



(12) **EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

- (43) Date of publication: **12.10.2005 Bulletin 2005/41**
- (44) Application number: **03780915.9**
- (45) Date of filing: **18.12.2003**
- (51) Int Cl.7: **C22C 38/00, C22C 38/58, C21D 6/00**
- (86) International application number: **PCT/JP2003/016288**
- (87) International publication number: **WO 2004/057050 (08.07.2004 Gazette 2004/28)**

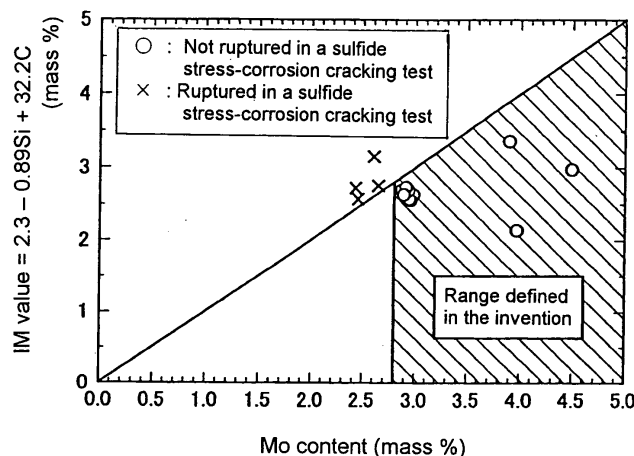
- (84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT RO SE SI SK TR**  
Designated Extension States:  
**AL LT LV MK**
- (30) Priority: **20.12.2002 JP 2002369595**
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(54) **HIGH-STRENGTH MARTENSITIC STAINLESS STEEL WITH EXCELLENT RESISTANCES TO CARBON DIOXIDE GAS CORROSION AND SULFIDE STRESS CORROSION CRACKING**

(57) The present invention provides a martensitic stainless steel in which specified elements in a steel composition are limited. The martensitic stainless steel can have high strength of 0.2 % proof stress of 860 MPa or more and excellent carbon dioxide gas corrosion resistance and sulfide stress-corrosion cracking resistance by limiting the steel composition of specified elements and defining Mo content in the steel by relation-

ships with IM values as well as by forming microstructure of the steel with main tempered martensite, carbide precipitated during tempering, and intermetallic compounds such as a Laves phase, a  $\sigma$  phase and the like. As a result the martensitic stainless steels of the present invention can be applied to practical steels, which can be widely used in oil well tubes and the like under environment including carbon dioxide gas, hydrogen sulfide, chlorine ions or two or more of them, in wide fields.

FIG.1



**Description**

## FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a steel material suitable for its use in severe corrosion environment containing corrosive materials such as carbon dioxide gas, hydrogen sulfide, chlorine ions and the like. Specifically, the present invention relates to a steel material for a seamless steel tube and a seam welded steel tube such as an electric resistance welding steel tube, a laser welding steel tube, a spiral welding tube or the like, which is used in applications for petroleum or natural gas production facilities, facilities for eliminating carbon dioxide gas, or for geo-thermal power generation, or for a tank for liquid containing carbon dioxide gas, especially to a steel material for oil well tubes for oil wells or gas wells.

## BACKGROUND ART

15 **[0002]** From the viewpoint of exhaustion of petroleum resources, which is expected in the near future, development of an oil well under severe environment that is an oil well in a deeper layer, of a sour gas field or the like, has often been performed. Thus, high strength and excellent corrosion resistance and sulfide stress corrosion cracking resistance are required for oil well steel tubes, which are used in such uses.

20 **[0003]** As a steel material for oil well tubes or the like, carbon steel or a low-alloy steel has been generally used. However, as the environment of the well becomes severe, steel which contains increased amount of alloying elements, has been used. For example, as oil wells for steel material which contain a large amount of carbon dioxide gas, 13 Cr series martensitic stainless steel such as typical SUS 420 and the like have been used.

25 **[0004]** However, although the SUS 420 steel has excellent corrosion resistance to carbon dioxide gas, it has poor corrosion resistance to hydrogen sulfide. Thus, the SUS 420 steel is liable to generate sulfide stress-corrosion cracking (SSCC) under the environment containing carbon dioxide gas and hydrogen sulfide simultaneously. Therefore various steel materials in place of the SUS 420 steel have been proposed.

30 **[0005]** Japanese Patent No. 2861024, Japanese Patent Application Publication No. 05-287455, and Japanese Patent Application Publication No. 07-62499 disclose steel having improved corrosion resistance by reducing carbon content of the SUS 420. However, such a low carbon-content steel described in these publications may not have the enough strength required for use in a deep well, that is proof stress of 860 MPa or more.

