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

(11) EP 1 103 626 A1

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

(43) Date of publication:
30.05.2001 Bulletin 2001/22

(21) Application number: **99925355.2**

(22) Date of filing: **16.06.1999**

(51) Int. Cl.^{7}: **C22C 38/32**

(86) International application number:
PCT/JP99/03231

(87) International publication number:
WO 00/03050 (20.01.2000 Gazette 2000/03)

(84) Designated Contracting States:
DE FR GB

(30) Priority: **08.07.1998 JP 19308498**

(71) Applicant:
Sumitomo Metal Industries Limited
Osaka-shi, Osaka 541-0041 (JP)

(72) Inventors:
- **SAWARAGI, Atsushi**
  Nishinomiya-shi, Hyogo 663-8104 (JP)
- **SENNBA, Hiroyuki**
  Nishinomiya-shi, Hyogo 663-8152 (JP)

(74) Representative:
Uchida, Kenji et al
S.A. Fedit-Loriot et Autres Conseils en Propriété
Industrielle,
38, avenue Hoche
75008 Paris (FR)

(54) HIGH Cr FERRITIC HEAT RESISTANCE STEEL

(57) A Cr ferritic heat resistance steel containing 0.02 to 0.15 % of C, 0.05 to 1.5 % of Mn, 0.03 % or less of P, 0.015 % or less of S, 8 to 13 % of Cr, 1.5 to 4 % of W, 2 to 6 % of Co, 0.1 to 0.5 % of V, 0.01 to 0.15 % of Ta, 0.01 to 0.15 % of Nb, 0.001 to 0.2 % of Nd, less than 0.02 % of N, 0.0005 to 0.02 % of B, 0.001 to 0.05 % of Al, with the proviso that the contents of Nb and N satisfy the formula, which is excellent in the creep strength under a condition of a high temperature and long duration and in toughness, and can be used under an extra supercritical pressure condition of 650°C or higher and 300 atm.

Printed by Xerox (UK) Business Services
2.16.7 (HRS)/3.6

Description

TECHNICAL FIELD

[0001] The present invention relates to a heat resistant high Cr ferritic steel, more particularly, a high Cr ferritic steel having excellent high temperature long term creep strength and toughness and being suitable for uses such as a heat resistant steel tube and pipe, a pressure vessel steel plate or a turbine steel member used under high temperature and high pressure conditions in a power boiler, in a nuclear power plant and in a chemical plant.

BACKGROUND ART

[0002] A heat resistant steel used under high temperature and high pressure condition such as those in a power boiler, a nuclear power plant and a chemical plant, is generally required to be excellent in high temperature strength, corrosion resistant property, oxidation resistant property and toughness.

[0003] An austenitic stainless steel such as JIS-SUS321H steel (Equivalent to AISI-TP321H), JIS-SUS347H steel (Equivalent to AISI-TP347H), a low alloy steel such as 2.1/4Cr-1Mo steel and a high Cr ferritic steel such as 9-12 Cr steel have been used in the past for these applications. Among them, a high Cr ferritic steel is superior to a low alloy steel in high temperature strength and corrosion resistant property at a temperature of 500 to 650°C. Furthermore, compared with an austenitic stainless steel, a high Cr ferritic steel has many advantages such that it is less expensive, high in thermal conductivity and excellent in thermal fatigue property because of low thermal expansion coefficient and also it does not cause stress corrosion cracking.

[0004] A steam condition of a power boiler has recently became higher and higher in temperature and pressure in order to improve a thermal efficiency further in a thermal power plant. An example of such steam condition is 538°C in temperature and 246atm in pressure, which is so-called a super critical condition. Furthermore, a steam condition such as 625°C or higher in temperature and 300atm or higher in pressure, so-called a ultra super critical condition, has been studied for a future operation. According to these changes in the steam condition, the properties required for a steel tube and pipe used in power boiler become severer. A ordinary high Cr ferritic steel, therefore, has faced the situation that it can not satisfy fully the requirement of a long term creep strength at a high temperature required for a higher steam condition.

[0005] An austenitic stainless steel has the properties which can satisfy the above-mentioned servere condition but it is expensive. Accordingly, many studies on an improvement of the properties of a high Cr ferritic steel has been carried out in order to utilize a high Cr ferritic steel which is less expensive compared with an austenitic stainless steel.

