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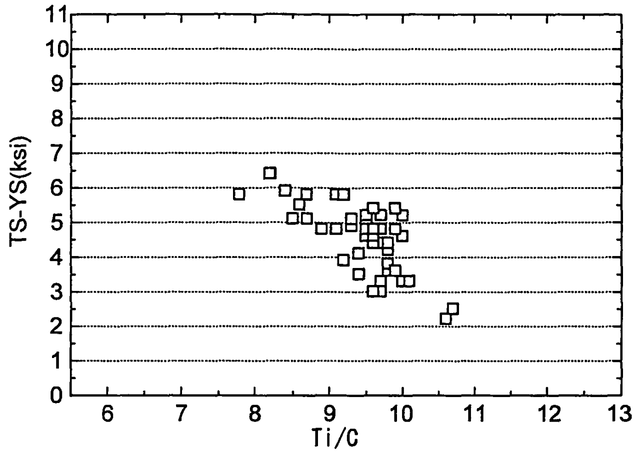
(54) **MARTENSITIC STAINLESS STEEL**

(57) The martensitic stainless steel according to the invention includes, in percent by mass, 0.010% to 0.030% C, 0.30% to 0.60% Mn, at most 0.040% P, at most 0.0100% S, 10.00% to 15.00% Cr, 2.50% to 8.00% Ni, 1.00% to 5.00% Mo, 0.050% to 0.250% Ti, at most 0.25% V, at most 0.07% N, and at least one of at most 0.50% Si and at most 0.10% Al, the balance consists of Fe and impurities, and the martensitic stainless steel satisfies Expression (1) and has a yield stress in the range from 758 MPa to 862 MPa. In this way, the martensitic stainless steel has a yield stress of 110 ksi grade (a yield stress in the range from 758 MPa to 862 MPa) and the value produced by subtracting the yield stress from the tensile stress is not less than 20.7 MPa.

$$6.0 \le Ti/C \le 10.1 \quad \ldots (1)$$

FIG.1



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Description

TECHNICAL FIELD

[0001] The present invention relates to martensitic stainless steel and more specifically to martensitic stainless steel for use in a corroding environment containing a corroding substance such as hydrogen sulfide, carbon dioxide gas, and chlorine ions.

BACKGROUND ART

[0002] In recent years, more and more oil wells and gas wells have been dug to deep levels. Steel products used as oil country tubular goods in these deep oil wells and gas wells (hereinafter collectively referred to as "oil wells") need high yield stress. Steel materials recently used for oil country tubular goods have a yield stress of 110 ksi grade (at which 0.6% total elongation yield stress is from 758 MPa to 862 MPa).
[0003] In addition, such oil wells contain hydrogen sulfide, carbon dioxide gas, and chlorine ions. Therefore, steel materials for the oil country tubular goods need high SSC (Sulfide Stress Corrosion Cracking) resistance and high carbon dioxide gas corrosion resistance.
[0004] In general, steel containing many alloy components is used for oil wells. For an oil well containing carbon dioxide gas, SUS420 martensitic stainless steel having carbon dioxide gas corrosion resistance is used. However, the SUS420 martensitic stainless steel is not suited for an oil well containing hydrogen sulfide because its SSC resistance against hydrogen sulfide is low.
[0005] To cope with the situation, martensitic stainless steel products having not only carbon dioxide gas corrosion resistance but also SSC resistance have been developed. JP 5-287455 A (hereinafter referred to as "Patent Document 1") discloses martensitic stainless steel for oil wells having high SSC resistance and high carbon dioxide gas corrosion resistance in an oil well containing substances such as hydrogen sulfide and carbon dioxide gas. In order to improve the SSC resistance, it is effective to reduce the tensile stress. Therefore, according to the disclosure of Patent Document 1, the tensile stress of the martensitic stainless steel is reduced, so that high SSC resistance is provided. Furthermore, variation in the tensile stress after tempering is reduced by reducing the tensile stress.
[0006] Recently in the field of stainless steel products for oil country tubular goods, there is a demand for a property that is not immediately fractured by plastic deformation of the steel products caused by externally applied force in addition to the high strength, SSC resistance and carbon dioxide gas corrosion resistance described above. More specifically, the value produced by subtracting the yield stress (0.6% total elongation yield stress) from the tensile stress must be at least 20.7 MPa (=3 ksi).
[0007] The martensitic stainless steel for oil wells disclosed by Patent Document 1 is designed to have low tensile stress. Therefore, when the yield stress of the steel is of 110 ksi grade (from 758 MPa to 832 MPa), the value produced by subtracting the yield stress from the tensile stress is less than 20.7 MPa.
[0008] Furthermore, a steel product for an oil country tubular good also needs the SSC resistance as described above. If the hardness of the same one steel product greatly varies, the SSC resistance is reduced. Therefore, the hardness variation of a steel product for an oil country tubular good must be suppressed.