35 **[0006]** Alternatively, Japanese Patent Application Publication No. 2000-192196 discloses steel of a martensitic single phase structure containing Co: 0.5 - 7 % and Mo: 3.1 - 7 % having high strength and excellent sulfide stress-corrosion cracking resistance. The invention described in the publication is a steel containing Co in the above-mentioned range to suppress the generation of retained austenite during cooling so that the structure is made to be a martensitic single phase. However, since Co is an expensive element, it is desirable not to use.

## SUMMARY OF THE INVENTION

40 **[0007]** The present invention was made in consideration of the above-mentioned circumstances. The object of the present invention is to provide a martensitic stainless steel having sufficient strength to use for oil well tubes for a deep well, that is high strength of a proof stress of 860 MPa or more, and excellent carbon dioxide gas corrosion resistance and sulfide stress-corrosion cracking resistance whereby it can be used even under the environment containing carbon dioxide gas, hydrogen sulfide or chlorine ions or two or more of them. The symbols of the respective elements in the following expression show the content (mass %) of each element.

45 **[0008]** Accordingly, the gist of the present invention is high strength martensitic stainless steels described in the following (a) and (b).

(a) A high strength martensitic stainless steel excellent in carbon dioxide gas corrosion resistance and sulfide stress-corrosion cracking resistance and having 0.2 % proof stress of 860 MPa or more, characterized by including, by mass %, C: 0.005 - 0.04 %, Si: 0.5 % or less, Mn: 0.1 - 3.0 %, P: 0.04 % or less, S: 0.01 % or less, Cr: 10 - 15 %, Ni: 4.0 - 8 %, Mo: 2.8 - 5.0 %, Al: 0.001- 0.10 % and N: 0.07 % or less, and the balance Fe and impurities, and also characterized by satisfying the expression (1) given below wherein the microstructure mainly comprises tempered martensite, carbide precipitated during tempering, and intermetallic compounds such as Laves phase,  $\sigma$  phase and the like finely precipitated during tempering.

$$\text{Mo} \geq 2.3 - 0.89 \text{ Si} + 32.2 \text{ C} \quad (1)$$

wherein the symbols of the respective elements in the expression (1) show the content (mass %) of each element.

Further, the gist of the present invention is martensitic stainless steels containing at least one of alloying elements selected from at least one group consisting of the following a first group, a second group and a third group, in addition to the components described in the above mentioned (a). In this steel said expression (1) is also satisfied and the microstructure is the same as mentioned above.

First group .... Ti: 0.005 - 0.25 %, V: 0.005 - 0.25 %, Nb: 0.005 - 0.25 %, and Zr: 0.005 - 0.25 %.

Second group ... Cu: 0.05 - 1 %

Third group ... Ca: 0.0002 - 0.005 %, Mg: 0.0002 - 0.005 %, La: 0.0002 - 0.005 %, and Ce: 0.0002 - 0.005 %.

(b) A high strength martensitic stainless steel excellent in carbon dioxide gas corrosion resistance and sulfide stress-corrosion cracking resistance and having 0.2 % proof stress of 860 MPa or more, characterized by including compositions defined in any one of (a) and characterized in that steel, which satisfies the above mentioned expression (1), is subjected to tempering in which  $(20 + \log t)(T + 273)$  satisfies 13500 - 17700 when, after quenching the steel at a quenching temperature of 880 °C - 1000 °C, a range of a tempering temperature is set to 450 °C - 620 °C, a tempering temperature is set to T (°C) and tempering time is set to t (hour), whereby the microstructure of said steel mainly comprises tempered martensite, carbide precipitated during tempering, and intermetallic compounds such as a Laves phase, a  $\sigma$  phase and the like finely precipitated during tempering.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0009]** FIG. 1 is a view showing relationships between Mo contents of various types of steels tested in examples and the right side in the expression (1), that is " $2.3 - 0.89 \text{ Si} + 32.2 \text{ C}$ " (IM value).

**[0010]** FIG. 2 is a view for explaining tempering conditions defined in the present invention, which shows relationships between 0.2 % proof stress obtained by changing values of  $(20 + \log t)(T + 273)$  while changing tempering temperatures in 400 - 650 °C after quenching steel at 920 °C, and the  $(20 + \log t)(T + 273)$ .

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0011]** The reasons for restrictions of contents of various elements defined in the present inventors will be described hereinbelow. "%" of the respective contents means mass %.

C: 0.005-0.04 %

**[0012]** Although C (carbon) is an effective alloying element to enhance strength of steel, from a viewpoint of corrosion resistance small C content is preferable. However, if the content of C is less than 0.005%, proof stress does not reach 860 Mpa or more. Thus, the lower limit of the C content was set to 0.005 %. On the other hand, if the C content exceeds 0.04 %, the hardness of the tempered steel becomes hard excessively, the steel has high sulfide stress-corrosion cracking sensibility. Accordingly, the C content was set to 0.005 - 0.04 %.