[0006] The inventors have already invented a heat resistant high Cr ferritic steel which is less expensive and excellent in creep strength and toughness when used for a long time under the ultra super critical condition with a high temperature and a high pressure. (Published Japan Patent Application No.8-85850, No.9-71845, No.9-71846)

[0007] However, a further improvement of creep strength has been required in order to use a high Cr ferrite steel in a thermal power boiler operated under more severe steam condition such as the above-mentioned ultra super critical condition.

DISCLOSURE OF THE INVENTION

[0008] The object of this invention is to provide a heat resistant high Cr ferritic steel which is excellent in long term creep strength at a high temperature and toughness and can be used under the condition of high temperature and high pressure such as 625°C or more and 300atm or more.

[0009] The gist of the present invention is a heat resistant high Cr ferritic steel as described below.

[0010] A heat resistant high Cr ferritic steel having excellent high temperature long term creep strength and toughness, which comprises, by mass %,

C : 0.02 to 0.15%	Mn: 0.05 to 1.5%
P : 0.03% or less	S : 0.015% or less
Cr: 8 to 13%	W : 1.5 to 4%
Co: 2 to 6%	V : 0.1 to 0.5%
Ta: 0.01 to 0.15%	Nb: 0.01 to 0.15%

(continued)

Nd: 0.001 to 0.2%	N : less than 0.02%
B : 0.0005 to 0.02%	Al: 0.001 to 0.05%
Mo: 0 to 1%	Si: 0 to 1%
Ca: 0 to 0.02%	La: 0 to 0.2%
Ce: 0 to 0.2%	Y : 0 to 0.2%
Hf: 0 to 0.2%,	

the contents of Nd and N satisfying the following formula, and the balance being Fe and incidental impurities.

$$\mathrm{Nd}(\%) \leqq 5 \times \mathrm{N}(\%) + 0.1(\%)$$

[0011] The inventors have studied in detail the effect of various alloy elements on high temperature long term creep strength and toughness of a heat resistant high Cr ferritic steel containing Nd, which was previously developed by the inventors, for its further improvement. As a result, the inventors have obtained the following findings and accomplished the present invention.

(a) Nd is effective in fixing an oxygen in a steel by forming Nd-oxides and thereby preventing a formation of oxides with some of Nd and V, which are the precipitation strengthening elements, and contribute to increase creep strength by precipitating fine carbides. Furthermore, Nd forms carbides such as NdC_2. These carbides precipitate finely and stably even after used for a long period of time at a high temperature and therefore contribute greatly to increase high temperature long term creep strength. However, Nd has strong affinity with N (Nitrogen) and produces inclusions of coarse NdN in a steel containing a large amount of nitrogen. Accordingly, in such steel, the effects of Nd in preventing a formation of oxides of Nb and V and in precipitating fine carbides such as NdC_2 for a precipitation strengthening become insufficient and Nd can not fully attain its effect in improving creep strength.

(b) A formation of coarse NdN can be prevented by controlling an amount of N to be less than 0.02% in a heat resistant high Cr ferritic steel containing Nd. As a result, fine carbides of Nb and V and fine carbides such as NdC_2 precipitate stably, even after exposed for a long time at a high temperature, and thereby a recovery and softening phenomena of a martensite structure is suppressed even after being used for a long time at a high temperature, which result in great improvement of creep strength.

(c) In order to ensure toughness of a heat resistant high Cr ferritic steel containing Nd, the balance of the amounts of Nd and N is important and must satisfy the formula mentioned above.

BEST MODE FOR CARRYING OUT THE INVENTION

[0012] The following are the reasons why the chemical composition of the heat resistant steel of the present invention is regulated. (hereinafter, the % represents a mass percent)

C: 0.02 to 0.15%

[0013] C forms MC type carbides (M represents an alloying element), such as M_7C_3 and $M_{23}C_6$ type carbides. These carbides contribute to increase creep strength and also C itself stabilizes a metallurgical structure by serving as an austenite-stabilizing element. However, when the C content is less than 0.02%, the precipitation of carbides is insufficient and the amount of δ-ferrite increases, which results in the failure to obtain the satisfactory creep strength and toughness. However, when C is contained excessively in an amount of more than 0.15%, a coarsening of carbides occurs from the early stage of service, thereby resulting in lowering long term creep strength and impairing formability and weldability. Therefore, the upper limit of the C content is set to 0.15%. As a result, the C content is preferably set to 0.05 to 0.13%.