DISCLOSURE OF THE INVENTION

[0009] It is an object of the invention to provide martensitic stainless steel of 110 ksi grade (having a yield stress from 758 MPa to 862 MPa) that allows the value produced by subtracting the yield stress from the tensile stress to be at least 20.7 MPa and can suppress hardness variation.
[0010] The inventors found that the ratio of the Ti content relative to the C content in steel and the value (hereinafter also referred to as TS-YS) produced by subtracting the yield stress (hereinafter also referred to as "YS") from the tensile stress (hereinafter also referred to as "TS") have a correlation. Now, the finding will be described.
[0011] The inventors produced a plurality of kinds of martensitic stainless steel containing, in percent by mass, 0.010% to 0.030% C, 0.30% to 0.60% Mn, at most 0.040% P, at most 0.0100% S, 10.00% to 15.00% Cr, 2.50% to 8.00% Ni, 1.00% to 5.00% Mo, 0.050% to 0.250% Ti, at most 0.25% V, at most 0.07% N, and at least one kind of at most 0.50% Si, and at most 0.10% Al, the balance consisted of Fe and impurities, and Ti/C was from 7.4 to 10.7. During the manufacture, quenching-tempering was carried out, and the tempering temperature was adjusted so that the yield stress of each kind of the martensitic stainless steel was of 110 ksi grade (from 758 MPa to 862 MPa). The produced martensitic stainless steel was subjected to tensile tests at room temperatures and their tensile stress and yield stress were obtained. Note that 0.6% total elongation yield stress according to the ASTM standard was defined as the yield stress.
[0012] The result of examination is given in Fig. 1. The abscissa in Fig. 1 represents Ti/C, and the ordinate represents TS-YS (ksi). As shown in Fig. 1, Ti/C and TS-YS indicated a negative correlation. More specifically, as Ti/C was reduced,

TS-YS increased. Based on this new finding, the inventors found that TS-YS≥20.7 MPa (3 ksi) can be satisfied by satisfying the following Expression (A):

$$Ti/C \leq 10.1 \quad \ldots (A)$$

where the element symbols represent the contents of these elements (% by mass).

[0013] Furthermore, the inventors newly found that when Ti/C is too small, the hardness greatly varies. More specifically, they found that when Ti/C is in an appropriate range, TS-YS is not less than 20.7 MPa and the hardness variation can be reduced.

[0014] Based on the foregoing technical ideas, the inventors have completed the following invention.

[0015] Martensitic stainless steel according to the invention includes, in percent by mass, 0.010% to 0.030% C, 0.30% to 0.60% Mn, at most 0.040% P, at most 0.0100% S, 10.00% to 15.00% Cr, 2.50% to 8.00% Ni, 1.00% to 5.00% Mo, 0.050% to 0.250% Ti, at most 0.25% V, at most 0.07% N, and at least one of at most 0.50% Si and at most 0.10% Al, and the balance consists of Fe and impurities. The martensitic stainless steel according to the present invention further satisfies Expression (1) and has a yield stress in the range from 758 MPa to 862 MPa. The yield stress herein means 0.6% total elongation yield stress according to the ASTM standards.

$$6.0 \leq Ti/C \leq 10.1 \quad \ldots (1)$$

where the symbols of the elements represent the contents of the elements in percent by mass.

[0016] The martensitic stainless steel preferably includes at least one of at most 0.25% Nb and at most 0.25% Zr instead of part of the Fe.

[0017] The martensitic stainless steel preferably further includes at most 1.00% Cu instead of part of the Fe.

[0018] The martensitic stainless steel preferably further includes at least one of at most 0.005% Ca, at most 0.005% Mg, at most 0.005% La, and at most 0.005% Ce instead of part of the Fe.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

Fig. 1 is a graph showing the relation between the value produced by subtracting the yield stress from the tensile stress and Ti/C; and
Fig. 2 is a cross sectional view of a steel pipe for showing locations

where the hardness is measured.

BEST MODE FOR CARRYING OUT THE INVENTION

[0020] Now, an embodiment of the invention will be described in detail in conjunction with the accompanying drawings.

1. Chemical Composition

[0021] Martensitic stainless steel according to the embodiment of the invention has the following composition. In the following description, "%" related to elements means "% by mass."
C: 0.010% to 0.030%

[0022] An excessive carbon (C) content raises the hardness after tempering too high, which increases the sulfide stress corrosion cracking sensitivity. When the C content is too small and the yield stress of the steel is of at least 110 ksi grade (from 758 MPa to 862 MPa), TS-YS≥20.7 MPa cannot be satisfied. Therefore, the C content is from 0.010% to 0.030%, preferably from 0.012% to 0.018%.
Mn: 0.30% to 0.60%

[0023] Manganese (Mn) improves the hot workability. However, with an excessive Mn content, the effect is saturated. Therefore, the Mn content is from 0. 30% to 0.60%.
P: 0.040% or less

[0024] Phosphorus (P) is an impurity and lowers the SSC resistance. Therefore, the P content is not more than 0.040%.
S: 0.0100% or less

[0025] Sulfur (S) is an impurity and lowers the hot workability. Therefore, the S content is preferably as small as possible. The S content is not more than 0.0100%.

Cr: 10.00% to 15.00%

[0026] Chromium (Cr) improves the carbon dioxide gas corrosion resistance. An excessive Cr content however prevents the structure after tempering from attaining a martensitic phase. Therefore, the Cr content is from 10.00% to 15.00%.

Ni: 2.50% to 8.00%

[0027] Nickel (Ni) effectively allows the structure after tempering to mainly attain a martensitic phase. When the Ni content is too small, a large amount of ferrite phase is deposited in the tempered structure. On the other hand, an excessive Ni content causes the tempered structure to mainly attain an austenite phase. Therefore, the Ni content is from 2.50% to 8.00%, preferably from 4.00% to 7.00%.

Mo: 1.00% to 5.00%

[0028] Molybdenum (Mo) improves the SSC resistance of high strength steel in an environment containing hydrogen sulfide. However, with an excessive Mo content, the effect is saturated. Therefore, the Mo content is from 1.00% to 5.00%.

