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

(11) EP 1 826 285 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
29.08.2007 Bulletin 2007/35

(21) Application number: **05799225.7**

(22) Date of filing: **26.10.2005**

(51) Int Cl.:
C22C 38/00 $^{(2006.01)}$ ***C21D 6/00*** $^{(2006.01)}$
C22C 38/58 $^{(2006.01)}$

(86) International application number:
PCT/JP2005/019685

(87) International publication number:
WO 2006/054430 (26.05.2006 Gazette 2006/21)

(84) Designated Contracting States:
DE FR

(30) Priority: **19.11.2004 JP 2004335241**

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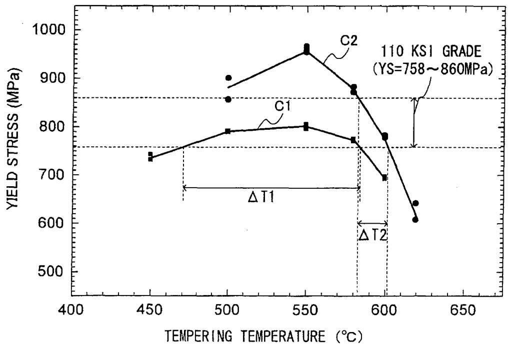
(54) MARTENSITIC STAINLESS STEEL

(57) Martensitic stainless steel according to the invention contains, by mass, 0.001% to 0.01% C, at most 0.5% Si, 0.1% to 3.0% Mn, at most 0.04% P, at most 0.01% S, 10% to 15% Cr, 4% to 8% Ni, 2.8% to 5.0% Mo, 0.001% to 0.10% Al, at most 0.07% N, 0% to 0.25% Ti, 0% to 0.25% V, 0% to 0.25% Nb, 0% to 0.25% Zr, 0% to 1.0% Cu, 0% to 0.005% Ca, 0% to 0.005% Mg, 0% to 0.005% La, and 0% to 0.005% Ce, with the balance being Fe and impurities, and the steel satisfies Expressions (1) and (2) and has a yield stress in the range from 758 MPa to 860 MPa. In this way, in the martensitic stainless steel according to the invention, the tempering temperature range at which a yield stress in the range from 758 MPa to 860 MPa can be obtained is increased,

$$922.6 - 554.5C - 50.9Mn + 2944.8P + 1.056Cr - 81.1Ni + 95.8Mo - 125.1Ti - 1584.9Al - 376.1N \geq 600 \quad \ldots(1)$$

$$30C + 0.5Mn + Ni + 0.5Cu - 1.5Si - Cr - Mo + 7.9 \geq 0 \quad \ldots(2)$$

FIG.2



EP 1 826 285 A1

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to martensitic stainless steel, and more specifically to martensitic stainless steel for use in a corrosive environment including corrosive substances such as hydrogen sulfide, carbon dioxide gas, and chloride ions.

BACKGROUND ART

[0002] As deeper oil wells and gas wells have come to be dug, there has been a demand for stronger and tougher martensitic stainless steel used as a steel material for oil well such as oil country tubular goods. Martensitic stainless steel having a yield stress (0.2% proof stress) in the range from 758 MPa to 860 MPa (hereinafter referred to as "110 ksi grade") and martensitic stainless steel having a strength equal to or higher than the 110 ksi grade have been developed.

[0003] Martensitic stainless steel for oil well must have high corrosion resistance such as SCC (Stress Corrosion Cracking) resistance and SSC (Sulfide Stress Cracking) resistance. This is because oil wells and gas wells exist in corrosive environments that include corrosive substances such as hydrogen sulfide, carbon dioxide gas, and cloride ions. More specifically, martensitic stainless steel for use in oil wells must have high strength, high toughness, and high corrosion resistance.

[0004] Martensitic stainless steel having high strength and high corrosion resistance is disclosed by JP 2003-3243 A. The disclosed martensitic stainless steel contains at least 1.5% by mass of Mo and allows higher SSC resistance than conventional martensitic stainless steel to be obtained.

[0005] If the Mo content is high, the tempering temperature range that allows the 110 ksi grade strength to be obtained (hereinafter referred to as "tempering temperature range") is very small. Fig. 1 shows the relation between the yield stress of martensitic stainless steel with a high Mo content (hereinafter referred to as "high Mo martensitic stainless steel) and the tempering temperature. The high Mo martensitic stainless steel in Fig. 1 contains, by mass, 0.016% C, 11.8% Cr, 7.2% Ni, and 2.9% Mo, with the balance being Fe and impurities. With reference to Fig. 1, the gradient of the tempering temperature curve C10 in the yield stress range from 758 MPa to 860 MPa is large. Therefore, the tempering temperature must be about in the range from 580˚C to 600˚C in order to obtain the 110 ksi grade strength for the high Mo martensitic stainless steel. More specifically, the tempering temperature range ΔT that allows the 110 ksi grade strength to be obtained is very small.

