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(72) Inventors:  
• **MINAMI, Yusuke**  
**Tokyo 100-0005 (JP)**  
• **MASAMURA, Katsumi**  
**Tokyo 100-0005 (JP)**  
• **SUZUKI, Toshio**  
**Tokyo 100-0005 (JP)**

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(71) Applicant: **NKK CORPORATION**  
**Tokyo 100-0005 (JP)**

(74) Representative: **HOFFMANN - EITLE**  
**Patent- und Rechtsanwälte**  
**Arabellastrasse 4**  
**81925 München (DE)**

(54) **MARTENSITIC STAINLESS STEEL**

(57) The martensitic stainless steel consists essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, by weight, and balance of Fe and inevitable impurities, and satisfies 0.02 to 0.04% (C + N) by weight. Even when the steel is used under an environment con-

taining both a moist carbon dioxide gas and a moist hydrogen sulfide, it gives excellent corrosion resistance, excellent field welding performance owing to less hardness increase after welding, and small variations in mechanical characteristics under different production conditions. Thus, the steel is suitable as a pipeline.

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**Description****Field of the Invention**

5 **[0001]** The present invention relates to a martensitic stainless steel suitable for pipelines or the like which are used under environments containing both moist carbon dioxide gas and moist hydrogen sulfide.

**Description of the Prior Art**

10 **[0002]** Steels for pipelines transporting oil and natural gas are requested to have excellent corrosion resistance and field welding performance responding to each use environment. In this respect, carbon steel pipes of X50 and X65 grades have often been adopted. The term "excellent field welding performance" referred to herein signifies the welding not requiring preheating and postheating that are applied to prevent welding crack generation observed during field welding of pipelines.

15 **[0003]** In recent years, environments containing moist carbon dioxide gas and moist hydrogen sulfide have increased, and the application of stainless steels are studied from the standpoint of corrosion resistance. Existing stainless steels, however, did not necessarily have sufficient performance for pipelines. Consequently, stainless steels such as those containing 0.2%C-13%Cr and two-phase stainless steels such as those containing 22%Cr and 25%Cr were developed. The former 0.2%C-13%Cr stainless steel was developed for oil well use that does not require welding. Therefore, the  
20 0.2%-13%Cr stainless steel is not suitable for the pipelines that need excellent field welding performance because the welding needs preheating and postheating at high temperatures to prevent weld crack generation. The latter two-phase stainless steel containing 22%Cr or 25%Cr does not need preheating and postheating on welding. However, the two-phase stainless steel is difficult in use as pipelines that need a large quantity of steels because the stainless steel is expensive.

25 **[0004]** To cope with the situation, stainless steel containing less C and containing 13%Cr is proposed in JP-A-6-100943, (the term "JP-A-" referred to herein signifies "Unexamined Japanese Patent Publication"), JP-A-4-266018, JP-A-8-100235, and JP-A-8-100236. However, that type of stainless steel cannot satisfy simultaneously the requirement of corrosion resistance to an environment containing both moist carbon dioxide gas and moist hydrogen sulfide and the requirement of field welding performance.

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**Summary of the Invention**

**[0005]** An object of the present invention is to provide a martensitic stainless steel applicable under environments containing both moist carbon dioxide gas and moist hydrogen sulfide, and having excellent field welding performance.

35 **[0006]** To attain the object, the inventors of the present invention carried out various investigations on the components of martensitic stainless steel, and obtained the following-given findings.

- Chromium is effective in corrosion resistance to an acid in a moist carbon dioxide gas.
- To prevent occurrence of sulfide stress corrosion cracking in an environment containing moist hydrogen sulfide,  
40 the suppression of quantity of invading hydrogen into the steel is required. To do this, it is effective to add a certain amount of Mo along with Cr, and further to reduce the amount of desulfurization and deoxidization elements.
- Control of C and N amount is effective to improve the welding and production performance.

45 **[0007]** Based on the findings, the inventors of the present invention have developed a martensitic stainless steel consisting essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, by weight, and balance of Fe and inevitable impurities, and satisfying 0.02 to 0.04% (C + N) by weight.

**[0008]** The object of the present invention can be achieved also by a martensitic stainless steel consisting essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, further one or both of 0.1 to 3% W and 0.1 to 3% Cu, by weight, and balance of Fe and inevitable impurities, and satisfying  
50 0.02 to 0.04% (C + N) by weight, a martensitic stainless steel consisting essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, further one or both of 0.01 to 0.1% Ti and Nb, by weight, and balance of Fe and inevitable impurities, and satisfying 0.02 to 0.04% (C + N) by weight, or a martensitic stainless steel consisting essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, further one or both of 0.1 to 3% W and 0.1 to 3% Cu, and one or both of 0.01  
55 to 0.1% Ti and Nb, by weight, and balance of Fe and inevitable impurities, and satisfying 0.02 to 0.04% (C + N) by weight.

