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(71) Applicant: **SUMITOMO METAL INDUSTRIES, LTD.**
Osaka-shi, Osaka-fu 540 (JP)

(72) Inventors:
- **Takabe, Hideki**
  Hannan-shi, Osaka, 599-02 (JP)
- **Sawaragi, Yoshiatsu**
  Nishinomiya-shi, Hyogo, 663 (JP)

(74) Representative: **TER MEER - MÜLLER - STEINMEISTER & PARTNER**
Mauerkircherstrasse 45
D-81679 München (DE)

(54) A high-chromium ferritic steel excellent in high-temperature ductility and strength

(57) A high Cr ferritic steel of this invention is excellent in ductility and strength at elevated temperatures and consists of by weight, 0.02 to 0.15% C, up to 0.5 Si, 0.1 to 1.5% Mn, up to 0.025% P, up to 0.015% S, up to 0.005% O, 8 to 14% Cr, 0.1 to 0.3% V, 0.01 to 0.2% Nb, 0.01 to 0.1% N, up to 0.05% Al, 0.001 to 0.02% B, 0.05 to 3.0% Cu, 1.0 to 5.0% Co, one or both of 0.01 to 1.2% Mo and 0.8 to 3.5% W, and the balance being Fe and incidental impurities, wherein the relationship between the Cu and Co content is defined so as to satisfy the following formula (1).

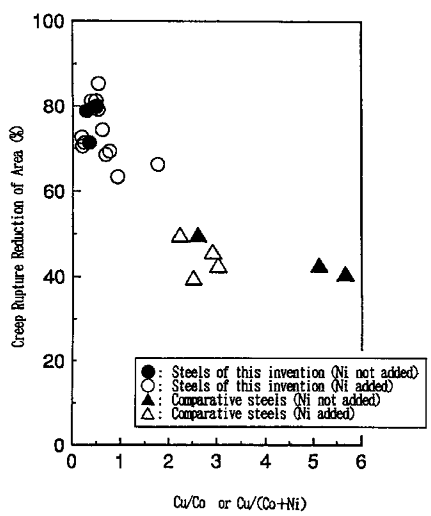
$$Cu/Co \leqq 2.0 \qquad (1)$$

The steel may further contain 0.1 to 1.5% Ni by weight, wherein the proportion of Ni, Cu and Co content is defined so as to satisfy the following formula (2).

$$Cu/(Co + Ni) \leqq 2.0 \qquad (2)$$

If Cu, Co and optionally Ni are contained in the steel in well-balanced proportions, the high creep rupture ductility and strength of the steel can be sustained at high temperatures and for long periods of time.

Fig—1



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Description

FIELD OF THE INVENTION

This invention relates to a high Cr ferritic heat resistant steel excellent in creep rupture strength and creep rupture ductility (elongation, reduction of area). The steel of this invention is particularly useful for heat resistant and high pressure resistant articles in boilers and chemical plants.

DESCRIPTION OF THE PRIOR ART

Heat resistant steels for use heat exchanger tubes, heat and high pressure resistant pipings or such equipment in boilers, chemical plants etc. are required to be excellent in high temperature strength, corrosion and oxidation resistance, toughness workability and weldability, as well. These heat resistant steels are also required to be economically produced and to be low cost.

Among the conventional materials for use in the above-mentioned applications, there are certain austenitic stainless steels, 2 · 1/4Cr-1Mo steel and similar low alloyed steels and high Cr ferritic steels containing 9 to 12% Cr. In particular, the high Cr ferritic steels are better from the point of view of tensile strength, corrosion resistance and oxidation resistance at temperatures between 500 and 650 °C when compared to ordinary low alloyed steels. The high Cr ferritic steels are also excellent for thermal fatigue resistance and stress corrosion cracking resistance due to their low thermal expansion coefficient and they can be produced more cheaply than austenitic stainless steels.

Known high Cr ferritic steels include 9Cr-1Mo steel (JIS STBA 26), modified 9Cr-1Mo steel (ASTM SA 213 T91) and 12Cr-1Mo steel (DIN X20CrMoV121).