Si: 0.5 % or less

**[0013]** Si (Silicon) is an alloying element necessary as a deoxidizer. An amount of Si retained in the steel may be a level of impurities. However, to obtain a large deoxidation effect it is preferred that the Si content is set to 0.01 % or more. On the other hand, if the Si content exceeds 0.5 %, the toughness of the steel is decreased and the workability of the steel is also decreased. Accordingly, the Si content was set to 0.5 % or less.

Mn: 0.1 - 3.0 %

**[0014]** Mn (Manganese) is an effective alloying element to enhance the hot workability. To obtain this effect Mn content of 0.1 % or more is needed. On the other hand, if the Mn content exceeds 3.0 %, the effect is saturated resulting in an increase in cost. Accordingly, the Mn content was set to 0.1- 3.0 %.

P: 0.04 % or less

**[0015]** P (Phosphorus) is an impurity element contained in the steel and the P content is better as low as possible. Particularly, if the P content exceeds 0.04 %, the sulfide stress-corrosion cracking resistance is remarkably decreased. Accordingly, the P content was set to 0.04 % or less.

S: 0.01 % or less

**[0016]** S (Sulfur) is an impurity element contained in the steel and the S content is better as low as possible. Particularly, if the S content exceeds 0.01 %, the hot workability, corrosion resistance and toughness are remarkably decreased. Accordingly, the S content was set to 0.01 % or less.

Cr: 10 - 15 %

**[0017]** Cr (Chromium) is an effective alloying element to enhance the carbon dioxide gas corrosion resistance. To obtain this effect Cr content of 10 % or more is needed. On the other hand, if the Cr content exceeds 15 %, it becomes difficult to make the microstructure of tempered steel a martensite phase mainly. Accordingly, the Cr content was set to 10 - 15 %.

Ni: 4.0 - 8 %

**[0018]** Ni (Nickel) is an alloying element, which is necessary for making the microstructure of tempered steel a martensite phase mainly. However, if the Ni content is 4.0 % or less, a number of ferrite phases were precipitated in the microstructure of tempered steel and the microstructure of tempered steel does not become a martensite phase mainly. On the other hand, if the Ni content exceeds 8 %, the microstructure of tempered steel becomes an austenite phase mainly. Accordingly, the Ni content was set to 4.0 - 8 %. More preferably the Ni content was set to 4 - 7 %.

Mo: 2.8 - 5.0 %

**[0019]** Mo (Molybdenum) is an effective alloying element to enhance the sulfide stress-corrosion cracking resistance for a high strength material. To obtain this effect Mo content of 2.8 % or more is needed. However, if the Mo content exceeds 5.0 %, this effect is saturated, resulting in an increase in cost. Accordingly, the Mo content was set to 2.8 - 5.0 %.

Al: 0.001- 0.10 %

**[0020]** Al (Aluminum) is an alloying element, which is used as a deoxidizer in a melting process. To obtain this effect Al content of 0.001 % or more is needed. However, if the Al content exceeds 0.10 %, many inclusions are formed in the steel so that the corrosion resistance is lost. Accordingly, the Al content was set to 0.001 - 0.10 %.

N: 0.07 % or less

**[0021]** N (Nitrogen) is an impurity element contained in the steel and the N content is better as low as possible. Particularly, if the N content exceeds 0.07 %, many inclusions are formed so that the corrosion resistance is lost. Accordingly, the N content was set to 0.07 % or less.

**[0022]** One of martensitic stainless steels according to the present invention consists the above-mentioned chemical composition as well as the balance Fe and indispensable impurities. Another martensitic stainless steel according to the present invention further contains, in addition to the above-mentioned components, at least one alloying element selected from at least one group consisting of a first group, a second group and a third group shown as follows. The components (elements) of the respective groups will be described below.

First group (Ti, V, Nb, Zr: 0.005 - 0.25 % respectively)

**[0023]** Since Ti, V, Nb and Zr have effect to fix C so as to reduce variations of strength, one or more selected from these elements may be optionally contained. However, if any one of the elements is less than 0.005%, the above-mentioned effect cannot be obtained. On the other hand, if any one of the elements exceeds 0.25 %, the microstructure of the steel cannot become a martensite phase mainly so that highly strengthening of the steel with a proof stress of 860 MPa or more cannot be attained. Accordingly, the respective contents in selectively containing these elements were set to 0.005 - 0.25 %.

Second group (Cu: 0.05 - 1 %)

**[0024]** Cu is an effective element to make the microstructure of tempered steel a martensite phase mainly like Ni. To obtain the effect by the addition of Cu the Cu content may be 0.05 % or more. However, if the Cu content exceeds 1 %, the hot workability of the steel is lowered. Accordingly, when Cu is contained in the steel the Cu content was set

to 0.05 - 1 %.

