP 4577457 B **[0008]**
- JP 4761008 B **[0008]**
- JP 4911266 B **[0008]**
- WO 2009119048 A **[0008]**