[0006] If the tempering temperature range ΔT is small, the productivity is reduced. In general, several hundred tons of such high Mo martensitic stainless steel is successively produced. In this case, the high Mo martensitic stainless steel is made by a plurality of heats (molten steel produced by a single steel making process) and the chemical compositions of the heats are not completely the same and slightly vary among them. If the tempering temperature range ΔT is small, the tempering temperature must be changed every time the chemical composition changes in order to obtain the 110 ksi grade strength for the steel. In short, in order to obtain the 110 ksi grade strength, the tempering temperature must be changed for each of the heats. The necessity of changing the tempering temperature setting in this manner lowers the productivity.

[0007] Note that International Publication No. WO 2004/57050 is a patent document related to the invention.

DISCLOSURE OF THE INVENTION

[0008] It is an object of the invention to provide martensitic stainless steel having a large tempering temperature range that allows a yield stress in the range from 758 MPa to 860 MPa to be obtained.

[0009] The inventor conducted various experiments and examinations and has obtained the following findings.

(A) If the martensitic stainless steel has such a chemical composition that the transformation point A_{c1} of the steel is high, the tempering temperature range that allows the yield stress to be from 758 MPa to 860 MPa increases. If the transformation point A_{c1} is lower, austenite forms during high temperature tempering process, which reduces the strength.

(B) In addition to the increase in the transformation point A_{c1}, the C content is reduced. In this way, the tempering temperature range that allows the yield stress to be from 758 MPa to 860 MPa even more increases. This is because as the C content is higher, the gradient of the tempering temperature curve in the yield stress range of 758 MPa to 860 MPa increases.

(C) If the C content is lowered, δ ferrite is more likely to be generated, which affects the strength and toughness of the steel. The 110 ksi grade martensitic stainless steel for use in environments where the atmospheric temperature is less than 0˚C must have both high strength and high toughness. If the steel has a composition that allows the structure of the steel to become martensitic even though the transformation point A_{c1} is raised and the C content is lowered, δ ferrite can be prevented from forming and the toughness can be prevented from being lowered while the 110 ksi grade strength is maintained.

[0010] As a result of consideration based on these findings, it was found that if the C content is 0.01% or less, and the following Expressions (1) and (2) are satisfied, the tempering temperature range that allows the yield stress to be from 758 MPa to 860 MPa can be larger than conventional cases.

$$922.6 - 554.5C - 50.9Mn + 2944.8P + 1.056Cr - 81.1Ni + 95.8Mo - 125.1Ti - 1584.9Al - 3\ 76.1N \geq 600 \quad ...(1)$$

$$30C + 0.5Mn + Ni + 0.5Cu - 1.5Si - Cr - Mo + 7.9 \geq 0 \quad ...(2)$$

where the contents of the elements in percentage by mass are substituted for the characters representing the elements.

[0011] The left side of Expression (1) (hereinafter the left side of Expression (1) = F1) is an expression used to estimate the A_{c1} transformation point of the martensitic stainless steel according to the invention. As described above, if the A_{c1} transformation point is high, retained austenite can be prevented from being precipitated during tempering process, so that the yield stress can be prevented from being abruptly lowered. Stated differently, the gradient of the tempering temperature curve in the yield stress range from 758 MPa to 860 MPa can be small.

[0012] Note that F1 ≥ 600 because the tempering process is carried out at 600˚C or less. If the tempering temperature is set to 600˚C or more, microscope carbide or intermetallic compounds in the steel become coarse, and this rather reduces the strength and toughness. Since the tempering temperature is 600˚C or less, it is only necessary that F1 be 600˚C or more.

[0013] Expression (2) is an expression used to make the steel after tempering martensitic. If the contents of C, Mn, and Ni that are austenite forming elements and the contents of Si, Cr, and Mo that are ferrite forming elements satisfy the relation defined by Expression (2), the structure becomes martensitic, and δ ferrite can be prevented from being produced. Therefore, the strength can be prevented from being lowered, and high toughness can be maintained.

[0014] Note that if the martensitic stainless steel does not contain optional elements Ti and Cu, the "Ti" and "Cu" in Expressions (1) and (2) are both "0."

[0015] If these expressions are satisfied, a tempering temperature curve as curve C1 shown in Fig. 2 can be obtained, and the gradient of the tempering temperature curve in the yield stress range from 758 MPa to 860 MPa can be smaller than that in the conventional cases. Therefore, the tempering temperature range ΔT1 that allows the yield stress to be in the range from 758 MPa to 860 MPa is larger than the tempering temperature range ΔT2 of the conventional tempering temperature curve C2. Therefore, the decrease in the productivity because of temperature setting changes during operation can be prevented.

[0016] The inventor completed the following invention based on the above-described findings.