Third group (Ca, Mg, La, Ce: 0.0002 - 0.005 % respectively)

5 **[0025]** Since Ca, Mg, La and Ce are effective elements to enhance the hot workability of the steel, one or more selected from these elements may be optionally contained. However, if any one of the elements is less than 0.0002 %, the above-mentioned effect cannot be obtained. On the other hand, if any one of the elements exceeds 0.005 %, coarse oxide is formed in the steel whereby the corrosion resistance of the steel is decreased. Accordingly, the respective contents in selectively containing these elements were set to 0.0002 - 0.005 %. Particularly, it is preferred to contain Ca and/or La in the steel.

10 **[0026]** The steel according to the present invention should have the above-mentioned chemical composition and satisfy the following expression (1). This is because, if the steel satisfies the expression (1), strength of the steel can be enhanced to proof stress of 860 MPa or more without deteriorating sulfide stress-corrosion cracking resistance.

$$15 \quad \text{Mo} \geq 2.3 - 0.89 \text{ Si} + 32.2 \text{ C} \quad (1)$$

wherein the symbols of the respective elements in the expression (1) show the content (mass %) of each element.

20 **[0027]** FIG. 1 is a view showing relationships between Mo contents of various types of steels tested in examples, which will be described later, and the right side in the expression (1), that is "2.3 - 0.89 Si + 32.2 C" (IM value). Specifically, the results shown in FIG. 1 are based on steels of the present invention and comparative steels (test Nos. 18 - 21). The mark "o" shows an example that did not generate rupture in a sulfide stress-corrosion cracking test, and the mark "x" shows an example that generated rupture therein. Even if the Mo content exceeds 2.8 %, if the Mo content does not satisfy the expression (1), the steel has a poor sulfide stress-corrosion cracking resistance.

25 **[0028]** When Mo content is out of a range (that is less than 2.8 %) defined in the present invention, the 0.2 % proof stress of the steel is less than 860 MPa. Further, even if Mo content is in a range (that is 2.8 - 5 %) defined in the present invention, if the Mo content does not satisfy the above-mentioned expression (1), the 0.2 % proof stress of the steel is less than 860 MPa.

30 **[0029]** However, if steel satisfies the above-mentioned expression (1), the 0.2 % proof stress of the steel reaches 860 MPa or more and the steel can endure the use of an oil well steel material due to its sufficient strength. Accordingly, the steel according to the present invention should be in a range of said chemical composition and satisfy the above-mentioned expression (1).

35 **[0030]** Further, the present inventors have checked the influences of microstructure. As a result the present inventors have found that if the microstructure is a structure mainly comprising tempered martensite, carbide precipitated during tempering, and intermetallic compounds such as Laves phase,  $\sigma$  phase and the like finely precipitated during tempering, the strength of the steel can be enhanced without deteriorating sulfide stress-corrosion cracking resistance.

**[0031]** It is noted that "mainly comprising tempered martensite" means that a 70 vol % or more of the microstructure of the steel is a tempered martensitic structure, and a retained austenitic structure and/or a ferritic structure other than a tempered martensitic structure may be present.

40 **[0032]** Further, the "intermetallic compounds such as Laves phase,  $\sigma$  phase and the like" may contain intermetallic compounds such as  $\mu$  phase and X phase other than Laves phase such as  $\text{Fe}_2\text{Mo}$  and the like and  $\sigma$  phase.

45 **[0033]** The microstructure of the steel according to the present invention contains carbide precipitated during tempering. Although carbide is an effective microstructure to ensure the strength of the steel, high strength of proof stress of 860 MPa or more cannot be realized by only carbide contained in the steel. Accordingly, in the present invention precipitation of carbide as well as fine precipitation of intermetallic compounds such as the above-mentioned Laves phase,  $\sigma$  phase and the like are needed.

**[0034]** Heat treatment for the steel of the present invention is typical quenching-tempering. To precipitate fine intermetallic compounds during tempering it is necessary to sufficiently dissolve the intermetallic compounds during quenching. The quenching temperature is preferably 880 - 1000 °C.

50 **[0035]** Further, conditions in which intermetallic compounds such as a fine Laves phase,  $\sigma$  phase and the like are precipitated and 0.2 % proof stress of 860 MPa or more can be obtained resides in a case where when a temperature range for tempering is 450 - 620 °C, as well as the tempering temperature is set to T(°C) and the tempering time is set to t (hour),  $(20 + \log t)(T + 273)$  can satisfy 13500 - 17700.

55 **[0036]** FIG. 2 is a view for explaining tempering conditions defined in the present invention. FIG. 2 shows relationships between 0.2 % proof stress obtained by changing values of  $(20 + \log t)(T + 273)$  while changing tempering temperatures in 400 - 650 °C after quenching steel at 920 °C, and the  $(20 + \log t)(T + 273)$ .