**Best Mode to Carry Out the Invention**

[0009] The reasons to limit the components of the martensitic stainless steels according to the present invention are described in the following.

**Carbon:**

[0010] Carbon is an element to form a carbide combining with Cr, thus strengthening the steel. Carbon, however, reduces the amount of chromium which is effective in corrosion resistance and increases the hardness at a weld heat-affected zone (HAZ), thus requiring heat treatment after welding. Accordingly, the C content is specified to 0.02 wt.% or less.

**Nitrogen**

[0011] Nitrogen combines with Cr to form a compound, thus reducing the amount of Cr which is effective in corrosion resistance, and increases the hardness at the HAZ. Consequently, the N content is specified to 0.02 wt.% or less.

**Silicon**

[0012] Silicon is added as a deoxidizer. The Si content of not more than 0.1 wt.% gives no effect of deoxidization. The Si content of more than 0.3 wt.% induces crystallization of delta ferrite, then an additional Ni amount are needed to maintain the phase balance. Therefore, the Si content is specified to a range of from 0.1 to 0.3 wt.%.

**Manganese**

[0013] Manganese is added as a desulfurizer. The Mn content of not more than 0.1 wt.% gives no effect of desulfurization, and degrades hot workability. The Mn content of more than 0.3 wt.% degrades the corrosion resistance under an environment containing carbon dioxide and hydrogen sulfide. Accordingly, the Mn content is specified to a range of from 0.1 to 0.3 wt.%.

**Chromium**

[0014] Chromium is an element which is effective to improve the corrosion resistance under an environment containing moist carbon dioxide gas. However, less than 10 wt.% of Cr content cannot attain the effect. With the increase in the Cr content, the corrosion resistance increases. Since Cr is a powerful element to produce ferrite, if the Cr content exceeds 13 wt.%, surplus addition of Ni which is an expensive element to produce austenite is required. Consequently, the Cr content is specified to a range of from 10 to 13 wt.%.

**Nickel**

[0015] Although Ni is an element necessary to form a martensitic structure, less than 5 wt.% of Ni content degrades toughness and corrosion resistance owing to generating a large quantity of ferritic phase. If the Ni content exceeds 8 wt.%, the economy degrades. Therefore, the Ni content is specified to a range of from 5 to 8 wt.%.

**Molybdenum**

[0016] Molybdenum is an effective element to attain corrosion resistance. However, less than 1.5 wt.% of Mo content gives insufficient effect. If Mo is added over 3 wt.%, addition of expensive Ni is required because Mo is an element to generate ferrite.

[0017] Adding to the above-described specification of each element, it is required that the amount of (C + N) is 0.02 wt.% or more to attain an aimed strength, and is not more than 0.04 wt.% to control the hardness at the HAZ.

[0018] Furthermore, one or both of W and Cu, one or both of Ti and Nb, or one or both of W and Cu and one or both of Ti and Nb may be added. In those cases, however, the amount of W, Cu, Ti, and Nb is requested to be limited as follows.

**Tungsten and copper**

[0019] Each of W and Cu is an element effective to attain strength and corrosion resistance. Addition of W or Cu to

less than 0.1 wt.% does not attain sufficient effect, and, to over 3 wt.% degrades the hot workability. Accordingly, the content of W and Cu is specified to a range of from 0.1 to 3 wt.%.

### Titanium and niobium

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**[0020]** Each of Ti and Nb forms a carbide with C in steel, and refines grains to improve the strength and toughness. Addition of Ti or Nb to less than 0.01 wt.% does not attain sufficient effect, and, to over 0.1 wt.% saturates the effect. Consequently, the content of Ti and Nb is specified to a range of from 0.01 to 0.1 wt.%.

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**[0021]** The steels with the components adjusted as described above according to the present invention are stable in their mechanical characteristics against variations of production conditions such as heat treatment.

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**[0022]** The steels according to the present invention may be prepared by melting using adequate methods such as converter, electric furnace, or combination of them, if only the components thereof are adjusted to a specified range. After prepared by melting, the steels are formed in billets and slabs by a continuous casting machine or a mold, then are worked into a specified shape such as steel pipes and steel plates by hot-rolling, followed by applying heat treatment to attain an aimed strength. After established a martensitic structure by a heat treatment, the steels are preferred to be subjected to a tempering to adjust the strength thereof.