There are certain ferritic steels containing some Cu in addition to 9 to 12% Cr, which were developed by the inventors of this invention, and disclosed in the Japanese Patent Public Disclosure (JPPD)2-232345 and JPPD 3-9783.

Such Cu containing high Cr steels exhibit not only the above-mentioned high oxidation resistance but also the following three kinds of excellent physical properties, i.e.,

(1) The formation of δ ferrite, which is detrimental to the toughness of the steel, can be suppressed.
(2) The lowering of the Ac_1 transformation point can be suppressed so that a high temperature tempering treatment can be applied to the steel, and a stable and lasting creep strength at elevated temperature can be obtained.
(3) The softening of the welded steel in HAZ (heat affected zone) can be suppressed.

If Cu and Ni in high Cr ferritic heat resistant steel are defined so as to satisfy the following relationship of

$$2.5\% \leqq Cu/Ni \leqq 4.5\%,$$

the resultant steel can be protected from a defect of copper checking, which results when the steel is subjected to hot working (JPPD 5-17850).

However, there still remain certain problems such as a reduction in creep rupture ductility and creep rupture strength, and three types of these steels are subject to creep rupture over long periods of time.

SUMMARY OF THE INVENTION

The purpose of this invention is to provide a high Cr ferritic steel with both improved creep rupture ductility and creep rupture strength sustainable, in conditions of long-sustained creep rupture, without diminishing the effect of Cu addition to the steel.

The high Cr ferritic steel according to this invention is excellent in ductility and strength at elevated temperatures and consists essentially of, by weight, 0.02 to 0.15% C, up to 0.5% Si, 0.1 to 1.5% Mn, up to 0.025% P, up to 0.015% S, up to 0.005% O (oxygen), 8 to 14% Cr, 0.1 to 0.3% V, 0.01 to 0.2% Nb, 0.01 to 0.1% N, up to 0.05% Al, 0.001 to 0.02% B, 0.05 to 3.0% Cu, 1.0 to 5.0% Co, one or both of 0.01 to 1.2% Mo and 0.8 to 3.5% W, the balance being Fe and incidental impurities, wherein the relationship between Cu and Co contents is defined so as to satisfy the following formula (1).

$$Cu/Co \leqq 2.0 \qquad (1)$$

The above-mentioned high Cr ferritic steel may additionally contain, 0.1 to 1.5% Ni by weight, and the relationship between the Ni, Cu and Co contents needs to be defined so as to satisfy the following formula (2).

$$Cu / (Co + Ni) \leqq 2.0 \qquad (2)$$

The following (1) and (2) have been discovered by replacing a part or whole of Ni with Co content in the high Cr ferritic steel:

(1) The lowering of Ac_1 transformation temperature can be suppressed, thus enabling tempering treatment at such elevated temperatures that are required to obtain lasting and stable creep rupture strength and accordingly improved creep rupture ductility, as well.

(2) Any intergranular precipitation of Cu containing compound can be suppressed without diminishing the effect of soluble Cu, as long as the relationship between the Cu and Co content is controlled according to the above-mentioned formula (1), and also as long as the relationship between the Ni, Cu and Co content is controlled according to formula (2) above. The result is the above-mentioned high quality high Cr ferritic steel.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 shows the relationship between the Co/Cu ratio or the [Cu/(Co + Ni)] ratio and the creep rupture reduction of area (%) in the creep rupture test conducted at 600 °C under $16kgf/mm^2$ applied stress.

Figure 2 shows the relationship between the Co/Cu ratio or the [Cu/(Co + Ni)] ratio and creep rupture time (in hours) in the creep rupture test conducted at 600 °C under $16kgf/mm^2$ applied stress.

Figure 3 shows both the relationship between the Ni/Co ratio and creep rupture time (in hours) in the creep rupture test conducted at 600°C under $16kgf/mm^2$ applied stress, and the relationship between the Ni/Co ratio and the creep rupture reduction of area (%) in the same creep rupture test.

DETAILED DESCRIPTION OF THE INVENTION

Now the behavior and function of each alloying element in the steel of this invention will be described in more detail as well as the technical reason for defining the content of each alloying element, wherein any " % " represents "weight percent".