[0017] Martensitic stainless steel according to the invention contains, by mass, 0.001% to 0.01% C, at most 0.5% Si, 0.1% to 3.0% Mn, at most 0.04% P, at most 0.01% S, 10% to 15% Cr, 4% to 8% Ni, 2.8% to 5.0% Mo, 0.001% to 0.10% Al, at most 0.07% N, 0% to 0.25% Ti, 0% to 0.25% V, 0% to 0.25% Nb, 0% to 0.25% Zr, 0% to 1.0% Cu, 0% to 0.005% Ca, 0% to 0.005% Mg, 0% to 0.005% La, and 0% to 0.005% Ce, with the balance being Fe and impurities, the steel satisfies Expressions (1) and (2) and has a yield stress in the range from 758 MPa to 860 MPa.

$$922.6 - 554.5C - 50.9Mn + 2944.8P + 1.056Cr - 81.1Ni + 95.8Mo - 125.1Ti - 1584.9Al - 376.1N \geq 600 \quad ...(1)$$

$$30C + 0.5Mn + Ni + 0.5Cu - 1.5Si - Cr - Mo + 7.9 \geq 0 \quad ...(2)$$

where the contents of the elements in percentage by mass are substituted for the characters representing the elements.

[0018] If the optional elements Ti and Cu are not contained, the "Ti" and "Cu" in Expressions (1) and (2) are both "0." The 0.2 % proof stress corresponds to the yield stress.

[0019] In the martensitic stainless steel according to the invention, the gradient of the tempering temperature curve can be reduced by setting the C content to 0.01% or less. In addition, the A_{C1} transformation point can be higher than the conventional examples if Expression (1) is satisfied. Therefore, the gradient of the tempering temperature curve is reduced, and the tempering temperature range that allows the yield stress to be in the range from 758 MPa to 860 MPa is increased as compared to the conventional examples.
[0020] The strength can be prevented from being less than 110 ksi as Expression (2) is satisfied, and the high toughness can be maintained. Since the Mo content is high, high corrosion resistance is obtained.
[0021] The martensitic stainless steel according to the invention preferably contains at least one of 0.005% to 0.25% Ti, 0.005% to 0.25% V, 0.005% to 0.25% Nb, and 0.005% to 0.25% Zr.
[0022] The martensitic stainless steel according to the invention preferably contains 0.05% to 1.0% Cu.
[0023] The martensitic stainless steel according to the invention preferably contains at least one of 0.0002% to 0.005% Ca, 0.0002% to 0.005% Mg, 0.0002% to 0.005% La, and 0.0002% to 0.005% Ce.
[0024] In this way, the hot workability of the martensitic stainless steel is improved. Note that these elements if contained do not affect the effects of the invention described above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025]

Fig. 1 shows the relation between the yield stress of a conventional high Mo martensitic stainless steel and the tempering temperature; and
Fig. 2 shows the relation between the yield stresses of sample materials 1 and 14 according to an embodiment of the invention and the tempering temperature.

BEST MODE FOR CARRYING OUT THE INVENTION

[0026] Now, an embodiment of the invention will be described in detail in conjunction with the accompanying drawings, in which the same or corresponding portions are denoted by the same reference characters, and their description will not be repeated.

1. Chemical Composition

[0027] Martensitic stainless steel according to an embodiment of the invention has the following composition. Hereinafter, "%" related to each element refers to "% by mass."
C: 0.001% to 0.01%
[0028] If the C content is excessive, the gradient of the tempering temperature curve becomes steep, and steel having a yield stress in the range from 758 MPa to 860 MPa cannot stably be produced. The C content should be limited to a small value. If the C content is less than 0.001%, on the other hand, the manufacturing cost increases. Therefore, the C content is in the range from 0.001% to 0.01%, preferably from 0.001% to 0.008%.
Si: 0.5% or less
[0029] Silicon is effectively applied as a deoxidizing agent. On the other hand, Si hardens steel and therefore an excessive Si content degrades the toughness and workability of the steel. Silicon is a ferrite forming element and therefore prevents the steel from becoming martensitic. Therefore, the Si content is not more than 0.5%, preferably 0.3% or less.
Mn: 0.1% to 3.0%
[0030] Manganese contributes to improvement in the hot workability of the steel. Furthermore, Mn is an austenite forming element and contributes to formation of a martensitic structure. However, an excessive Mn content degrades the toughness. Therefore, the Mn content is in the range from 0.1% to 3.0%, preferably from 0.3% to 1.0%.
P: 0.04% or less
[0031] Phosphorus is an impurity and causes SSC to be generated, and therefore the P content is limited as much as possible. The P content is 0.04% or less.
S: 0.01% or less
[0032] Sulfur is an impurity and lowers the hot workability. Therefore, the S content is limited as much as possible. The S content is 0.01% or less.
Cr: 10% to 15%
[0033] Chromium contributes to improvement in corrosion resistance in a wet carbon dioxide gas environment. On the other hand, Cr is a ferrite forming element and an excessive Cr content makes it difficult to form tempered martensite, which lowers the strength and the toughness. Therefore, the Cr content is in the range from 10% to 15%, preferably from 11% to 14%.

Ni: 4% to 8%

[0034] Nickel is an austenite forming element and necessary for the structure after tempering to become martensitic. If the Ni content is too small, the structure after the tempering contains much ferrite. On the other hand, an excessive Ni content causes the structure after the tempering to have much austenite. Therefore, the Ni content is in the range from 4% to 8%, preferably from 4% to 7%.