**[0037]** As shown in FIG. 2, when  $(20 + \log t)(T + 273)$  is in a range of 13500 - 17700, 0.2 % proof stress reaches 860 MPa or more.

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**[0038]** When tempering is performed at a condition that  $(20 + \log t)(T + 273)$  exceeds 17700, dislocation density is reduced or intermetallic compounds are dissolved in microstructure of the steel, whereby high strengthening of 0.2 % proof stress of 860 MPa or more cannot be attained. On the other hand, when the steel is tempered at a condition of less than 13500, intermetallic compounds and carbide are not precipitated. Accordingly, 0.2 % proof stress of 860 MPa or more cannot be attained.

**[0039]** From the above-mentioned principal, the steel of the present invention should have the above-mentioned chemical compositions and satisfy the expression (1) and the microstructure of the steel should be mainly comprising tempered martensite, carbide precipitated during tempering, and intermetallic compounds such as a Laves phase,  $\sigma$  phase and the like finely precipitated during tempering.

(Examples)

**[0040]** Steels having chemical compositions shown in Tables 1 (1) and 1 (2) were melted and cast, and the obtained cast ingots were forged and hot rolled to prepare steel plates each having a thickness of 15 mm, a width of 120 mm and a length of 1,000 mm. These steel plates were subjected to quenching (water cooling at 920 °C) and tempering [air cooling after soaking at 550 °C for 30 min.  $((20 + \log t)(T + 273) = 16212]$ , and the obtained steel plates were provided in various tests as testing steel plates.

Table 1 (1)

Test No.	Chemical composition (mass %)																Mo/IM value				
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Al	N	Nb	V	Ti	Zr	Ca		Mg	La	Ce	IM value
1	0.014	0.17	0.43	0.015	0.0010		11.81	6.85	2.93	0.030	0.0055									2.60	0.33
2	0.016	0.17	0.46	0.015	0.0010		12.08	6.90	2.93	0.030	0.0055		0.060							2.66	0.27
3	0.026	0.18	0.87	0.016	0.0011	0.08	12.02	7.67	4.50	0.028	0.0050		0.040	0.003						2.98	1.52
4	0.034	0.04	0.44	0.015	0.0010	0.04	12.01	7.39	3.88	0.034	0.0062		0.040	0.091						3.36	0.52
5	0.008	0.48	0.41	0.011	0.0010	0.98	11.98	7.87	3.98	0.024	0.0050		0.05	0.105	0.040			0.0009	0.0010	2.13	1.85
6	0.015	0.17	0.98	0.015	0.0010		10.11	4.21	2.98	0.030	0.0055		0.004			0.0005				2.63	0.35
7	0.017	0.17	1.02	0.015	0.0010		14.10	7.92	2.88	0.030	0.0066		0.060							2.70	0.18
8	0.016	0.15	0.23	0.013	0.0009		12.10	6.87	2.86	0.025	0.0065		0.004							2.68	0.28
9	0.015	0.15	1.44	0.012	0.0008		12.07	6.85	2.91	0.025	0.0066		0.060							2.65	0.26
10	0.014	0.18	0.44	0.015	0.0008	0.28	12.01	6.91	2.96	0.034	0.0062		0.040	0.091						2.59	0.37
11	0.014	0.21	0.44	0.015	0.0010	0.85	12.01	6.55	2.97	0.034	0.0062		0.040	0.092						2.56	0.41
12	0.014	0.20	0.44	0.015	0.0010	1.54	12.01	6.25	2.97	0.034	0.0062		0.040	0.091						2.57	0.40
13	0.015	0.18	0.43	0.017	0.0090	2.70	12.08	5.85	2.96	0.030	0.0642		0.060	0.088						2.62	0.34
14	0.014	0.17	0.47	0.014	0.0012	0.48	12.08	6.90	2.96	0.027	0.0074									2.60	0.36
15	0.016	0.15	0.67	0.015	0.0010		12.01	6.78	2.94	0.030	0.0059					0.0005				2.68	0.26
16	0.014	0.02	0.46	0.012	0.0009		11.99	6.89	2.91	0.025	0.0065			0.098		0.0004				2.74	0.17
17	0.015	0.17	0.44	0.014	0.0010	0.43	12.01	6.88	2.88	0.027	0.0067								0.0007	2.63	0.23

Note 1) Mark \* shows out of range defined in the present invention.

Note 2) IM value shows  $(2.3 - 0.89 \text{ Si} + 32.2\text{C})$

Note 3) Mo - IM value shows a calculated value of (Mo content - IM value), and if this value is 0 or more, it satisfied the expression (1) defined in the present invention.