C ; 0.02 to 0.15%

Part of the C combines with any alloying element of Cr, Fe, Mo, W, V and Nb to form a carbide thereof, and consequently increasing the resultant steel's high temperature strength. The remainder of the C forms a solid solution in a matrix of the steel and serves to stabilize an austenite in the matrix. If the C content is not more than 0.02%, precipitation of the carbide is not enough and an amount of δ ferrite unfavorably increases in the matrix, resulting in a lowering of the strength and toughness of the steel. On the other hand, if the C content exceeds 0.15%, excess amounts of the carbides will be precipitated in the matrix, and the resultant steel will be too hard, which will result in a lowering of weldability and the workability thereof. The C content is therefore restricted to a range of 0.02 to 0.15%.

Si ; up to 0.5%

Si serves as a deoxidizing agent in molten steel and increases the resistance of the steel to an attack of oxidizing water vapor. If the Si content exceeds 0.5%, the toughness of the resultant steel is markedly reduced. An excessive amount of Si is also detrimental to the creep rupture strength of steel. In order to avoid causing an embrittlement of steel, particularly on thicker steel sheets, due to long sustained heating, the Si content should be suppressed to a lower level. Accordingly, the Si content is restricted so that it does not exceed 0.5%.

Mn ; 0.1 to 1.5%

Mn serves to improve the hot workability of steel and also to stabilize the structure. The addition of less than 0.1% Mn cannot fully produce these effects on steel. On the other hand, the addition of more than 1.5% Mn needlessly hardens steel and results in a decrease in workability and weldability. Accordingly, the Mn content is defined to a range of 0.1 to 1.5%.

Cr ; 8 to 14%

Cr is one of the indispensable elements for maintaining oxidation and corrosion resistance at high temperatures. If the Cr content is not more than 8%, the desired degree of oxidation and high temperature corrosion resistance is not obtained. On the other hand, if the Cr content exceeds 14%, the amount of δ ferrite increases to such an extent that the strength, workability and toughness of steel is lowered. In view of the circumstances, the Cr content is defined to a range of 8 to 14%.

V ; 0.1 to 0.3%

V combines with the C and N to form fine precipitates of V(C,N), which contribute to increase the creep strength at a high temperature and under long sustained applied stress. If the V content is less than 0.1%, these effects will not be fully obtained. On the other hand, if the V content is higher than 0.3%, the V will tend to form a solid solution in the matrix resulting in diminished strength. The V content is therefore defined to a range of 0.1 to 0.3%.

Nb ; 0.01 to 0.2%

Nb also combines with the C and N to form fine precipitates of the Nb(C,N) which contribute to heighten the creep strength of the resultant steel. The fine precipitate of Nb(C,N) is also effective in improving the toughness of the steel.

Less than 0.01% of Nb cannot achieve the above-mentioned effects, while more than 0.2% of Nb increases NbC in the unsolved or precipitated state, resulting in a reduction of strength, ductility and weldability. Accordingly, the Nb content is restricted to a range of 0.01 to 0.2%.

N (nitrogen); 0.01 to 0.1%

N combines with the V and Nb to form a carbonitride thereof, which increases the creep strength of the steel. If the N content is less than 0.01%, the above-mentioned effects will not result. On the other hand, an addition of more than 0.1% N markedly decreases the creep ductility, weldability and workability. The N content is therefore restricted to a range of 0.01 to 0.1%.

Al ; up to 0.05%

Al is added to the molten steel as a deoxidizing agent. If the Al exceeds 0.05%, the creep strength is reduced. The Al content is therefore restricted to a range of not more than 0.05%.

B (boron); 0.001 to 0.2%

An additional very small amount of B improves the hardenability of the resultant steel and serves to strengthen the grain boundaries of the structure of the steel due to the B carbide which is precipitated uniformly along the grain boundaries, thus enabling the steel to have a high tensile strength at elevated temperatures for long periods of time.

Less than 0.001% of B cannot achieve the above-mentioned effects, while more than 0.2% of B decreases workability and weldability.

Cu ; 0.05 to 3.0%

Cu is a characteristic element of this steel. It exhibits the following effects:

(1) The formation of δ ferrite is suppressed, and the toughness of steel is improved.
(2) Oxidation and corrosion resistance at temperatures higher than 600 °C are improved.
(3) The formation of any softened layer in an HAZ (heat affected zone) is suppressed thereby improving the creep strength of welded joints.