Mo: 2.8% to 5.0%

[0035] Molybdenum is a critical element that contributes to improvement in SSC resistance and strength. In the martensitic stainless steel according to the embodiment, the lower limit for the Mo content to allow high SSC resistance to be obtained is 2.8%. Molybdenum is a ferrite forming element and excessive addition of the element prevents the structure from becoming martensitic. The upper limit for the Mo content is therefore 5.0%. The Mo content is preferably in the range from 2.8% to 4.0%.

Al: 0.001% to 0.10%

[0036] Aluminum is effectively applicable as a deoxidizing agent. On the other hand, an excessive Al content causes many inclusions to be generated, and the corrosion resistance is lowered. Therefore, the Al content is from 0.001% to 0.10%, preferably from 0.001% to 0.06%.

N: 0.07% or less

[0037] Nitrogen forms a nitride and lowers the corrosion resistance. Therefore, the N content is 0.07% or less.

[0038] Note that the balance consists of Fe and impurities. The impurities are mixed in the manufacturing process for various reasons.

[0039] The martensitic stainless steel according to the embodiment further contains at least one of Ti, V, Nb, and Zr if required.

Ti: 0% to 0.25%
V: 0% to 0.25%
Nb: 0% to 0.25%
Zr: 0% to 0.25%

Note that Ti, V, Nb, and Zr are optional elements. These elements fix C and reduce variations in strength. On the other hand, an excessive content of any of these elements prevents the structure after tempering from becoming martensitic. Therefore, the content of each of these elements is set to the range from 0% to 0.25%, preferably from 0.005% to 0.25%, more preferably from 0.005% to 0.20%.

[0040] The martensitic stainless steel according to the embodiment contains Cu if required.

Cu: 0% to 1.0%

[0041] Copper is an optional element and an austenite forming element as with Ni suitable for making the structure after tempering martensitic. On the other hand, an excessive Cu content lowers the hot workability. Therefore, the Cu content is from 0% to 1.0%, preferably from 0.05% to 1.0%.

[0042] The martensitic stainless steel according to the embodiment further contains at least one of Ca, Mg, La, and Ce if required.

Ca: 0% to 0.005%
Mg: 0% to 0.005%
La: 0% to 0.005%
Ce: 0% to 0.005%

[0043] Note that Ca, Mg, La, and Ce are optional elements. These optional elements contribute to improvement in hot workability. On the other hand, excessive contents of these elements cause coarse oxides to be generated, which lowers the corrosion resistance. Therefore, the contents of these elements are all in the range from 0% to 0.005%, preferably from 0.0002% to 0.005%. Among these elements, Ca and La are elements that particularly contribute to improvement in hot workability.

2. Manufacturing Method

[0044] Steel having the above-described chemical composition is melted and refined by well-known refining process. Then, the molten steel is formed into a continuos casting material by a continuos casting method. The continuos casting material is for example a slab, bloom, or billet. Alternatively, the molten steel may be made into ingots by an ingot casting method.

[0045] The slab, bloom, or ingot is formed into billets by hot working. At the time, the billets may be formed by hot rolling or by hot forging.

[0046] The billets produced by the continuos casting or hot working are subjected to further hot working and formed into oil country tubular goods. For example, Mannesmann process may be performed as the hot working. Alternatively, Ugine-Sejournet hot extrusion process may be employed as the hot working, while a forged pipe making method such as Ehrhardt method may be employed. The oil country tubular good after the hot working is subjected to quenching process and tempering process. The quenching process is carried out according to a well-known method. The quenching temperature is for example from 900°C to 950°C, while other temperature ranges may be employed.

[0047] In the tempering process, the lower limit for the tempering temperature is preferably 500°C. If the tempering temperature is too high, retained austenite is precipitated, so that the yield stress cannot be in the range from 758 MPa to 860 MPa. Therefore, the upper limit for the tempering temperature is preferably 600°C.

[0048] The martensitic stainless steel according to the embodiment of the invention satisfies the following Expressions (1) and (2):

$$922.6 - 554.5C - 50.9Mn + 2944.8P + 1.056Cr - 81.1Ni + 95.8Mo - 125.1Ti - 1584.9Al - 376.1N \geq 600 \quad \ldots(1)$$

$$30C + 0.5Mn + Ni + 0.5Cu - 1.5Si - Cr - Mo + 7.9 \geq 0 \quad \ldots(2)$$

[0049] If Expression (1) is satisfied, the A_{c1} transformation point is high, and therefore the gradient of the tempering curve in the yield stress range from 758 MPa to 860 MPa can be reduced. If Expression (2) is satisfied, the structure can become martensitic in an accelerated manner. Therefore, if both Expressions (1) and (2) are satisfied, the tempering temperature range that allows the yield stress to be in the range from 758 MPa to 860 MPa can be larger than those of the conventional examples. Therefore, a decrease in productivity based on changes in the temperature setting during operation can be reduced.

[0050] High toughness necessary for steel for use in an oil well can be obtained by satisfying Expression (2).

[0051] Note that if the martensitic stainless steel does not contain Ti and Cu as optional elements, "Ti" and "Cu" in Expressions (1) and (2) are "zero."