Table 1 (2)

Test No.	Chemical composition (mass %)																IM value	MoIM value			
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Al	N	Nb	V	Ti	Zr	Ca			Mg	La	Ce
18	0.018	0.17	0.45	0.012	0.0012	0.04	10.50	6.11	2.44	0.048	0.0064		0.030	0.101	—	—	—	—	—	2.73	*-0.29
19	0.012	0.11	0.44	0.011	0.0010	0.03	12.08	6.15	2.46	0.043	0.0062		0.080	0.098	—	—	—	—	—	2.59	*-0.13
20	0.028	0.05	0.45	0.015	0.0011	0.03	12.70	6.45	2.61	0.058	0.0055		0.040	0.067	—	—	—	—	—	3.16	*-0.55
21	0.020	0.21	0.45	0.015	0.0011	0.03	12.70	6.45	2.65	0.058	0.0055		0.040	0.067	—	—	—	—	—	2.76	*-0.11
22	0.018	0.15	0.46	0.015	0.0009	0.03	12.30	6.34	*1.51	0.032	0.0060		0.040	0.003	—	—	—	—	—	2.75	*-1.24
23	0.017	0.16	0.45	0.015	0.0011	0.03	11.98	6.38	*0.98	0.035	0.0061	0.050	0.100	0.098	—	—	—	—	—	2.71	*-1.73
24	0.023	0.17	0.43	0.014	0.0011	0.03	11.97	6.48	*2.04	0.034	0.0058		0.040	0.097	—	—	—	—	—	2.89	*-0.85
25	0.015	0.35	0.44	0.013	0.0011	0.03	*9.50	6.01	2.46	0.011	0.0053		0.050	0.088	—	—	—	—	—	2.47	*-0.01

Note 1) Mark \* shows out of range defined in the present invention.

Note 2) IM value shows (2.3 – 0.89 Si + 32.2C)

Note 3) Mo – IM value shows a calculated value of (Mo content – IM value), and if this value is 0 or more, it satisfied the expression (1) defined in the present invention.

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**[0041]** First, round bar test pieces each having a diameter of 6.35 mm and a length of the parallel portion of 25.4 mm were taken from the respective testing steel plates and subjected to tensile tests at normal temperatures. The obtained 0.2 % proof stresses are shown in Table 2.

5 **[0042]** Then, test pieces each having a thickness of 3 mm, a width of 20 mm and a length of 50 mm were taken from the respective testing steel plates and these testing pieces were polished with a No. 600 emery paper and degreased and dried. Then the obtained testing pieces were immersed into 25% NaCl water solution saturated with 0.973 MPa CO<sub>2</sub> gas and 0.0014 MPa H<sub>2</sub>S gas (temperature: 165 °C) for 720 hours.

10 **[0043]** After the immersion weight reductions of the test pieces by corrosion [(mass before testing) - (mass after testing)] were measured and the presence and absence of local corrosion on surfaces of the testing pieces were confirmed by a visual test. As a result the corrosion rate of the steel according to the present invention is 0.5 mm/year or less, and no local corrosion on its surface could be found.

15 **[0044]** Subsequently, examples in which 0.2 % proof stresses were 860 MPa or more in the tensile tests were subjected to fixed load tests by use of a spring type (proof ring type) testing machine in accordance with TM0177-96 Method A of NACE. Specifically, round bar test pieces each having a diameter of 6.3 mm and a length of the parallel portion of 25.4 mm were taken from the respective testing steel plates and subjected to 0.2 % proof stress-85 % (test stress) fixed load tests at a test temperature of 25 °C, for 720 hours by use of 0.003 MPa H<sub>2</sub>S gas (CO<sub>2</sub> bal.) saturated 25% NaCl water solution (pH 4.0). As a result all test pieces were not ruptured.

20 **[0045]** The Microstructures of the test pieces were observed by an optical microscope and an extraction replica. These results are also shown in Table 2.

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Table 2

	Test No.	0.2 % Proof stress (MPa)	Carbon dioxide gas corrosion test	SSC Corrosion test	Microstructure
Steels of the invention	1	951	o	o	M + IM + C
	2	944	o	o	M + IM + C
	3	1,007	o	o	M + IM + C
	4	1,027	o	o	M + IM + C
	5	1,020	o	o	M + IM + C
	6	910	o	o	M + IM + C
	7	882	o	o	M + F + IM + C
	8	944	o	o	M + IM + C
	9	965	o	o	M + IM + C
	10	972	o	o	M + IM + C
	11	958	o	o	M + IM + C
	12	951	o	o	M + IM + C
	13	965	o	o	M + IM + C
	14	958	o	o	M + IM + C
	15	972	o	o	M + IM + C
	16	882	o	o	M + IM + C
	17	979	o	o	M + IM + C
Comparative steels	18	841	o	×	M + C
	19	843	o	×	M + C
	20	858	o	×	M + C
	21	840	o	×	M + C
	22	829	o	×	M + C
	23	832	o	×	M + C
	24	849	o	×	M + C
	25	841	×	×	M + C

Note 1) In carbon dioxide gas corrosion test a steel, whose corrosion rate is 0.5 mm/y or less, and which did not generate local corrosion, is shown by "o" and otherwise "x".