Mn: 0.05 to 1.5%

[0014] Mn is an element effective in serving as a deoxidizer and fixing S, and also serves as an austenite-stabilizing element. In order to obtain these effects, the Mn content must be 0.05% or more. However, the Mn content exceeding 1.5% deteriorates tougness of the steel. Therefore the Mn content is set to 0.05 to 1.5%, preferably 0.05 to 0.7%.

P: 0.03% or less S: 0.015% or less

[0015] P and S, which are impurity elements, are detrimental to hot workability, weldability and toughness. Therefore, it is preferable that the P and S contents are as low as possible but the P content of 0.03% or less and the S content of 0.015% or less do not directly affect the properties of the steel of this invention. Accordingly, the upper limits of P and S contents are set to 0.03% and 0.015%, respectively.

Cr: 8 to 13%

[0016] Cr is an essential element for the steel of this invention to ensure corrosion resistance and oxidation resistance, particularly steam oxidation resistance, at a high temperature. Besides, Cr forms carbides and thereby increases creep strength. Cr also forms tight oxide-film to thereby improve corrosion resistance and oxidation resistance. In order to obtain these effects, the Cr content must be 8% or more. However, an excessive Cr content promotes the formation of δ-ferrite to thereby deteriorate toughness of the steel. Therefore, the upper limit of Cr content is set to 13%. The Cr content is preferably set to 9 to 12%.

W: 1.5 to 4%

[0017] W is one of the main elements serving as a strengthening element of the steel of this invention. W precipitates finely and dispersively in a form of inter-metallic compounds such as the Fe_7W_6 type μ-phase and the Fe_2W type Laves phase during high temperature service, thereby contributing to the improvement of long term creep strength. Furthermore, W is also dissolved partially into Cr-carbides and prevents the carbides from gathering and coarsening, thereby contributing to maintaining strength of the steel. However, an excessive amount of W promotes the formation of δ-ferrite. Therefore, the W content is set to 1.5 to 4%, preferably 2 to 3.5%.

Co: 2 to 6%

[0018] Co is an austenite-stabilizing element and essential for the steel of this invention into which W is intentionally added. Co does not impair creep strength and rather increase creep strength. In this respect, Co differs from Ni which is also an austenite-stabilizing element. In order to attain these effects, Co must be added in an amount of 2% or more but an excessive Co content exceeding 6% lowers remarkably Ac_1 transformation temperature of the steel and impairs creep strength of the steel. Therefore, the Co content is preferably set to 2 to 4%.

V: 0.1 to 0.5%

[0019] V is an important element for the steel of this invention in order to form the fine carbonitrides, thereby contributing to the improvement of creep strength. In order to obtain this effect, the V content must be 0.1% or more, but the effect saturates when the V content is more than 0.5%. Therefore, the V content is set to 0.1 to 0.5%, preferably 0.15 to 0.35%.

Ta: 0.01 to 0.15% Nb: 0.01 to 0.15%

[0020] Ta and Nb, as well as V, form the fine carbonitrides, contributing to the improvement of creep strength. In order to obtain this effect, each of the contents of Ta and Nb must be 0.01% or more, respectively, but the effect saturates when each content is more than 0.15%. Therefore, each of the contents of Ta and Nb is set to 0.01 to 0.15%, preferably 0.01 to 0.1%.

Nd: 0.001 to 0.2%

[0021] Nd is effective to precipitate the carbides such as NdC_2 finely and stably even after used for a long term at a high temperature, thereby contributing greatly to prevent the recovery and softening of a martensite structure and to increase creep strength. In order to obtain these effects, the Nd content must be 0.001% or more but an excessive Nd content exceeding 0.2% deteriorates toughness of the steel. Therefore, the Nd content is set to 0.001 to 0.2%, preferably 0.005 to 0.15%.