Less than 0.05% of Cu cannot achieve the above-mentioned effects. On the other hand, more than 3.0 % of Cu will precipitate along the grain boundaries of the steel while it is exposed to creep forming conditions, and the ductility of the resultant steel will be markedly reduced. Therefore, the Cu content is restricted to a range of 0.05 to 3.0%.

Co ; 1.0 to 5.0%

Co is also a characteristic element in steel, which suppresses the diffusion of Cu in the steel matrix while steel is exposed to a creep forming circumstance, thereby preventing a decrease in creep ductility. The Co combines with the C to form fine precipitates of the resultant Co carbide, which contributes to improving the creep strength of the steel. Since Co in steel hardly lowers the Ac_1 transformation point unlike in the case of Ni, the steel can be subjected to a high temperature tempering treatment which also contributes to improving the creep strength. All these effects can not be obtained if the Co content is less than 1.0%. On the other hand, if the Co content exceeds 5.0%, the Co carbide is coarsened so that the creep strength of steel is lowered. Accordingly, the Co content is restricted to a range of 1.0 to 5.0%.

Ni ; 0.1 to 1.5%

Ni is an optional element and added to the steel of Claim 2 of this invention. Ni is also a characteristic element of steel, which suppresses the diffusion of Cu in the steel matrix while steel is exposed to a creep forming circumstance, thereby preventing a decrease in creep ductility. Ni is one of the austenite stabilizing elements and suppresses the formation of δ ferrite and stabilizes the martensitic structure. These effects cannot be obtained when the Ni content is less than 0.1%, whereas more than 1.5% Ni undesirably lowers the Ac_1 transformation point, which makes the resultant steel incapable of being fully tempered and produces a precipitation of coarse carbide, resulting in a lowering of the creep strength. The Ni content is therefore restricted to a range of 0.1 to 1.5%.

$Cu/Co \leq 2.0$; $[Cu/(Co + Ni)] \leq 2.0$:

The contents of Cu, Ni or Co must be in accordance with the above-mentioned two relationships, and the contents must be within the restricted ranges. All these three elements are concerned with creep ductility. If the Cu is exclusively added to steel without adding the other two elements, the Cu will precipitate along the grain boundaries of the steel while it is exposed to creep forming conditions, and the ductility of the resultant steel will be markedly reduced. On the other hand, if Cu is added to the steel together with suitable amounts of Co or Co and Ni, the precipitation of the Cu along the grain boundaries of the steel, which is detrimental to the ductility, can be controlled. If the Co content or Co plus Ni content is suppressed to a low level and the above-mentioned relationships are not satisfied by these alloying elements, the precipitation of Cu along the grain boundaries will not be suppressed even by adding Co + Ni. The content of these three elements is therefore restricted to satisfy the above-mentioned relationships.

As mentioned before, Co, which is almost incapable of lowering the Ac_1 point but capable of accelerating the precipitation of fine carbide, makes it possible to apply a tempering treatment to the resultant steel at higher temperatures and also improves the creep strength, whereas Ni cannot exhibit such behavior and can not have the same effect on steel. Therefore, if Co and Ni are both added to steel, in order to improve the creep strength and keep the creep strength as it is, the Co content should be much higher than the Ni content.

Mo ; 0.01 to 1.2%

The steel of this invention further contains either or both Mo and W. Mo improves the creep strength of steel by strengthening the matrix with a solid solution of Mo therein and by dispersing the precipitates of the fine carbide in the matrix. These effects are not obtained with less than 0.01% Mo content. On the other hand, if the Mo content exceeds 1.2%, the δ ferrite is produced excessively and the steel hardens which diminishes toughness, ductility and workability.

Mo content is therefore restricted to a range of 0.01 to 1.2%.