Ti: 0.050% to 0.250%

[0029] Titanium (Ti) improves the toughness by suppressing the structure from being coarse-grained. However, an excessive Ti content prevents the structure after tempering from mainly attaining a martensitic phase, so that the toughness and the corrosion resistance (the SSC resistance and the carbon dioxide gas corrosion resistance) are lowered. Therefore, the Ti content is from 0.050% to 0.250%, preferably from 0.050% to 0.150%.

N: 0.07% or less

[0030] Nitrogen (N) is an impurity. An excessive N content causes a lot of nitrogen-based inclusions to be deposited in the steel, which lowers the corrosion resistance. Therefore, the N content is not more than 0.07%, preferably not more than 0.03%, more preferably not more than 0.02%, even more preferably not more than 0.01%.

V: 0.25% or less

[0031] Vanadium (V) fixes C in the steel by forming a carbide and thus raises the tempering temperature and enhances the SSC resistance. However, an excessive V content prevents a martensitic phase from being attained. Therefore, the V content is not more than 0.25%. The lower limit for the V content is preferably 0.01%.

[0032] The martensitic stainless steel according to the embodiment contains at least one of Si and Al.

Si: 0.50% or less

Al: 0.10% or less

[0033] Silicon (Si) and aluminum (Al) both effectively work as a deoxidizing agent. However, an excessive Si content lowers the toughness and the hot workability. An excessive Al content causes a lot of inclusions to be produced in the steel, which lowers the corrosion resistance. Therefore, the Si content is not more than 0.50% and the Al content is not more than 0.10%. The lower limit for the Si content is preferably 0.10%, and the lower limit for the Al content is preferably 0.001%. Note that if the Si and/or Al content is less than the described lower limits, the above-described effect is provided to some extent.

[0034] The balance of the martensitic stainless steel according to the embodiment includes Fe. Note that impurities other than the above-described impurities may be contained for various causes.

[0035] Furthermore, the Ti content and the C content in the chemical composition described above satisfy the following Expression (1):

$$6.0 \leq Ti/C \leq 10.1 \qquad (1)$$

where the element symbols represent the contents of the elements (% by mass).

[0036] As shown in Fig. 1, as Ti/C decreases, TS-YS increases. When Ti/C exceeds 10.1, TS-YS≥20.7 MPa cannot be satisfied.

[0037] On the other hand, when Ti/C is too small, the hardness variation increases. More specifically, the hardness variation (HRC) determined by the following Expression (2) is not less than 2.5.

$$\text{Hardness variation (HRC)} = \text{Hmax} - \text{Hmin} \qquad \ldots (2)$$

[0038] Here, Hmax and Hmin are measured by the following method. In a cross section corresponding to the center of the steel pipe as shown in Fig. 2, the Rockwell hardness C scale (which is hereinafter simply referred to as "Rockwell hardness" and expressed in the unit HRC) is measured at the thickness central parts P1 to P4 at intervals of 90° in the circumferential direction. Among the four measured Rockwell hardness values, the maximum value is Hmax and the minimum value is Hmin.

[0039] When the hardness variation is not less than 2.5, the SSC resistance tends to decrease. When Ti/C is not less than 6.0, the hardness variation is less than 2.5 and can be suppressed. While the reason is not clearly determined, this may be for the following reason. If Ti/C is too small, the Ti content in the steel is small. Therefore, a plurality of VCs are deposited during tempering. The deposited VCs have unequal sizes depending on where they are deposited in the steel pipe. As a result, the hardness greatly varies. On the other hand, if Ti/C is large, the Ti content in the steel is large. Therefore, TiC is deposited during tempering and the deposition of VCs is suppressed. Consequently, the hardness variation is reduced.

[0040] The martensitic stainless steel according to the invention satisfies Expression (1), so that TS-YS is not less than 20.7 MPa and the hardness variation is less than 2.5.

[0041] The upper limit for Ti/C is preferably 9.6, more preferably 9.0.

[0042] The martensitic stainless steel according to the embodiment further contains at least one of Nb and Zr instead of part of Fe as required.

Nb: 0.25% or less

Zr: 0.25% or less

[0043] Niobium (Nb) and Zirconium (Zr) are both optional elements. These elements both form a carbide to fix C in the steel and reduce the hardness variation after tempering. However, excessive contents of these elements prevent the tempered structure from mainly attaining a martensitic phase. Therefore, the Nb content and the Zr content are both not more than 0.25%. The preferred lower limits for the Nb content and the Zr content are each 0.005%. Note that when the Nb and Zr contents are each less than 0.005%, the above-described effect can be provided to some extent.

[0044] The martensitic stainless steel according to the embodiment further contains Cu instead of part of Fe as required.

Cu: 1.00% or less

[0045] Copper (Cu) is an optional element. Similarly to Ni, Cu effectively allows the structure after tempering to attain a martensitic phase. However, an excessive Cu content lowers the hot workability. Therefore, the Cu content is not more than 1.00%. The lower limit for the Cu content is preferably 0.05%. Note that if the Cu content is less than 0.05%, the above-described effect can be provided to some extent.

[0046] The martensitic stainless steel according to the embodiment further contains at least one of Ca, Mg, La, and Ce instead of part of Fe as required.