N: less than 0.02%

[0022] N, as well as C, serves as an austenite-stabilizing element. However, in the steel containing Nd, when an amount of N increases, a coarse NdN remains as an inclusion in the steel, thereby impairing the improvement effect of creep strength by Nd and also toughness of the steel. Therefore, in order to secure the effect of Nd fully, the upper limit of the N content in the steel must be less than 0.02%. When toughness of the steel is particularly important, it is preferable that the balance of the Nd content and the N content is controlled to satisfy the following formula. The N content is preferably not more than 0.017%.

$$Nd(\%) \leqq 5 \times N(\%) + 0.1(\%)$$

B: 0.0005 to 0.02%

[0023] B has an effect of precipitating the $M_{23}C_6$ type carbide finely and dispersively when B is added in a small amount. Thus, B contributes to the improvement of the high temperature long term creep strength. B is also effective in increasing the quench-hardening property, especially for a steel product having a heavy wall whose cooling speed after a heat-treatment is slow, thereby attaining an important role in securing high temperature strength. This effect becomes remarkable when the B content is 0.0005% or more, but the B content exceeding 0.02% forms the coarse precipitations, thereby lowering toughness of the steel. Therefore, the B content is set to 0.0005 to 0.02%, preferably 0.002 to 0.01%.

Al: 0.001 to 0.05%

[0024] Al must be contained in an amount of 0.001% or more for serving as a deoxidizer in the molten steel. However, an excessive Al content exceeding 0.05% lowers creep strength. Therefore, the Al content is set to 0.001 to 0.05%, preferably 0.001 to 0.03%.

Si: 0 to 1%

[0025] Si is optionally added to serve as a deoxidizer in the molten steel. Si is effective to increase steam oxidation resistance at a high temperature. However, since an excessive Si content exceeding 1% deteriorates toughness of the steel, the Si content is set to 0 to 1%. When steam oxidation resistance is particularly important, it is preferable that the Si content is 0.1% or more.

Mo: 0 to 1%

[0026] Mo is an optional element which contributes to the improvement of creep strength by serving as a solution strengthening element. However, the Mo content exceeding 1% accelerates to precipitate an inter-metallic compound such as the Laves phase. In the steel containing Mo, the inter-metallic compound precipitates very coarsely, which thereby does not contribute to the improvement of creep strength and also lowers toughness of the steel after aging. Therefore, the Mo content is set to 0 to 1%.

Ca: 0 to 0.02%	La: 0 to 0.2%	Ce: 0 to 0.2%
Y : 0 to 0.2%	Hf: 0 to 0.2%	

[0027] At least one element selected from Ca, La, Ce, Y and Hf is optionally added. These elements are effective in improving creep strength and also hot workability of the steel by strengthening the grain boundaries even if the amount of the addition is very little. However, excessive amount of these elements deteriorates hot workability of the steel. Therefore, the upper limit of the Ca content is set to 0.02% and each of the upper limits of La, Ce, Y and Hf is set to 0.2%, respectively.

Examples

[0028] The present invention will next be described in detail by way of various examples but these examples should not be construed as limiting the invention.

[0029] The steels having the chemical composition shown in Table 1 and Table 2 were melted in a vacuum induction furnace and cast into the 50Kg ingots with a diameter of 144mm. In the tables, the steel No.1 to No.23 are the examples of the steel of this invention and the steel A to Q are the comparative examples.

Table 1

(Balance: Fe, mass %)