[0052] In the above-described example, the martensitic stainless steel is made into a steel pipe, but the steel may be formed into a steel plate.

Example 1

[0053] Sample materials having chemical compositions given in Table 1 were produced and each examined for the tempering temperature range that allows the yield stress to be in the range from 758 MPa to 860 MPa. The sample materials were also examined for toughness and corrosion resistance.

Table 1

	No	Chemical Compositions (unit: % by mass, the balance is Fe and impurities)																			F1	F2
	.	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	sol.AL	N	Nb	V	Ti	Zr	Ca	Mg	La	Ce		
Inventive Steel	1	0.006	0.14	0.46	0.012	0.0008	0.02	11.79	6.79	2.91	0.020	0.0053	0.002	0.11	0.075	0	0	0	0	0	628.7	0.20
	2	0.006	0.14	0.47	0.012	0.0008	0.02	11.75	6.78	2.90	0.027	0.0030	0.002	0.06	0.081	0	0	0	0	0	617.0	0.25
	3	0.007	0.17	0.40	0.014	0.0011	0.02	11.88	6.90	2.95	0.029	0.0075	0.002	0.05	0	0	0.0007	0	0	0	626.4	0.14
	4	0.006	0.15	0.47	0.012	0.0008	0.26	11.79	6.72	2.91	0.025	0.0038	0.002	0.06	0.079	0	0	0	0	0	626.0	0.24
	5	0.006	0.20	0.46	0.011	0.0010	0.03	11.88	7.01	3.12	0.035	0.0053	0	0.06	0.093	0	0	0	0	0	602.1	0.03
	6	0.007	0.16	0.47	0.012	0.0009	0.93	11.78	6.37	2.90	0.025	0.0037	0.002	0.06	0.079	0.0003	0	0	0	0	652.9	0.26
	7	0.008	0.14	0.30	0.017	0.0010	0	11.00	7.90	4.80	0.035	0.0060	0	0.04	0.100	0	0	0.0006	0	0	713.5	0.18
	8	0.004	0.15	0.45	0.011	0.0010	0	11.90	7.98	3.80	0.025	0.0099	0	0.05	0.088	0	0	0	0	0	604.9	0.30
	9	0.006	0.16	0.46	0.012	0.0008	0.03	11.90	6.79	2.91	0.020	0.0501	0.002	0.11	0.075	0	0	0	0.0009	0	611.9	0.06
	10	0.006	0.14	0.46	0.012	0.0010	0.02	11.70	6.56	2.91	0.020	0.0450	0	0.04	0.082	0	0	0	0	0.0008	631.4	0.06
	11	0.007	0.14	0.35	0.012	0.0008	0	11.91	6.81	2.94	0.020	0.0065	0	0	0	0	0	0	0	0	644.0	0.04
Comparative Steel	12	0.008	0.14	0.46	0.013	0.0010	0.02	11.84	7.21	2.91	0.025	0.0061	0.002	0.06	0.084	0	0.0006	0	0	0	587.2	0.63
	13	0.007	0.20	0.45	0.010	0.0010	0.02	11.96	6.93	2.89	0.028	0.0051	0	0.06	0.089	0	0	0	0	0	595.3	0.12
	14	0.016	0.17	0.71	0.015	0.0010	0.03	11.80	7.20	2.92	0.030	0.0055	0.004	0.06	0.001	0	0	0	0	0	580.3	0.98
	15	0.013	0.22	0.44	0.011	0.0010	0.02	12.55	6.12	3.08	0.026	0.0050	0	0.06	0.088	0	0	0	0	0	683.3	-1.32
	16	0.013	0.15	0.71	0.012	0.0009	0.26	11.83	6.54	2.92	0.022	0.0053	0.002	0.06	0.079	0	0	0	0	0	629.7	0.34

$F1=922.6 - 554.5C - 50.9Mn + 2944.8P + 1.056Cr - 81.1Ni + 95.8Mo - 125.1Ti - 1584.9Al - 376.1N$

$F2=30C + 0.5Mn + Ni + 0.5Cu - 1.5Si - Cr - Mo + 7.9$

[0054] Steel having the chemical compositions given in Table 1 were melted. As shown in Table 1, the chemical compositions of the sample materials 1 to 11 were within the range of the chemical compositions according to the invention.

[0055] The left sides of Expressions (1) and (2) are represented as F1 and F2, respectively, and F1 and F2 were obtained for each of the sample materials. For the sample materials without Ti, "0" is entered in the box for "Ti" in F1 and for those without Cu, "0" is entered in the box for "Cu" in F2.

[0056] As for all the sample materials 1 to 11, F1 and F2 were both within the range according to the invention. More specifically, F1 was 600 or more and F2 was zero or more.

[0057] As for the sample materials 12 and 13, while the chemical compositions were within the range according to the invention, F1 was less than 600. As for the sample materials 14 to 16, the C content exceeded the upper limit according to the invention. Furthermore, as for the sample material 14, F1 was less than 600, and as for the sample material 15, F2 was less than zero.