Note 2) In SSC test, a steel, which did not generate rupture, is shown by "o" and a steel, which generated rupture, is shown by "x".

Note 3) In microstructure, tempered martensite is shown by "M", ferrite is shown by "F", intermetallic compounds are shown by "IM" and carbide is shown by "C".

**[0046]** As shown in Table 2, examples Nos. 1 to 17 of the present invention each have 0.2 % proof stress of 860 MPa or more and excellent carbon dioxide gas corrosion resistance and sulfide stress-corrosion cracking resistance. On the other hand, comparative examples Nos. 22 to 25, which have Cr and/or Mo contents out of range defined in the present invention, and comparative examples Nos. 18 to 21, which have the content ranges of the respective components are in the range defined in the present invention but the expression (1) previously described was not satisfied, were not sufficient in carbon dioxide gas resistance and/or stress cracking resistance.

#### INDUSTRIAL APPLICABILITY

**[0047]** The martensitic stainless steel according to the present invention can have high strength of 0.2 % proof stress of 860 MPa or more and excellent carbon dioxide gas corrosion resistance and sulfide stress-corrosion cracking resistance by limiting the steel composition of specified elements and defining Mo content in the steel by relationships with IM values as well as by forming microstructure of the steel with tempered martensite mainly, carbide precipitated during tempering, and intermetallic compounds such as a Laves phase, a  $\sigma$  phase and the like. As a result the mar-

tensitic stainless steels of the present invention can be applied to practical steels, which can be widely used in oil well tubes and the like under environment including carbon dioxide gas, hydrogen sulfide, chlorine ions or two or more of them, in wide fields.

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## Claims

1. A high strength martensitic stainless steel excellent in carbon dioxide gas corrosion resistance and sulfide stress-corrosion cracking resistance and having 0.2 % proof stress of 860 MPa or more, **characterized by** including, by mass %, C: 0.005 - 0.04 %, Si: 0.5 % or less, Mn: 0.1 - 3.0 %, P: 0.04 % or less, S: 0.01 % or less, Cr: 10 - 15 %, Ni: 4.0 - 8 %, Mo: 2.8 - 5.0 %, Al: 0.001 - 0.10 % and N: 0.07 % or less, and optionally further containing Cu: 0.05 - 1 %, and/or one or more selected from Ti: 0.005 - 0.25 %, V: 0.005 - 0.25 %, Nb: 0.005 - 0.25 %, and Zr: 0.005 - 0.25 %, and/or one or more selected from Ca: 0.0002 - 0.005 %, Mg: 0.0002 - 0.005 %, La: 0.0002 - 0.005 %, and Ce: 0.0002 - 0.005 %, and the balance Fe and impurities, and also **characterized by** satisfying the expression (1) given below wherein the microstructure mainly comprises tempered martensite, carbide precipitated during tempering, and intermetallic compounds finely precipitated during tempering:

$$\text{Mo} \geq 2.3 - 0.89 \text{ Si} + 32.2 \text{ C} \quad (1)$$

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wherein the symbols of the respective elements in the expression (1) show the content (mass %) of each element.

2. A steel according to claim 1 further containing, by mass %, one or more selected from Ti: 0.005 - 0.25 %, V: 0.005 - 0.25 %, Nb: 0.005 - 0.25 %, and Zr: 0.005 - 0.25 %.
3. A steel according to claim 1 or 2 containing 0.05 - 1 mass % Cu.
4. A steel according to any one of claims 1 to 3 further containing, by mass %, one or more selected from Ca: 0.0002 - 0.005 %, Mg: 0.0002 - 0.005 %, La: 0.0002 - 0.005 %, and Ce: 0.0002 - 0.005 %.
5. A steel according to any one of claims 1 to 4 **characterized in that** the steel is obtainable by subjecting a steel of the composition defined in one of claims 1 to 4 to tempering in which  $(20 + \log t)(T + 273)$  satisfies 13500 - 17700 when, after quenching the steel at a quenching temperature of 880 °C - 1000 °C, a range of a tempering temperature is set to 450 °C - 620 °C, a tempering temperature is set to T (°C) and tempering time is set to t (hour).
6. A process for producing a steel according to any one of claims 1 to 5 which comprises tempering a steel having the composition defined in any one of claims 1 to 4, wherein  $(20 + \log t)(T + 273)$  satisfies 13500 - 17700 when, after quenching the steel at a quenching temperature of 880 °C - 1000 °C, a range of a tempering temperature is set to 450 °C - 620 °C, a tempering temperature is set to T (°C) and tempering time is set to t (hour).