Steel No.	C	Si	Mn	P	S	Cr	Co	W	Mo	Nd	V	Ta	Nb	N	B	Al	others	Nd-5N-0.10 value
1	0.082	0.18	0.20	0.015	0.003	10.95	2.90	3.05	-	0.05	0.20	0.05	0.06	0.005	0.0025	0.008		-0.065
2	0.083	0.17	0.18	0.015	0.003	10.90	2.87	3.07	-	0.05	0.21	0.05	0.05	0.012	0.0027	0.006		-0.110
3	0.079	0.16	0.22	0.016	0.003	10.98	2.93	3.10	-	0.05	0.21	0.06	0.06	0.018	0.0025	0.006		-0.140
A	0.080	0.18	0.25	0.015	0.002	10.90	2.90	3.05	-	0.05	0.21	0.05	0.06	0.045*	0.0030	0.007		-0.275
4	0.091	0.25	0.23	0.017	0.003	10.45	2.33	2.85	-	0.10	0.19	0.05	0.06	0.004	0.0045	0.005		-0.020
5	0.093	0.25	0.26	0.016	0.002	10.40	2.36	2.86	-	0.11	0.21	0.05	0.05	0.012	0.0043	0.006		-0.050
6	0.090	0.23	0.24	0.015	0.002	10.45	2.30	2.90	-	0.12	0.20	0.06	0.06	0.017	0.0040	0.006		-0.065
B	0.093	0.26	0.25	0.016	0.001	10.48	2.35	2.90	-	0.12	0.20	0.05	0.06	0.043*	0.0042	0.005		-0.195
7	0.102	0.35	0.45	0.013	0.001	10.85	3.50	3.25	-	0.18	0.17	0.08	0.06	0.010	0.0028	0.010		0.030
C	0.103	0.37	0.48	0.013	0.001	10.80	3.52	3.27	-	0.18	0.17	0.08	0.05	0.038*	0.0027	0.008		-0.110
8	0.100	0.23	0.25	0.015	0.001	10.40	3.50	2.52	0.15	0.05	0.22	0.05	0.06	0.013	0.0038	0.010		-0.115
D	0.098	0.23	0.24	0.014	0.001	10.35	3.52	2.54	0.17	0.05	0.21	0.05	0.06	0.043*	0.0040	0.008		-0.265
9	0.050	0.11	0.27	0.018	0.003	8.63	2.30	1.75	-	0.08	0.15	0.05	0.06	0.015	0.0018	0.007		-0.095
E	0.053	0.10	0.24	0.019	0.003	8.58	2.32	1.79	-	0.08	0.15	0.05	0.06	0.055*	0.0018	0.006		-0.295
10	0.135	0.55	0.27	0.013	0.001	12.13	5.38	3.50	-	0.08	0.22	0.10	0.07	0.007	0.0070	0.013		-0.055
F	0.137	0.57	0.24	0.010	0.001	12.15	5.36	3.55	-	0.08	0.21	0.11	0.07	0.042*	0.0073	0.015		-0.230
11	0.090	0.26	1.35	0.013	0.002	10.85	3.20	3.03	-	0.05	0.22	0.02	0.05	0.007	0.0030	0.010		-0.085
G	0.088	0.26	1.38	0.010	0.001	10.90	3.16	3.05	-	0.04	0.23	0.02	0.06	0.028*	0.0033	0.009		-0.200
12	0.090	0.26	0.35	0.013	0.001	10.45	3.25	3.15	-	0.05	0.22	0.05	0.06	0.010	0.0028	0.008	Ca:0.0045	-0.100
H	0.093	0.23	0.32	0.015	0.001	10.35	3.28	3.10	-	0.05	0.22	0.06	0.06	0.045*	0.0030	0.011	Ca:0.0048	-0.275

The mark* shows outside the range defined by the present invention.
Steels No.1 to 12: Examples of the present invention. Steels No. A to H: Comparative examples

Table 2

(Balance:Fe, mass %)