Ca: 0.005% or less

Mg: 0.005% or less

La: 0.005% or less

Ce: 0.005% or less

[0047] Calcium (Ca), magnesium (Mg), lanthanum (La) and cerium (Ce) are optional elements. These elements improve the hot workability. However, if these elements are excessively contained, coarse oxides are produced, and the corrosion resistance is lowered. Therefore, the contents of these elements are each not more than 0.005%. The lower limit for each of these elements is preferably 0.0002%. Note that if the contents of Ca, Mg, La, and Ce are less than 0.0002%, the above-described effect can be provided to some extent. Among these elements, Ca and/or La is preferably contained.

2. Manufacturing Method

[0048] A method of manufacturing martensitic stainless steel according to the embodiment will be described. Molten steel having the chemical composition described in the above 1. is made into a slab or billet by a method such as continuous casting. Alternatively, the molten steel is made into an ingot by ingot-making. The slab or ingot is subjected to hot working by a method such as blooming and made into a billet.

[0049] The manufactured billet is heated in a heating furnace, and the billet extracted from the heating furnace is axially pierced by a piercing mill. Then, the strand or billet is made into a seamless steel pipe having a prescribed size by a mandrel mill, a reducer, or the like. Then, heat treatment (quenching and tempering) is carried out. At the time, the quenching and tempering temperatures are adjusted so that the 0.6% total elongation yield stress of the tempered martensitic stainless steel is in the range from 758 MPa to 862 MPa (110 ksi grade).

[0050] Note that the above description is about a method of manufacturing a seamless pipe of martensitic stainless steel, while a welded steel pipe of martensitic stainless steel may be produced by any of other well-known manufacturing methods.

Example

[0051] Seamless steel pipes having various chemical compositions were produced and the produced seamless steel pipes were examined for TS-YS and hardness variation.

Examination Method

[0052] Various kinds of steel having chemical compositions in Table 1 were each formed into a billet by melting on a test number basis. The manufactured billets were each subjected to hot forging and hot rolling, and seamless steel pipes were produced.

Table 1

No.	Chemical Composition (unit: mass %, the balance consisting of Fe and impurities)													Ti/C	TS (MPa)	YS (MPa)	TS-YS (MPa)	hardness variation (HRC)
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Ti	V	Al	N					
1	0.010	0.23	0.39	0.014	0.0013	0.21	11.98	5.37	1.92	0.092	0.06	-	0.0105	9.2	839.0	805.0	34.0	0.4
2	0.010	0.25	0.39	0.017	0.0007	0.08	11.99	5.83	1.94	0.091	0.05	0.032	0.0068	9.1	888.0	848.0	40.0	1.2
3	0.010	0.18	0.45	0.016	0.0008	0.25	11.93	5.42	1.92	0.100	0.07	-	0.0120	10.0	839.0	816.0	23.0	0.6
4	0.010	0.18	0.39	0.016	0.0012	0.23	12.06	5.56	1.93	0.097	0.07	-	0.0070	9.7	838.0	817.0	21.0	0.5
5	0.010	0.19	0.40	0.015	0.0012	0.23	11.99	5.41	1.95	0.096	0.06	0.033	0.0060	9.6	847.0	816.0	31.0	0.8
6	0.010	0.19	0.41	0.015	0.0010	0.23	11.92	5.39	1.92	0.095	0.06	0.033	0.0066	9.5	860.0	824.0	36.0	0.5
7	0.010	0.19	0.42	0.016	0.0011	0.24	11.97	5.41	1.92	0.093	0.05	0.034	0.0067	9.3	849.0	815.0	34.0	1.2
8	0.010	0.22	0.42	0.015	0.0009	0.23	11.97	5.44	1.92	0.091	0.06	0.042	0.0060	9.1	854.0	821.0	33.0	1.2
9	0.010	0.23	0.42	0.016	0.0009	0.23	11.92	5.42	1.92	0.100	0.06	-	0.0087	10.0	844.0	812.0	32.0	1.4
10	0.010	0.19	0.42	0.016	0.0005	0.22	11.97	5.45	1.92	0.099	0.06	0.031	0.0074	9.9	859.0	826.0	33.0	0.7
11	0.010	0.25	0.39	0.019	0.0007	0.23	12.00	5.37	1.94	0.086	0.06	0.035	0.0057	8.6	856.0	818.0	38.0	1.7
12	0.010	0.24	0.42	0.017	0.0017	0.23	12.16	5.45	1.94	0.095	0.06	0.040	0.0068	9.5	857.0	817.0	40.0	1.2
13	0.010	0.23	0.44	0.016	0.0008	0.22	12.07	5.53	1.94	0.100	0.06	0.039	0.0064	10.0	859.0	823.0	36.0	1.1
14	0.010	0.25	0.43	0.018	0.0005	0.24	12.04	5.43	1.96	0.095	0.06	0.039	0.0064	9.5	852.0	816.0	36.0	0.7
15	0.010	0.24	0.43	0.018	0.0006	0.23	12.08	5.48	1.95	0.099	0.06	0.038	0.0072	9.9	844.0	807.0	37.0	1.2
16	0.010	0.22	0.43	0.014	0.0010	0.25	11.99	5.39	1.92	0.095	0.06	0.034	0.0061	9.5	823.0	789.0	34.0	0.5
17	0.010	0.24	0.41	0.016	0.0012	0.24	12.03	5.43	1.93	0.097	0.06	0.033	0.0065	9.7	839.0	809.0	30.0	1
18	0.010	0.22	0.44	0.014	0.0009	-	12.10	5.83	1.94	0.096	0.06	0.039	0.0069	9.6	836.0	805.0	31.0	0.5
19	0.010	0.27	0.42	0.016	0.0006	0.25	12.04	5.47	1.94	0.092	0.06	0.019	0.0066	9.2	865.0	841.0	24.0	1.4
20	0.010	0.22	0.43	0.015	0.0008	0.25	11.98	5.43	1.92	0.094	0.06	0.040	0.0057	9.4	852.0	824.0	28.0	0.5
21	0.010	0.21	0.42	0.016	0.0008	-	12.05	5.89	1.94	0.097	0.06	0.039	0.0060	9.7	829.0	793.0	36.0	0.3
22	0.011	0.26	0.41	0.019	0.0006	-	12.00	5.83	1.93	0.104	0.06	0.046	0.0060	9.5	847.0	815.0	32.0	0.6
23	0.010	0.23	0.43	0.019	0.0007	0.23	12.10	5.48	1.95	0.098	0.06	0.040	0.0063	9.8	858.0	833.0	25.0	1.1