### Example 1

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**[0023]** Steels A through Q having respective chemical compositions given in Table 1 were prepared by melting in a vacuum melting furnace. Each of the steels was hot-rolled to a steel plate having 12 mm in thickness. The steel plate was quenched by water from  $9.00^{\circ}\text{C} \pm 10^{\circ}\text{C}$ . and then tempered at  $640^{\circ}\text{C} \pm 5^{\circ}\text{C}$  to obtain aimed proof stresses of from 600 to 700 MPa. For each of thus prepared steel plates, the corrosion resistance and the field welding performance described below were tested.

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**[0024]** The corrosion resistance to a moist carbon dioxide gas was evaluated in terms of plate thickness loss by immersing a steel plate in a solution of 5%NaCl-30atmCO<sub>2</sub> at 180°C for 96 hours. If the corrosion rate converted to one-year value is not more than 0.3 mm/y, no practical application problem occurs.

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**[0025]** The corrosion resistance to a moist hydrogen sulfide was evaluated in terms of presence/absence of fracture on the steel plate by the stress corrosion crack test for a sulfide, (Resistant SSC test) of TM0177 specified by NACE. That is, a steel plate was immersed in an aqueous solution of 5%NaCl+0.5%acetic acid saturated with latmH<sub>2</sub>S for 720 hours while applying a load of 60% of the proof stress. If no fracture occurs under the test, no practical application problem occurs.

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**[0026]** The field welding performance was evaluated by the hardness at a reproduced HAZ section. If the hardness is not more than 350 Hv, no preheating and postheating treatment are required.

**[0027]** Table 2 shows the results of the investigation.

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**[0028]** The steels A through J, which are the Example Steels according to the present invention, gave 600 to 700 MPa of proof stress, 0.3 mm/y or less of corrosion rate in a moist carbon dioxide gas, and 350 Hv or less of hardness, giving no fracture in a moist hydrogen sulfide, being applicable in an environment containing both a moist carbon dioxide gas and a moist hydrogen sulfide, giving excellent field welding performance, thus showing adaptability to pipelines.

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**[0029]** On the other hand, the Comparative Steel K contained less amount of Cr content and showed no sufficient corrosion resistance to a moist carbon dioxide. The Comparative Steel L contained large amount of Si which is a deoxidizer, the Comparative Steel M contained large amount of Mn as a desulfurizer, and the Comparative Steel N contained less amount of Mo, so that these comparative steels were inferior in corrosion resistance to a moist hydrogen sulfide. The Comparative Steel O contained less amount of Ni, so a delta ferrite deposited, which degraded the corrosion resistance to a moist carbon dioxide gas. The Comparative Steel P contained less amount of (C + N), and failed to attain satisfactory strength. The Comparative Example Q contained large amount of C and N, so that the strength was high and that the field welding performance was inferior.

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Table 1

Steel	C	Si	Mn	Cr	Ni	Mo	W	Cu	Ti	Nb	N	C+N	Remark
A	0.013	0.22	0.27	12.6	7.3	2.3	-	-	-	-	0.012	0.025	Example Steel
B	0.011	0.28	0.15	10.8	5.4	2.7	-	-	-	-	0.016	0.027	Example Steel
C	0.008	0.15	0.24	11.6	7.6	2.5	1.8	-	-	-	0.018	0.026	Example Steel
D	0.018	0.13	0.19	12.7	5.8	2.1	-	1.5	-	-	0.012	0.030	Example Steel
E	0.016	0.20	0.21	12.3	6.2	1.8	-	-	0.02	-	0.008	0.024	Example Steel
F	0.012	0.18	0.23	11.8	5.7	1.9	-	-	-	0.05	0.016	0.028	Example Steel
G	0.015	0.12	0.16	12.2	6.0	2.1	0.5	0.7	-	-	0.011	0.027	Example Steel
H	0.011	0.20	0.26	11.7	5.8	2.2	0.4	-	0.03	0.04	0.016	0.027	Example Steel
I	0.018	0.17	0.14	12.4	5.5	1.7	-	0.5	0.04	-	0.008	0.026	Example Steel
J	0.014	0.21	0.23	12.6	6.5	1.8	1.0	0.3	0.05	0.03	0.018	0.032	Example Steel
K	0.013	0.26	0.18	9.3*	5.6	2.0	-	-	-	-	0.015	0.028	Comparative Steel
L	0.011	0.53*	0.20	12.4	5.3	2.6	-	-	-	-	0.014	0.025	Comparative Steel
M	0.018	0.14	0.48*	11.7	6.2	1.9	-	-	-	-	0.008	0.026	Comparative Steel
N	0.014	0.20	0.26	12.1	5.7	0.7*	-	-	-	-	0.011	0.025	Comparative Steel
O	0.011	0.27	0.13	12.7	4.2*	2.7	-	-	-	-	0.011	0.022	Comparative Steel
P	0.007	0.19	0.20	11.6	5.3	2.1	-	-	-	-	0.009	0.014*	Comparative Steel
Q	0.025*	0.22	0.23	12.0	6.2	2.5	-	-	-	-	0.025*	0.050*	Comparative Steel