Steel No.	C	Si	Mn	P	S	Cr	Co	W	Mo	Nd	V	Ta	Nb	N	B	Al	Others	Nd-5N-0.10 value
13	0.078	0.20	0.35	0.017	0.003	10.30	3.02	2.86	-	0.10	0.20	0.10	0.05	0.006	0.0052	0.004	La:0.050	-0.030
I	0.081	0.19	0.35	0.016	0.003	10.32	3.05	2.83	-	0.11	0.20	0.09	0.06	0.054*	0.0053	0.006	La:0.053	-0.260
14	0.105	0.28	0.37	0.012	0.002	10.78	3.26	3.12	-	0.07	0.22	0.03	0.05	0.008	0.0042	0.014	Ce:0.034	-0.070
J	0.105	0.26	0.40	0.012	0.001	10.73	3.34	3.12	-	0.08	0.20	0.02	0.06	0.038*	0.0043	0.012	Ce:0.036	-0.210
15	0.110	0.20	0.23	0.015	0.001	10.23	3.13	3.50	-	0.07	0.18	0.05	0.07	0.013	0.0040	0.011	Y:0.017	-0.095
K	0.113	0.19	0.20	0.013	0.001	10.20	3.17	3.62	-	0.08	0.19	0.04	0.07	0.058*	0.0044	0.008	Y:0.020	-0.310
16	0.090	0.20	0.25	0.010	0.001	9.80	2.98	2.87	-	0.09	0.25	0.07	0.05	0.010	0.0022	0.004	Hf:0.025	-0.060
L	0.093	0.20	0.28	0.010	0.001	9.78	2.95	2.83	-	0.09	0.24	0.07	0.04	0.046*	0.0020	0.006	Hf:0.028	-0.240
17	0.097	0.28	0.46	0.015	0.001	10.60	3.26	3.03	-	0.11	0.22	0.05	0.06	0.006	0.0032	0.007		-0.020
18	0.100	0.29	0.45	0.015	0.001	10.55	3.28	3.08	-	0.18	0.21	0.04	0.06	0.006	0.0032	0.009		0.050
19	0.088	0.25	0.40	0.014	0.001	10.85	2.75	2.53	-	0.15	0.20	0.03	0.06	0.014	0.0054	0.013		-0.020
20	0.091	0.26	0.44	0.016	0.001	10.81	2.70	2.47	-	0.19	0.20	0.03	0.06	0.014	0.0056	0.014		0.020
21	0.078	0.38	0.34	0.013	0.001	10.38	3.10	1.80	0.45	0.13	0.24	0.07	0.07	0.010	0.0032	0.027		-0.020
22	0.080	0.40	0.43	0.015	0.001	10.41	3.14	1.76	0.43	0.17	0.24	0.07	0.06	0.010	0.0032	0.029		0.020
23	0.062	0.25	0.41	0.008	0.001	10.12	5.23	3.78	-	0.10	0.22	0.10	0.05	0.004	0.0010	0.005	Ca:0.0075, Y:0.0087	-0.020
24	0.065	0.26	0.36	0.009	0.001	10.10	5.20	3.78	-	0.15	0.23	0.11	0.07	0.004	0.0009	0.007	Ca:0.0073, Y:0.0090	0.030

The mark* shows outside the range defined by the present invention.
Steels No. 13 to 23 : Examples of the present invention Steels No. I to Q : Comparative examples

[0030] These steel ingots were hot-forged and then hot-rolled to the steel plates with a thickness of 20mm. The steel plates were heated at 1050°C for 1 hour and then air-cooled. After that, the steel plates were heated for a temper treatment at 780°C for 1 hour and air-cooled. The creep rupture test specimens and the Charpy impact test specimens were prepared from the thus-obtained steel plates and the creep rupture tests and the Charpy impact tests were carried out under the following conditions.

(1) Creep rupture test

Specimen: Diameter 6.0mm, Gage length 30mm
Test temperature: 650°C
Applied stress: 98 MPa

(2) Chary impact test

Specimen: 10mmX10mmX55mm, 2mm V-notch
Test temperature: 0°C

[0031] The creep rupture time and the Charpy impact value(J/cm^2) obtained by the above-mentioned tests are shown in Table 3 and Table 4.

Table 3

(Examples of the present invention)		
Steel No.	Creep rupture time 650° C x 98 MPa (hrs)	Charpy impact value* at 0° C (J/cm^2)
1	18789.5	186
2	18502.3	190
3	17462.0	196
4	19711.2	178
5	19465.7	170
6	19396.0	175
7	20035.3	150
8	17690.0	185
9	16683.7	205
0	21475.5	160
1	17180.3	178
2	19334.0	195
3	18863.7	202
4	20181.5	195
5	22430.0	170
6	20003.7	175
7	19499.0	183
8	19023.0	150
9	18753.7	178
0	18552.5	148
1	17263.5	195
2	17022.0	165
3	23176.3	170
4	23105.3	150

* : The specimens were prepared from the steel in normalized and tempered condition.