[0058] The molten steel for the sample materials 1 to 16 were cast into continuous casting materials. The produced continuous casting materials were subjected to hot forging and hot rolling and made into a plurality of steel plates each having a thickness of 15 mm, a width of 120 mm, and a length of 1000 mm. The steel plates after the hot forging and hot rolling were cooled by air to room temperatures. Using the obtained steel plates, the following tests were conducted.

1. Tempering Temperature Range

[0059] To start with, the obtained plurality of steel plates were quenched. At the time, the quenching temperature was 910˚C. Then, the quenched steel plates were subjected to tempering. At the time, the tempering temperature was varied within the temperature range from 450˚C to 650˚C. The steel plates after the tempering at various temperatures were subjected to tensile tests. More specifically, a round-bar test piece having a diameter of 6.35 mm and a length of 25.4 mm for the parallel part was produced from each of the steel plates. Using the produced round-bar test pieces, tensile tests were conducted at room temperatures based on JIS Z2241 and the yield stresses were obtained. After the tensile tests, the tempering temperature range ΔT in which the yield stress was in the range from 758 MPa to 860 MPa was obtained for each of the sample materials. Note that the 0.2% proof stress was set as the yield stress.

[0060] The tempering temperature ranges of the sample materials that allow the yield stress to be in the range from 758 MPa to 860 MPa are given in Table 2.

Table 2

	No.	ΔT(˚C)
Inventive Steel	1	110
	2	80
	3	100
	4	110
	5	45
	6	80
	7	50
	8	55
	9	40
	10	110
	11	100
	12	10
Comparative Steel	13	10
	14	20
	15	25
	16	20

[0061] In Table 2, ΔT represents the difference between the maximum temperature and the minimum temperature among the tempering temperatures at which the yield stresses of the sample materials are from 758 MPa to 860 MPa. The unit is "˚C."

[0062] As shown in Table 2, ΔT was 40˚C or more for each of the sample materials 1 to 11. Meanwhile, ΔT was less than 40˚C for the sample materials 12 and 13 because F1 was less than 600 for them. The sample material 14 had a high C content, F1 was less than 600, and therefore ΔT was less than 40˚C. The sample materials 15 and 16 each had a high C content, and therefore ΔT was less than 40˚C.

[0063] Fig. 2 shows the relation between the tempering temperature and the yield stress in the sample materials 1 and 14. As shown in Fig. 2, the gradient of the tempering temperature curve C1 of the sample material 1 whose F1 was 600 or more was small in the yield stress range of 758 MPa to 860 MPa and the tempering temperature range ΔT1 was 110˚C. Meanwhile, for the sample material 14 whose F1 was less than 600, the gradient of the tempering temperature curve C2 was large in the yield stress range from 758 MPa to 860 MPa, and the tempering temperature range ΔT2 was as small as 20˚C.

2. Toughness

[0064] The toughness values of the sample materials are given in Table 3.

Table 3

	No.	F2	yield stress (MPa)	absorbed energy at -40˚C (J)
Inventive Steel	1	0.20	804.0	185
	2	0.25	782.0	182
	3	0.14	812.0	176
	4	0.24	805.0	185
	5	0.03	813.0	188
	6	0.26	838.0	187
	7	0.18	854.0	192
	8	0.30	808.0	190
	9	0.06	841.0	188
	10	0.06	807.0	190
	11	0.04	773.0	194
	12	0.63	848.0	160
Comparative Steel	13	0.12	815.0	165
	14	0.98	851.0	167
	15	-1.32	844.0	81
	16	0.34	841.0	171

[0065] The toughness tests were conducted as follows. The obtained steel plates were quenched at 910˚C and tempered so that the yield stresses become values given in Table 3. From each of the tempered steel plates, a V-notch test piece as wide as 10 mm according to JISZ2202 was produced.

[0066] The produced V-notch test pieces were subjected to Charpy impact tests according to JISZ2242 at -40˚C and examined for absorbed energy.

[0067] The unit of the absorbed energy in Table 3 is J. Since the F2 values of the sample materials 1 to 11 are all at least zero, the values of the absorbed energy exceeded 100 J, in other words, high toughness resulted. Meanwhile, the F2 value of the sample material 15 was less than zero, and therefore the absorbed energy was low.

3. Corrosion Resistance

[0068] Corrosion resistance in a wet carbon dioxide gas environment was evaluated by conducting carbon dioxide gas corrosion tests. A test piece having a width of 20 mm, a thickness of 3 mm, and a length of 50 mm was cut from each of steel plates quenched and tempered in the same conditions as the above toughness evaluation. The surface of each test piece was polished with No. 600 emery paper, then degreased, and dried.

[0069] The produced test pieces were immersed for 720 hours in a 25% NaCl aqueous solution in which CO_2 gas at 9.73 atm and H_2S at 0.014 atm were saturated. Note that the aqueous solution was kept at 165˚C during the tests.