(continued)

No.	Chemical Composition (unit: mass %, the balance consisting of Fe and impurities)													Ti/C	TS (MPa)	YS (MPa)	TS-YS (MPa)	hardness variation (HRC)
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Ti	V	Al	N					
24	0.010	0.22	0.42	0.020	0.0010	0.23	12.14	5.44	1.92	0.096	0.06	0.041	0.0067	9.6	890.0	860.0	30.0	1.2
25	0.011	0.24	0.43	0.016	0.0010	0.20	11.99	5.46	1.89	0.094	0.06	0.043	0.0080	8.5	870.0	835.0	35.0	0.7
26	0.010	0.25	0.44	0.018	0.0009	0.25	12.08	5.47	1.91	0.092	0.06	0.035	0.0083	9.2	852.0	812.0	40.0	1.5
27	0.010	0.25	0.44	0.018	0.0008	0.25	12.08	5.46	1.92	0.095	0.06	0.040	0.0064	9.5	834.0	798.0	36.0	0.7
28	0.011	0.23	0.44	0.016	0.0009	0.24	12.03	5.44	1.90	0.090	0.06	0.032	0.0075	8.2	844.0	800.0	44.0	1.3
29	0.010	0.23	0.39	0.018	0.0010	0.22	12.04	5.44	1.91	0.084	0.06	0.037	0.0084	8.4	826.0	785.0	41.0	0.5
30	0.012	0.22	0.43	0.019	0.0007	0.22	12.23	5.51	1.90	0.094	0.04	0.034	0.0085	7.8	846.0	806.0	40.0	0.9
31	0.010	0.24	0.42	0.015	0.0006	0.24	11.99	5.42	1.92	0.096	0.06	0.036	0.0076	9.6	842.0	810.0	32.0	0.8
32	0.010	0.26	0.43	0.015	0.0005	0.24	12.06	5.45	1.93	0.101	0.06	0.036	0.0080	10.1	848.0	825.0	23.0	1.1
33	0.010	0.25	0.42	0.017	0.0009	0.25	12.04	5.43	1.92	0.096	0.06	0.037	0.0076	9.6	852.0	823.0	29.0	0.7
34	0.010	0.22	0.43	0.018	0.0009	0.23	12.04	5.43	1.94	0.097	0.06	0.038	0.0061	9.7	833.0	800.0	33.0	0.9
35	0.010	0.27	0.42	0.017	0.0007	0.22	12.02	5.44	1.93	0.096	0.06	0.036	0.0062	9.6	862.0	825.0	37.0	0.7
36	0.010	0.22	0.44	0.015	0.0010	0.23	11.98	5.44	1.94	0.097	0.06	0.035	0.0068	9.7	852.0	829.0	23.0	1.2
37	0.010	0.24	0.41	0.020	0.0005	0.27	12.11	5.46	1.91	0.095	0.07	-	0.0110	9.5	864.0	831.0	33.0	1
38	0.013	0.23	0.43	0.018	0.0007	0.22	11.99	5.39	1.91	0.096	0.06	0.037	0.0081	7.4	856.0	816.0	40.0	0.3
39	0.010	0.27	0.41	0.015	0.0005	0.23	12.00	5.42	1.91	0.098	0.06	0.039	0.0070	9.8	837.0	807.0	30.0	0.8
40	0.010	0.24	0.41	0.016	0.0012	0.25	11.96	5.39	1.92	0.089	0.06	0.034	0.0070	8.9	830.0	797.0	33.0	0.5
41	0.010	0.22	0.44	0.017	0.0007	0.27	12.03	5.44	1.93	0.096	0.06	0.037	0.0078	9.6	848.0	815.0	33.0	1.1
42	0.010	0.23	0.42	0.017	0.0005	0.25	11.94	5.43	1.91	0.096	0.07	0.037	0.0071	9.6	839.0	818.0	21.0	0.8
43	0.010	0.22	0.43	0.016	0.0006	0.24	11.97	5.42	1.92	0.095	0.06	0.036	0.0074	9.5	829.0	788.0	41.0	0.4
44	0.010	0.25	0.43	0.018	0.0006	0.24	12.02	5.43	1.90	0.093	0.06	0.032	0.0075	9.3	855.0	820.0	35.0	1.1
45	0.010	0.23	0.42	0.016	0.0005	0.24	12.03	5.45	1.92	0.098	0.06	0.036	0.0049	9.8	844.0	818.0	26.0	0.9
46	0.010	0.25	0.42	0.016	0.0005	0.23	11.98	5.47	1.94	0.099	0.06	0.034	0.0063	9.9	854.0	829.0	25.0	0.2
47	0.010	0.22	0.43	0.014	0.0008	0.24	11.96	5.43	1.91	0.087	0.06	0.032	0.0064	8.7	833.0	798.0	35.0	0.6