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FIG.1

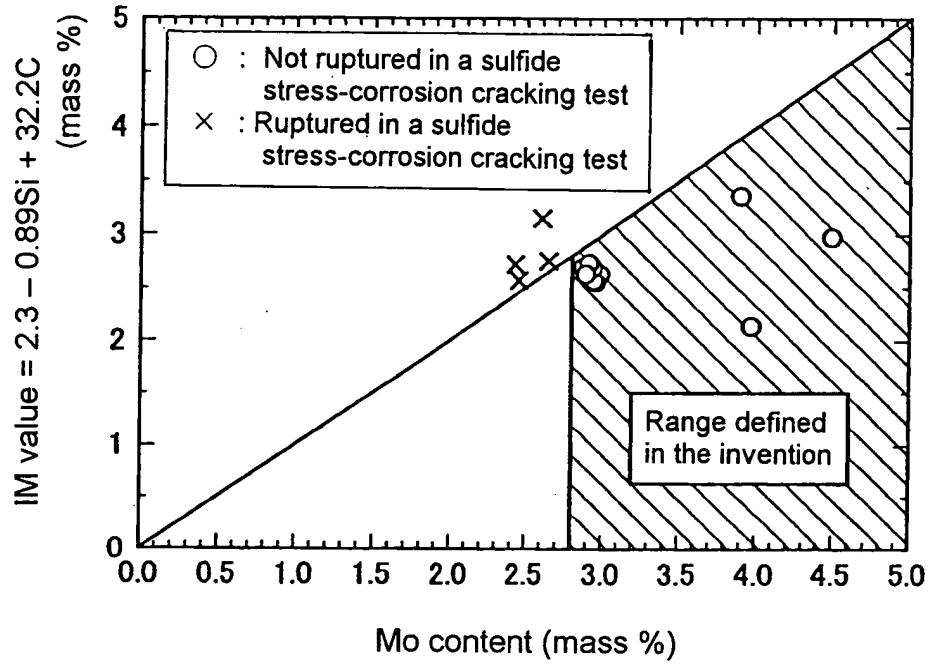
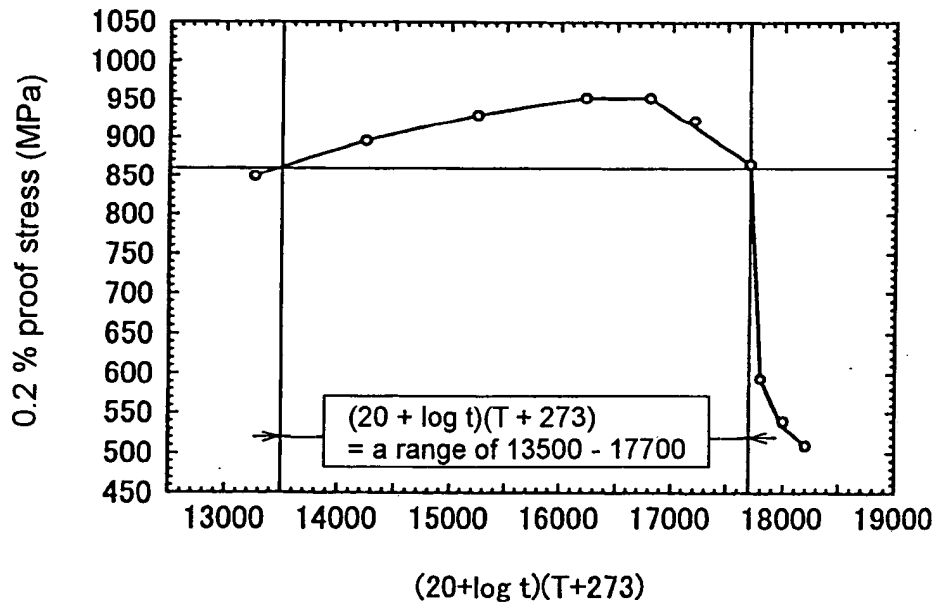


FIG.2



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/16288

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl. <sup>7</sup> C22C38/00, C22C38/58, C21D6/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>7</sup> C22C38/00, C21D6/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2004 Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 5-156409 A (Nippon Steel Corp.), 22 June, 1993 (22.06.93), Claims; table 1 (Family: none)	1-9
X	JP 2-243740 A (Sumitomo Metal Industries, Ltd.), 27 September, 1990 (27.09.90), Claims; tables 1, 2, 3 (Family: none)	2, 4, 6, 8, 9
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> 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 document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search 02 February, 2004 (02.02.04)		Date of mailing of the international search report 17 February, 2004 (17.02.04)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)