W ; 0.8 to 3.5%

W is also effective in increasing the creep strength of steel by strengthening the matrix with a solid solution of W therein and by dispersing the precipitates of the fine W carbide in the matrix. The W content usually needs to be twice as high as the Mo content. If the W content exceeds 3.5%, the toughness of the resultant steel will be significantly decreased due to the formation of δ ferrite. On the other hand, less than 0.8% of W content cannot fully produce the above-mentioned properties. Accordingly, the W content is confined to a range of 0.8 to 3.5%. In addition, the combined addition of Mo and W is much more effective in exhibiting such properties than the sole addition of Mo or W. The relationship between the Mo and W contents is preferably defined as $Mo + 1/2\ W = 1.2$ to 2.0%.

P ; up to 0.025%

P is a detrimental impurity in steel, and the toughness, workability and weldability of steel can be maintained at a desired level by maintaining the P content at or below 0.025%.

S ; up to 0.015%

S is also a detrimental impurity in steel, and the toughness, workability and weldability of the steel can be maintained at a desired level by suppressing the S content to not more than 0.015%.

O (oxygen) ; up to 0.005%

O is also a detrimental impurity in steel, and the toughness, workability and weldability of steel can be maintained at a desired level by suppressing the O content to not more than 0.005%.

EXAMPLE

Two series of steel ingots having the chemical compositions listed in Table 1, which were obtained from a vacuum melting furnace of 150kg capacity, were forged at 1150 to 950 °C into plates of 15mm thickness. Marks A to Q refer to the steel plate test specimens according to this invention and Marks 1 to 11 refer to test specimens of comparative examples.

Test Specimens A to Q and 1 to 11 were normalized by heating them at a temperature of 1050 °C for 1 hour and they were then air cooled, and tempered at 750°C to 830 °C for 3 hours.

After being heat-treated as above, each test specimen of 6mm diameter and 30mm gauge length was shaved off from the steel plates, and subjected to a creep rupture test wherein the test specimen was kept at 600°C under 16kgf/mm^2 applied stress for 250,000 hours at the longest.

The creep rupture time, elongation and reduction of area were measured and the test results are set forth in Table 2.