(continued)

No.	Chemical Composition (unit: mass %, the balance consisting of Fe and impurities)													Ti/C	TS (MPa)	YS (MPa)	TS-YS (MPa)	hardness variation (HRC)
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Ti	V	Al	N					
48	0.010	0.27	0.44	0.015	0.0008	0.22	12.13	5.59	1.93	0.097	0.06	0.034	0.0062	9.7	866.0	825.0	41.0	0.9
49	0.018	0.19	0.42	0.019	0.0007	-	11.99	5.52	1.95	0.110	0.06	0.028	0.0088	6.1	889.0	843.0	46.0	1.2
50	0.010	0.22	0.42	0.017	0.0010	0.24	12.03	5.43	1.90	0.1060	0.06	-	0.0120	**10.6**	850.0	835.0	15.0	0.3
51	0.010	0.20	0.35	0.018	0.0009	0.20	12.00	5.40	1.92	0.107	0.06	-	0.0144	**10.7**	839.0	822.0	17.0	0.8
52	**0.007**	0.23	0.40	0.019	0.0005	0.22	11.90	5.39	1.92	0.097	0.06	-	0.0098	**13.9**	861.0	847.0	14.0	1
53	**0.006**	0.22	0.40	0.016	0.0006	0.22	11.97	5.43	1.95	0.099	0.06	0.041	0.0064	**16.5**	861.0	847.0	14.0	0.8
54	**0.008**	0.18	0.42	0.015	0.0011	0.23	12.02	5.42	1.94	0.098	0.05	-	0.0110	**12.3**	847.0	832.0	15.0	1
55	**0.006**	0.21	0.42	0.016	0.0005	0.24	11.90	5.43	1.92	0.097	0.06	-	0.0151	**16.2**	853.0	837.0	16.0	0.9
56	**0.009**	0.20	0.42	0.012	0.0014	0.22	11.90	5.33	1.91	0.086	0.06	-	0.0087	**9.6**	851.0	835.0	16.0	1.4
57	**0.007**	0.20	0.44	0.017	0.0009	0.24	12.03	5.44	1.92	0.071	0.06	-	0.0077	**10.1**	866.0	850.0	16.0	0.3
58	**0.007**	0.20	0.42	0.015	0.0006	-	11.87	5.82	1.91	0.100	0.06	0.030	0.0076	**14.3**	856.0	840.0	16.0	1.6
59	**0.007**	0.20	0.44	0.017	0.0009	0.24	12.05	5.43	1.92	0.069	0.06	-	0.0065	**9.9**	862.0	845.0	17.0	1.1
60	**0.006**	0.22	0.42	0.016	0.0005	0.24	11.89	5.42	1.91	0.097	0.06	-	0.0130	**16.2**	848.0	831.0	17.0	0.5
61	**0.008**	0.21	0.41	0.013	0.0007	0.23	11.94	5.41	1.91	0.095	0.06	-	0.0133	**11.9**	856.0	839.0	17.0	1.0
62	**0.006**	0.23	0.41	0.017	0.0008	0.25	11.98	5.42	1.92	0.098	0.06	0.037	0.0075	**16.3**	848.0	831.0	17.0	0.4
63	**0.006**	0.21	0.41	0.019	0.0007	0.24	12.14	5.48	1.93	0.094	0.06	-	0.0111	**15.7**	845.0	827.0	18.0	1.0
64	**0.009**	0.21	0.41	0.015	0.0010	0.21	11.99	5.43	1.92	0.097	0.06	-	0.0125	**10.8**	823.0	805.0	18.0	0.7
65	**0.009**	0.20	0.40	0.014	0.0008	0.22	11.98	5.42	1.93	0.093	0.06	0.030	0.0068	**10.3**	837.0	819.0	18.0	0.6
66	**0.006**	0.20	0.43	0.014	0.0006	-	11.96	5.83	1.92	0.099	0.06	0.032	0.0074	**16.5**	833.0	815.0	18.0	0.7
67	**0.007**	0.22	0.42	0.018	0.0006	0.25	12.12	5.48	1.93	0.099	0.06	0.037	0.0071	**14.1**	831.0	814.0	17.0	1.2
68	**0.007**	0.22	0.42	0.018	0.0009	0.25	12.07	5.45	1.91	0.095	0.06	0.037	0.0071	**13.6**	837.0	820.0	17.0	1.6
69	**0.008**	0.20	0.45	0.017	0.0011	0.23	12.10	5.48	1.91	0.101	0.06	0.042	0.0086	**12.6**	841.0	823.0	18.0	1.1
70	**0.020**	0.21	0.42	0.017	0.0007	-	11.98	5.51	1.99	0.009	0.06	0.030	0.0077	**0.5**	924.0	839.0	85.0	3.6
71	0.018	0.21	0.43	0.015	0.0006	-	12.01	5.53	1.98	0.040	0.06	0.029	0.0084	**2.2**	912.0	820.0	92.0	3.3

(continued)

No.	Chemical Composition (unit: mass %, the balance consisting of Fe and impurities)													Ti/C	TS (MPa)	YS (MPa)	TS-YS (MPa)	hardness variation (HRC)
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Ti	V	Al	N					
72	0.019	0.23	0.42	0.017	0.0009	-	11.97	5.49	1.96	0.072	0.06	0.031	0.0072	**<u>3.8</u>**	905.0	817.0	88.0	3.2
73	0.017	0.22	0.40	0.017	0.0007	-	12.08	5.48	1.95	0.084	0.06	0.028	0.0075	**<u>4.9</u>**	897.0	848.0	49.0	2.6

[0053] Then, quenching and tempering was carried out so that the 0.6% total elongation yield stress of each of the manufactured seamless steel pipes was within the range from 758 MPa to 862 MPa. More specifically, the quenching temperature was 910°C and the tempering temperature was adjusted in the range from 560°C to 630°C.