Table 4

(Comparative examples)		
Steel No.	Creep rupture time 650° C x 98 MPa (hrs)	Charpy impact value* at 0° C (J/cm^2)
A	15172.0	180
B	16123.5	170
C	16547.7	143
D	15120.3	183
E	13489.3	200
F	16362.0	150
G	13896.7	175
H	16501.3	187
I	15141.4	195
J	15859.7	187
K	16724.0	165
L	15879.5	173

* : The specimens were prepared from the steel in normalized and tempered condition.

[0032] It can be found that the creep rupture times of the steel No.1 to 3 and No.4 to 6, which are the examples of this invention containing N of less than 0.02%, are significantly improved in comparison with the steels A and B, which are the comparative examples containing N exceeding the amount defined by this invention. The effect of the improvement in creep rupture life by reducing the N content is obvious in the steels No.7 to 17, which are the examples of this invention, when they are compared with the steels C to M, which are the comparative examples corresponding to the steels No.7 to 17, respectively.

[0033] In the steels N, O, P and Q, which are the comparative examples, the contents of Nd and N do not satisfy the following formula. In this case, comparing with the steels No.17, 19, 21 and 23, which are the examples of this invention and satisfy the following formula, it can be found that there is almost no difference in creep rupture life, but the impact value is lower. Therefore, when toughness of the steel is important, it is preferable to control the contents of Nd and N within the range satisfying the following formula.

$$\mathrm{Nd}(\%) \leqq 5 \times \mathrm{N}(\%) + 0.1(\%)$$

INDUSTRIAL APPLICABILITY

[0034] The heat resistant high Cr ferritic steel according to the present invention is excellent in high temperature long term creep strength at a high temperature of 625°C or more and in toughness at room temperature and thus can achieve superior performance as a material for a heat resistant steel tube and pipe, a pressure vessel steel plate and a turbine steel member used in a field of a nuclear power plant and a chemical plant. Therefore, this steel has a great advantage for an industrial application.

Claims

1. A heat resistant high Cr ferritic steel excellent in high temperature long term creep strength and toughness, which comprises, in mass %,

C : 0.02 to 0.15%	Mn: 0.05 to 1.5%
P : 0.03% or less	S : 0.015% or less
Cr: 8 to 13%	W : 1.5 to 4%
Co: 2 to 6%	V : 0.1 to 0.5%
Ta: 0.01 to 0.15%	Nb: 0.01 to 0.15%
Nd: 0.001 to 0.2%	N : less than 0.02%
B : 0.0005 to 0.02%	Al: 0.001 to 0.05%
Mo: 0 to 1%	Si: 0 to 1%
Ca: 0 to 0.02%	La: 0 to 0.2%
Ce: 0 to 0.2%	Y : 0 to 0.2%
Hf: 0 to 0.2%,	

the contents of Nd and N satisfying the following formula, and the balance being Fe and incidental impurities.

$$Nd(\%) \leqq 5 \times N(\%) + 0.1(\%)$$

2. A ferritic steel according to claim 1, wherein the W content is 2 to 3.5%.

3. A ferritic steel according to claim 1 or 2, wherein the V content is 0.15 to 0.35% and the Nd content is 0.005 to 0.15%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/03231

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^6 C22C38/32

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)
Int.Cl^6 C22C38/00-38/32

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	1994-1999
Kokai Jitsuyo Shinan Koho	1971-1999	Jitsuyo Shinan Toroku Koho	1994-1999

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 8-85849, A (Sumitomo Metal Industries,Ltd.), 2 June, 1996 (02. 06. 96), Page 2, column 1 & EP, 703301, A	1-3
A	JP, 7-331389, A (Kawasaki Steel Corp.), 19 December, 1995 (19. 12. 95), Page 2, column 1 (Family: none)	1-3
A	JP, 9-71845, A (Sumitomo Metal Industries,Ltd.), 18 March, 1997 (18. 03. 97), Page 2, column 1 (Family: none)	1-3
A	JP, 9-71846, A (Sumitomo Metal Industries,Ltd.), 18 March, 1997 (18. 03. 97), Page 2, column 1 (Family: none)	1-3
A	JP, 8-85850, A (Sumitomo Metal Industries,Ltd.), 2 April, 1996 (02. 04. 96), Page 2, column 1 (Family: none)	1-3

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier 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 14 September, 1999 (14. 09. 99)	Date of mailing of the international search report 28 September, 1999 (28. 09. 99)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)