[0070] After the tests, the test pieces were each examined for quantity loss caused by corrosion. More specifically, the corrosion loss was obtained as a value produced by subtracting the weight of a test piece after the test from the weight of the test piece before the test. The presence/absence of local corrosion at the surfaces of the test pieces was visually inspected. It was determined that the piece had high corrosion resistance in a wet carbon dioxide gas environment if the corrosion loss was less than 7.7 g and there was no local corrosion found.

[0071] The following SSC tests were conducted to examine SSC resistance in a wet hydrogen sulfide environment. Tensile test pieces each having a diameter of 6.3 mm and a length of 25.4 mm for the parallel part were cut from steel plates quenched and tempered in the same conditions as the above toughness evaluation. The produced tensile test pieces were subjected to proof ring tests based on NACE TM0177-96 Method A. At the time, the test pieces were immersed for 720 hours in a 20% NaCl aqueous solution in which H_2S (CO_2 bal.) at 0.03 atm was saturated. The pH of the NaCl aqueous solution was 4.5 and the temperature of the aqueous solution was kept at 25˚C. After the tests, the presence/absence of crackings was visually inspected.

[0072] The result of the corrosion resistance tests is given in Table 4.

Table 4

No.	carbon dioxide gas corrosion tests	SSC tests
1	○	○
2	○	○
3	○	○
4	○	○
5	○	○
6	○	○
7	○	○
8	○	○
9	○	○
10	○	○
11	O	O

[0073] In Table 4, "O " in the carbon dioxide gas corrosion tests indicates that the corrosion loss was less than 7.7 g and there was no local corrosion. In the SSC corrosion tests, "O " indicates that there was no cracking generated. The sample materials 1 to 11 each had high corrosion resistance.

[0074] Although the embodiment of the present invention has been described and illustrated in detail, it is clearly understood that 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 as required without departing from the spirit and scope of the invention.

INDUSTRIAL APPLICABILITY

[0075] The martensitic stainless steel according to the invention is applicable as a steel material for use in a corrosive environment including corrosive substances such as hydrogen sulfide, carbon dioxide gas, and chloride ions. The steel is particularly applicable to steel materials for production facilities, geothermal power generation facilities, and carbon dioxide gas removing facilities, and steel pipes used as oil country tubular goods in a wet hydrogen sulfide environment and a wet carbon dioxide gas environment such as oil wells or gas wells.

Claims

1. Martensitic stainless steel, comprising, by mass, 0.001% to 0.01% C, at most 0.5% Si, 0.1% to 3.0% Mn, at most 0.04% P, at most 0.01% S, 10% to 15% Cr, 4% to 8% Ni, 2.8% to 5.0% Mo, 0.001% to 0.10% Al, at most 0.07% N, 0% to 0.25% Ti, 0% to 0.25% V, 0% to 0.25% Nb, 0% to 0.25% Zr, 0% to 1.0% Cu, 0% to 0.005% Ca, 0% to 0.005% Mg, 0% to 0.005% La, and 0% to 0.005% Ce, the balance being Fe and impurities, said steel satisfying Expressions (1) and (2) and having a yield stress in the range from 758 MPa to 860 MPa.

$$922.6 - 554.5C - 50.9Mn + 2944.8P + 1.056Cr - 81.1Ni + 95.8Mo - 125.1Ti - 1584.9Al - 376.1N \geq 600 \quad \ldots(1)$$

$$30C + 0.5Mn + Ni + 0.5Cu - 1.5Si - Cr - Mo + 7.9 \geq 0 \quad \ldots(2)$$

where the contents of the elements in percentage by mass are substituted for the characters representing the elements.

2. The martensitic stainless steel according to claim 1, comprising at least one of 0.005% to 0.25% Ti, 0.005% to 0.25% V, 0.005% to 0.25% Nb, and 0.005% to 0.25% Zr.

3. The martensitic stainless steel according to claim 1, comprising 0.05% to 1.0% Cu.

4. The martensitic stainless steel according to claim 2, comprising 0.05% to 1.0% Cu.

5. The martensitic stainless steel according to any one of claims 1 to 4, comprising at least one of 0.0002% to 0.005% Ca, 0.0002% to 0.005% Mg, 0.0002% to 0.005% La, and 0.0002% to 0.005% Ce.