[0054] After the quenching and tempering was carried out, the 0.6% total elongation yield stress (YS) and the tensile stress (TS) of each of the seamless steel pipes were measured. A round rod specimen (according to the ASTM A370 standard) was sampled from each of the seamless steel pipes along the axial direction and the parallel part of the specimen had a length of 25.4 mm and a sectional diameter of 6.35 mm along the axial direction of the seamless steel pipe. The sampled round rod specimens were subjected to tensile tests at room temperatures and measured for the 0.6% total elongation yield stress YS (MPa) and the tensile stress TS (MPa) according to the ASTM standard. After the measurement, TS-YS was obtained for each of the specimens with the test numbers.

[0055] The hardness variation of each of the seamless steel pipes was obtained. More specifically, each of the seamless steel pipes was cut in the transverse direction in the center. In a cross section of the cut seamless steel pipe as shown in Fig. 2, the Rockwell hardness C scale (HRC) was measured at the thick center parts P1 to P4 at intervals of 90° in the circumferential direction. Among the four measured Rockwell hardness values, the maximum value was represented by Hmax and the minimum value by Hmin. Using the thus obtained Hmax and Hmin, the hardness variation (HRC) was obtained from Expression (2).

Result of Examination

[0056] The examination result is given in Table 1. In the table, "Ti/C" is the ratio of the Ti content (% by mass) to the C content (% by mass) for each of the specimens with the test numbers. In the table, "TS" represents the tensile stress (MPa) of each of the specimens with the test numbers, and "YS" represents the 0.6% total elongation yield stress (MPa). In the table, "TS-YS" represents the value (MPa) obtained by subtracting the 0.6% total elongation yield stress from the tensile stress. In the table, the "hardness variation" represents hardness variation (HRC) obtained by Expression (2). Note that the underlined numerical values are outside the range defined by the invention.

[0057] With reference to Table 1, the 0.6% total elongation yield stress (YS) was in the range from 758 MPa to 862 MPa.

[0058] The seamless steel pipes with Nos. 1 to 49 had chemical compositions within the range defined by the invention, and their Ti/Ci values satisfied Expression (1). Therefore, TS-YS was not less than 20.7 MPa and the hardness variation (HRC) was less than 2.5 for any of the seamless steel pipes.

[0059] On the other hand, the seamless steel pipes with Nos. 50 and 51 had chemical compositions within the range defined by the invention, but their Ti/C values did not satisfy Expression (1) or Ti/C exceeded 10.1 for each of the pipes. Therefore, TS-YS was less than 20.7 MPa.

[0060] The C contents of the seamless steel pipes with Nos. 52 to 69 were all less than the lower limit for the C content defined by the invention. Therefore, TS-YS was less than 20.7 MPa for any of the pipes.

[0061] The seamless steel pipes with Nos. 70 to 73 had chemical compositions within the range defined by the invention but their Ti/C values were all less than 6.0. Therefore, the hardness variation was not less than 2.5.

[0062] The seamless steel pipes with Nos. 1 to 49 and 70 to 73 in Table 1 were subjected to SSC tests and appreciated for their SSC resistance. More specifically, a tensile test specimen with a parallel part having a diameter of 6.3 mm and a length of 25.4 mm was produced from each of the seamless steel pipes. Using the produced tensile test specimens, proof ring tests were carried out according to the NACE TM0177-96 Method A. At the time, the specimens were immersed for 720 hours in a 20% NaCl aqueous solution saturated with '0.03 atm H_2S (CO_2bal.). The pH of the NaCl aqueous solution was 4.5 and the temperature of the aqueous solution was kept at 25°C during the tests. After the tests, the specimens were examined for cracks by visual inspection.

[0063] According to the test result, no crack was generated in any of the tensile test specimens with Nos. 1 to 49. On the other hand, cracks were discovered in the tensile test specimens with Nos. 70 to 73.

[0064] Although the embodiment of the present invention has been described, the same is by way of illustration and example only and is not to be taken by way of limitation. The invention may be embodied in various modified forms without departing from the spirit and scope of the invention.

INDUSTRIAL APPLICABILITY

[0065] Martensitic stainless steel according to the invention is widely applicable as steel products for use in a corroding environment containing a corroding substance such as hydrogen sulfide, carbon dioxide gas, and chlorine ions. More specifically, the steel is suitably used for steel products for use in a production facility for oil or natural gas, a carbon dioxide removing device, and geothermal power generation installment. The steel is particularly suitably used as an oil country tubular good used in an oil well and a gas well.

Claims

1. Martensitic stainless steel, comprising, in percent by mass, 0.010% to 0.030% C, 0.30% to 0.60% Mn, at most 0.040% P, at most 0.0100% S, 10.00% to 15.00% Cr, 2.50% to 8.00% Ni, 1.00% to 5.00% Mo, 0.050% to 0.250% Ti, at most 0.25% V, at most 0.07% N, and at least one of at most 0.50% Si and at most 0.10% Al, the balance consisting of Fe and impurities, said martensitic stainless steel satisfying Expression (1) and having a yield stress in the range from 758 MPa to 862 MPa.

$$6.0 \leq Ti/C \leq 10.1 \quad \ldots (1)$$

where the symbols of the elements represent the contents of the elements in percent by mass.