TABLE 1

* Mark	Chemical Composition (weight %, balance : Fe and impurities, oxygen content is below 0.0005 %)															** Formula 1	*** Formula 2
	C	Si	Mn	P	S	Ni	Cr	Mo	W	V	Nb	Al	Cu	N	Co	B		
A	0.11	0.072	0.49	0.016	0.001	0.35	10.78	0.29	2.25	0.26	0.069	0.034	0.98	0.068	1.10	0.0027	0.68	0.318
B	0.12	0.068	0.48	0.016	0.003	0.19	11.02	0.30	1.83	0.25	0.070	0.030	0.51	0.056	1.95	0.0025	0.24	0.097
C	0.12	0.070	0.49	0.018	0.002	0.38	10.85	0.27	2.21	0.23	0.069	0.025	1.32	0.060	1.35	0.0041	0.76	0.281
D	0.10	0.069	0.50	0.015	0.001	0.95	9.98	0.29	2.42	0.19	0.091	0.032	2.76	0.055	2.01	0.0033	0.93	0.475
E	0.11	0.052	0.48	0.015	0.003	0.32	13.21	0.26	1.98	0.22	0.069	0.027	1.01	0.067	4.83	0.0015	0.20	0.066
F	0.07	0.45	0.53	0.021	0.002	0.28	11.05	0.15	2.21	0.17	0.056	0.045	0.98	0.035	2.11	0.0025	0.41	0.133
G	0.10	0.020	0.21	0.027	0.002	0.15	10.69	0.31	3.21	0.22	0.072	0.004	0.52	0.002	2.54	0.0043	0.19	0.059
H	0.09	0.067	0.52	0.017	0.001	0.68	10.72	0.68	2.12	0.22	0.068	0.023	2.98	0.078	1.01	0.0022	1.76	0.673
I	0.12	0.053	1.32	0.005	0.003	0.83	12.15	0.34	2.15	0.25	0.031	0.015	2.10	0.055	2.59	0.0055	0.61	0.320
J	0.12	0.055	0.56	0.011	0.004	0.61	8.53	0.27	2.83	0.26	0.120	0.031	1.62	0.063	3.52	0.0100	0.39	0.173
K	0.08	0.42	0.49	0.017	0.001	–	11.07	0.55	1.69	0.21	0.066	0.022	0.51	0.066	1.51	0.0152	0.34	0
L	0.11	0.051	0.46	0.015	0.001	–	10.86	0.25	2.24	0.18	0.071	0.011	1.02	0.052	3.66	0.0064	0.28	0
M	0.10	0.055	0.47	0.016	0.003	0.98	11.07	0.41	1.67	0.23	0.065	0.017	0.96	0.059	1.01	0.0025	0.48	0.970
N	0.09	0.049	0.49	0.011	0.002	0.49	11.05	0.42	1.98	0.22	0.066	0.023	1.01	0.060	1.44	0.0023	0.52	0.340
O	0.11	0.052	0.51	0.009	0.004	0.31	11.07	0.40	2.01	0.22	0.066	0.015	0.98	0.070	1.68	0.0023	0.49	0.185
P	0.08	0.048	0.48	0.010	0.003	0.12	11.12	0.42	1.97	0.21	0.063	0.022	1.02	0.063	1.81	0.0025	0.53	0.066
Q	0.10	0.051	0.50	0.012	0.003	–	11.06	0.39	1.99	0.20	0.065	0.020	0.97	0.056	1.97	0.0026	0.49	0
1	0.10	0.48	0.47	0.024	0.002	0.55	10.54	0.30	2.02	0.22	0.069	0.030	2.41	0.063	0.41	0.0008	2.51	1.341
2	0.11	0.061	0.48	0.021	0.002	0.41	11.02	0.28	2.09	0.18	0.120	0.015	1.30	0.070	0.02	0.0023	3.02	20.500
3	0.10	0.060	0.56	0.004	0.001	0.53	10.54	0.28	2.01	0.20	0.090	0.008	1.54	0.045	–	0.0060	2.91	–
4	0.08	0.053	0.43	0.013	0.002	0.42	11.15	0.27	2.01	0.19	0.115	0.007	1.78	0.052	0.38	0.0033	2.23	1.105
5	0.11	0.064	0.49	0.021	0.003	2.07	12.01	0.31	2.41	0.25	0.069	0.005	0.31	0.060	4.65	0.0045	0.05	0.445
6	0.09	0.062	0.50	0.024	0.001	0.45	10.78	0.25	2.35	0.24	0.070	0.036	1.15	0.073	6.35	0.0027	0.17	0.071
7	0.07	0.061	0.29	0.022	0.002	1.25	12.15	0.31	2.55	0.19	0.069	0.005	5.01	0.055	2.91	0.0055	1.20	0.430
8	0.14	0.070	0.48	0.007	0.001	0.28	10.86	0.30	2.38	0.19	0.068	0.004	1.07	0.052	4.53	–	0.22	0.062
9	0.10	0.30	0.40	0.019	0.001	–	11.03	0.26	2.20	0.18	0.065	0.009	2.55	0.055	0.98	0.0062	2.60	0
10	0.09	0.052	0.49	0.017	0.002	–	10.98	0.21	2.25	0.24	0.050	0.016	2.81	0.058	0.55	0.0058	5.11	0
11	0.11	0.15	0.49	0.017	0.002	–	12.07	0.23	2.21	0.27	0.050	0.007	1.81	0.061	0.32	0.0067	5.66	0

Note * Marks A–Q : examples of this invention. Marks 1–11 : comparative examples
** Formula 1 : Cu/(Co+Ni)
*** Formula 2 : Ni/Co

TABLE 2

* Mark	Creep Properties at 600°C, 16kgf/mm^2		
	Rupture Time hr.	Elongation %	Reduction of Area %
A	23923.8	25.0	68.5
B	19787.3	22.1	71.3
C	25527.3	27.1	69.3
D	15193.9	24.3	63.3
E	17599.5	25.4	70.5
F	18859.3	32.4	79.4
G	19032.9	22.5	72.6
H	18932.7	24.0	66.2
I	17225.4	19.2	74.4
J	16424.5	20.5	81.2
K	20119.3	23.3	71.3
L	17321.4	17.5	78.8
M	15336.1	33.5	81.3
N	16903.4	27.3	79.1
O	17395.2	22.3	79.8
P	17892.3	25.7	85.3
Q	18503.2	20.1	80.1
1	10356.3	19.0	39.2
2	11270.9	15.7	42.1
3	14211.9	15.2	45.3
4	13095.4	22.4	49.3
5	5321.4	27.3	65.2
6	8083.1	22.5	72.9
7	8503.4	11.4	30.1
8	8361.5	25.3	71.5
9	11380.9	15.8	49.3
10	9873.4	14.7	42.2
11	9600.3	15.2	40.1

Note
* Marks A-Q : examples of this invention Marks 1-11 : comparative examples

It is apparent from Table 2 that all the steels in this invention exhibit excellent creep characteristics.