Unit is wt. %.

Value with (\*) mark indicates that the value is outside of the range of the present invention.

Table 2

Steel	Proof stress (MPa)	Corrosion in a moist carbon dioxide gas (mm/y)	Presence/absence of fracture in a moist hydrogen sulfide gas (Hv)	Hardness	Remark
A	625	0.11	Absent	315	Example Steel
B	690	0.15	Absent	316	Example Steel
C	684	0.08	Absent	314	Example Steel
D	630	0.05	Absent	320	Example Steel
E	622	0.14	Absent	310	Example Steel
F	625	0.20	Absent	320	Example Steel
G	644	0.12	Absent	318	Example Steel
H	651	0.18	Absent	315	Example Steel
I	614	0.22	Absent	314	Example Steel
J	660	0.15	Absent	325	Example Steel
K	602	0.75	Absent	321	Comparative Example Steel
L	622	0.15	Present	313	Comparative Example Steel
M	618	0.14	Present	315	Comparative Example Steel
N	613	0.21	Present	312	Comparative Example Steel
O	656	0.42	Absent	309	Comparative Example Steel
P	575	0.16	Absent	297	Comparative Example Steel
Q	720	0.23	Absent	380	Comparative Example Steel

#### Claims

1. A martensitic stainless steel consisting essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, by weight, and balance of Fe and inevitable impurities, and satisfying 0.02 to 0.04% (C + N) by weight.
2. A martensitic stainless steel consisting essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, further one or both of 0.1 to 3% W and 0.1 to 3% Cu, by weight, and balance of Fe and inevitable impurities, and satisfying 0.02 to 0.04% (C + N) by weight.
3. A martensitic stainless steel consisting essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, further one or both of 0.01 to 0.1% Ti and Nb, by weight, and balance of Fe and inevitable impurities, and satisfying 0.02 to 0.04% (C + N) by weight.
4. A martensitic stainless steel consisting essentially of 0.02% or less C, 0.02% or less N, 0.1 to 0.3% Si, 0.1 to 0.3% Mn, 10 to 13% Cr, 5 to 8% Ni, 1.5 to 3% Mo, further one or both of 0.1 to 3% W and 0.1 to 3% Cu, and one or both of 0.01 to 0.1% Ti and Nb, by weight, and balance of Fe and inevitable impurities,

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/07067

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl <sup>7</sup> C22C 38/00, 38/44, 38/50		
According to International Patent Classification (IPC) or to both national classification and IPC		
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Minimum documentation searched (classification system followed by classification symbols) Int.Cl <sup>7</sup> C22C 38/00~38/60		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) JICST, WPI		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, Y	EP, 0798394, A1 (KAWASAKI STEEL CORPORATION), 01 October, 1997 (01.10.97), Claims & JP, 9-316611, A & US, 5985209, A & NO, 9701434, A	1-4
X Y	JP, 8-41599, A (Sumitomo Metal Industries, Ltd.), 13 February, 1996 (13.02.96), Claims (Family: none)	1, 3 2, 4
Y	JP, 10-204587, A (NKK CORPORATION), 04 August, 1998 (04.08.98), Par. No. [0014] (Family: none)	1-4
A	JP, 9-327721, A (NKK CORPORATION), 22 December, 1997 (22.12.97) (Family: none)	1-4
A	JP, 7-310143, A (Sumitomo Metal Industries, Ltd.), 28 November, 1995 (28.11.95) (Family: none)	1-4
A	JP, 9-125141, A (Sumitomo Metal Industries, Ltd.), 13 May, 1997 (13.05.97) (Family: none)	1-4
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document but published on or after the international filing date 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) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"
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