2. The martensitic stainless steel according to claim 1, further comprising at least one of at most 0.25% Nb and at most 0.25% Zr instead of part of said Fe.

3. The martensitic stainless steel according to claim 1, comprising at most 1.00% Cu instead of part of said Fe.

4. The martensitic stainless steel according to claim 2, comprising at most 1.00% Cu instead of part of said Fe.

5. The martensitic stainless steel according to any one of claims 1 to 4, comprising at least one of at most 0.005% Ca, at most 0.005% Mg, at most 0.005% La, and at most 0.005% Ce instead of part of said Fe.

FIG.1

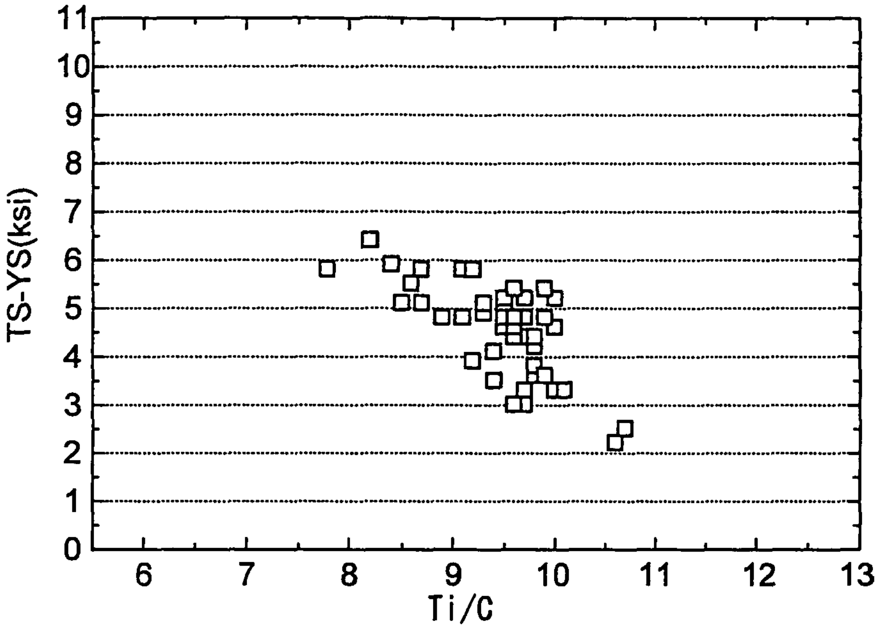
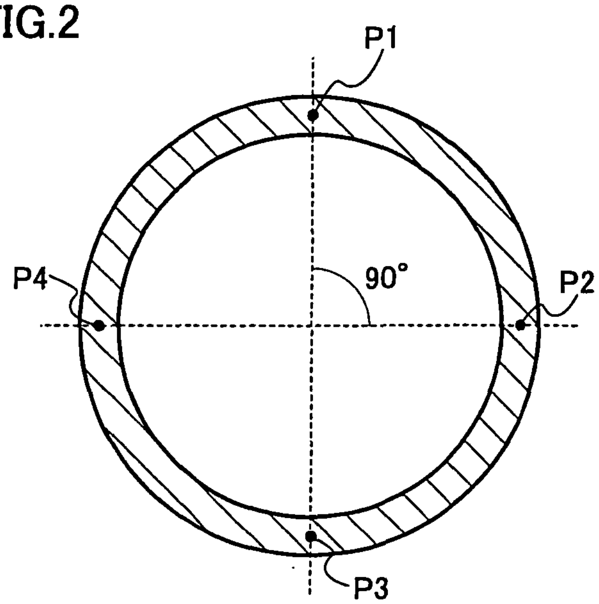


FIG.2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/066194

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/50*(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

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	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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.
Y	JP 2003-3243 A (Sumitomo Metal Industries, Ltd.), 08 January, 2003 (08.01.03), Invention examples 7, 9 (Family: none)	1-5
Y	JP 2000-192203 A (Sumitomo Metal Industries, Ltd.), 11 July, 2000 (11.07.00), Table 3; kind of steel No.9 (Family: none)	1-5
Y	JP 10-130785 A (Sumitomo Metal Industries, Ltd.), 19 May, 1998 (19.05.98), Invention example 3 (Family: none)	1-5

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 November, 2007 (12.11.07)	20 November, 2007 (20.11.07)

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/JP2007/066194

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2006-144069 A (Sumitomo Metal Industries, Ltd.), 08 June, 2006 (08.06.06), Claims & EP 1826285 A1 & WO 2006/54430 A1	1-5
A	JP 5-287455 A (Sumitomo Metal Industries, Ltd.), 02 November, 1993 (02.11.93), Table 1 & EP 565117 A1 & US 5383983 A	1-5
A	JP 2003-129190 A (Sumitomo Metal Industries, Ltd.), 08 May, 2003 (08.05.03), Kind of steel L & EP 1446512 A1 & US 2003/217789 A1 & WO 03/35921 A1	1-5
A	WO 2004/01082 A1 (JFE Steel Corp.), 31 December, 2003 (31.12.03), Table 3 & EP 1514950 A1 & US 2004/238079 A1	1-5

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- JP 5287455 A **[0005]**