FIG.1

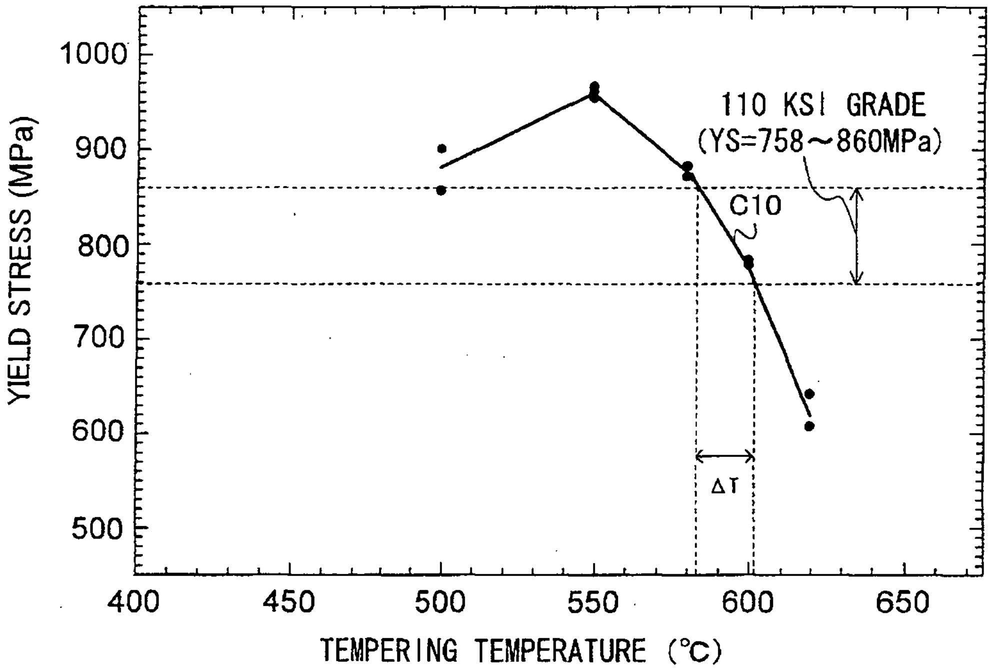
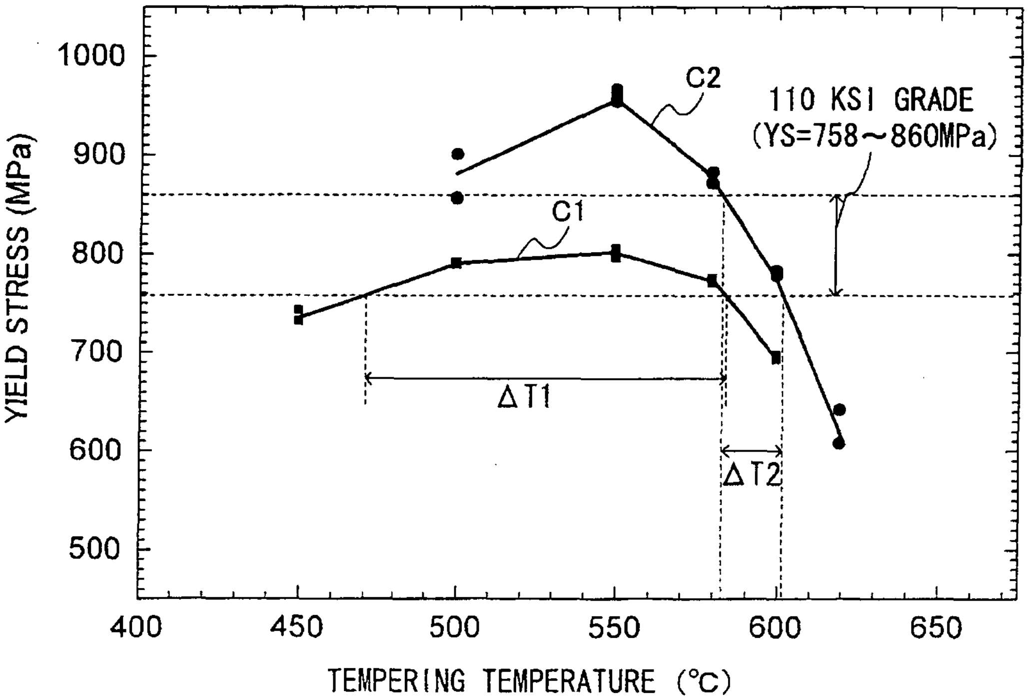

1000
900
800
700
600
500
YIELD STRESS (MPa)
400
450
500
550
600
650
TEMPERING TEMPERATURE (°C)
110 KSI GRADE
(YS=758~860MPa)
C10
ΔT

FIG.2


1000
900
800
700
600
500
YIELD STRESS (MPa)
400
450
500
550
600
650
TEMPERING TEMPERATURE (°C)
C2
110 KSI GRADE
(YS=758~860MPa)
C1
ΔT1
ΔT2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/019685

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01), *C21D6/00*(2006.01), *C22C38/58*(2006.01)

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(2006.01), *C21D6/00*(2006.01)

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	1996-2006
Kokai Jitsuyo Shinan Koho	1971-2006	Toroku Jitsuyo Shinan Koho	1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 5-156409 A (Nippon Steel Corp.), 22 June, 1993 (22.06.93), Full text (Family: none)	1-5
A	JP 3427387 B2 (Sumitomo Metal Industries, Ltd.), 14 July, 2003 (14.07.03), Table 1 (basic material No.M4) & EP 864663 A1 & US 6129999 A1 & WO 97/12072 A1	1-5
A	JP 2001-107198 A (Nippon Steel Corp.), 17 April, 2001 (17.04.01), Table 1; steel No.C (Family: none)	1-5

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

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search 23 January, 2006 (23.01.06)	Date of mailing of the international search report 31 January, 2006 (31.01.06)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2003003243 A **[0004]**
- WO 200457050 A **[0007]**