On the other hand, the Cu, Co and Ni content of Specimens 1 to 4 of the comparative examples, do not satisfy the relationship between the Cu, Co and Ni content, i.e.,

$$[Cu/(Co + Ni)] > 2.0$$

Since the content of these three elements is not well balanced, Specimens 1 to 4 show high creep strength but undesirably low creep ductility.

Test Specimens 5 and 6 satisfy the relationship between Cu, Co and Ni, but the Ni and Co contents are outside the ranges defined in the claims of this invention. Accordingly, the carbides are unfavorably coarsened in creep causing conditions, resulting in a lowering of the creep rupture strength of test specimens 5 and 6.

Specimen 7 has a Cu content which exceeds the upper limit of the range defined in the claims of this invention, and the ductility is therefore not satisfactory. Since Specimen 8 does not contain B which is essential for increasing both creep rupture strength and the hardenability of steel, the creep rupture strength of Specimen 8 is not satisfactory.

Since Test Specimens 9 to 11 in the comparative example do not satisfy the relationship between Cu and Co, i.e., (Cu/Co) > 2.0, and since the contents of these elements are not well balanced, the creep strength and ductility of Test Specimens 9 to 11 are decreased.

The relationship between various creep characteristics and the contents of Cu, Co and Ni is shown in Figures 1 to 3. The relationship between the Cu/Co ratio or the Cu/(Co + Ni) ratio and the creep rupture reduction of area is shown in Figure 1. The relationship between the Cu/Co ratio or the Cu/(Co + Ni) ratio and the creep rupture time is shown in Figure 2. The comparative test specimens plotted by △ and ▲ in Figure 2 have chemical compositions within the scope of this invention.

The relationship between the Ni/Co ratio and the creep rupture time and the creep rupture reduction of area is shown in Figure 3. All the specimens plotted contain about 1% Cu and satisfy the formula: Co + Ni = 2%.

It is apparent from Figures 1 and 2 that the excellent creep rupture reduction of area and creep rupture strength are obtained when the formula $(Cu/Co) \leqq 2.0$ or $[Cu/(Co + Ni)] \leqq 2.0$ is applied. Figure 3 shows that creep rupture time increases relative to the replacement of Ni with Co. This means that the lowering of the Ac_1 transformation point is reduced and that it becomes possible to apply high temperature tempering treatment in order to improve creep rupture strength.

As noted above, by adding Cu and Co, or Cu, Co and Ni to the steel in balanced proportions the resultant high Cr ferritic steel is able to exhibit excellent creep rupture ductility and creep rupture strength for long periods of time at elevated temperatures. The steel of this invention can be widely used for equipments in boilers or chemical plants such as pipes, sheets and forgings, all of which operate at high temperatures and at high pressures.

Although this invention has been shown and described with respect to a preferred embodiment thereof, it should be understood by those skilled in the area that various changes and modifications in the details thereof may be made therein and thereto without departing from the spirit and scope of the invention.

Claims

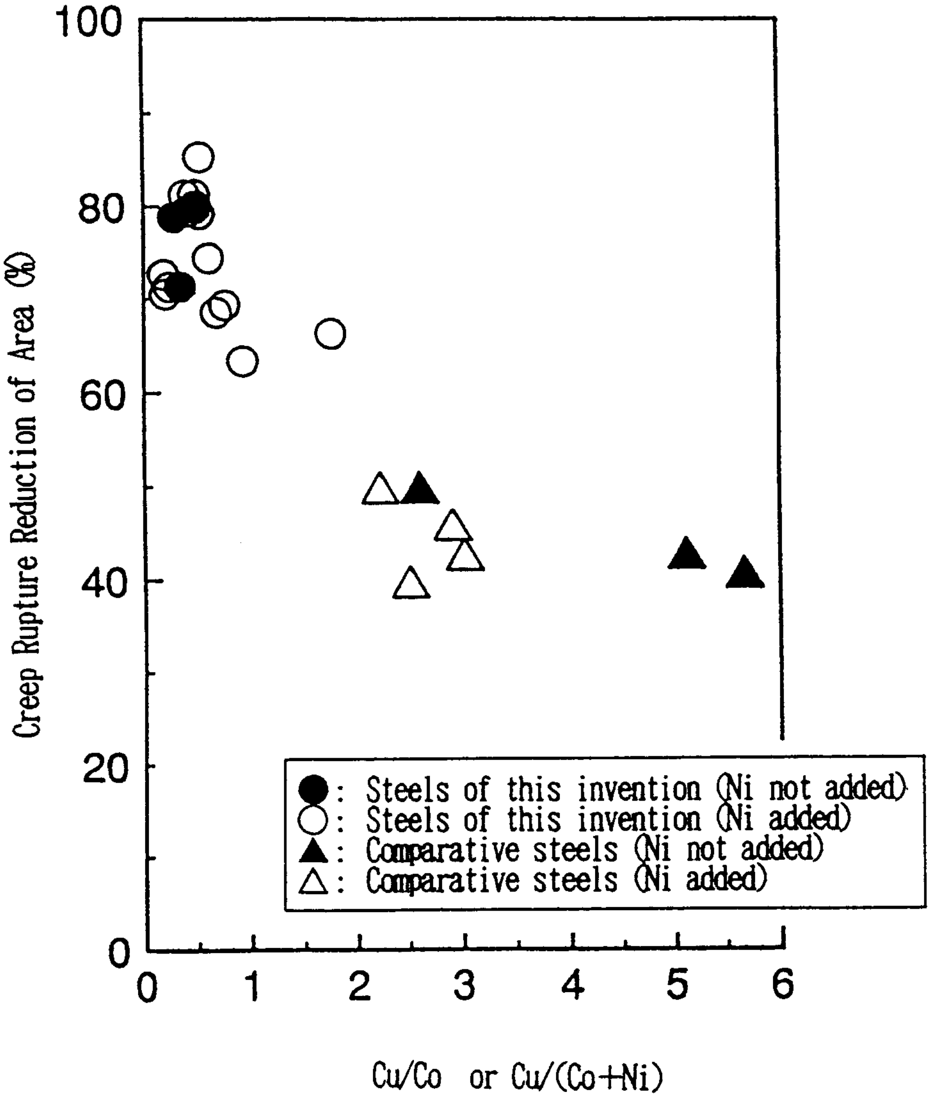
1. A high Cr ferritic steel excellent in ductility and strength at elevated temperature which consists essentially of, by weight, 0.02 to 0.15% C, up to 0.5 Si, 0.1 to 1.5% Mn, up to 0.025% P, up to 0.015% S, up to 0.005% O(oxygen), 8 to 14% Cr, 0.1 to 0.3% V, 0.01 to 0.2% Nb, 0.01 to 0.1% N, up to 0.05% Al, 0.001 to 0.02% B, 0.05 to 3.0% Cu, 1.0 to 5.0% Co, one or both of 0.01 to 1.2% Mo and 0.8 to 3.5% W, and the balance being Fe and incidental impurities, wherein the relationship between Cu and Co content is defined so as to satisfy the following formula (1).

$$Cu/Co \leqq 2.0 \quad (1)$$

2. The high Cr ferritic steel according to Claim 1, further contains 0.1 to 1.5% Ni by weight, wherein the relationship among Ni, Cu and Co contents is defined so as to satisfy the following formula (2).

$$Cu/(Co + Ni) \leqq 2.0 \quad (2)$$

Fig-1


100
80
60
40
20
0
Creep Rupture Reduction of Area (%)
●: Steels of this invention (Ni not added)
○: Steels of this invention (Ni added)
▲: Comparative steels (Ni not added)
△: Comparative steels (Ni added)
0
1
2
3
4
5
6
Cu/Co or Cu/(Co+Ni)

Fig－2

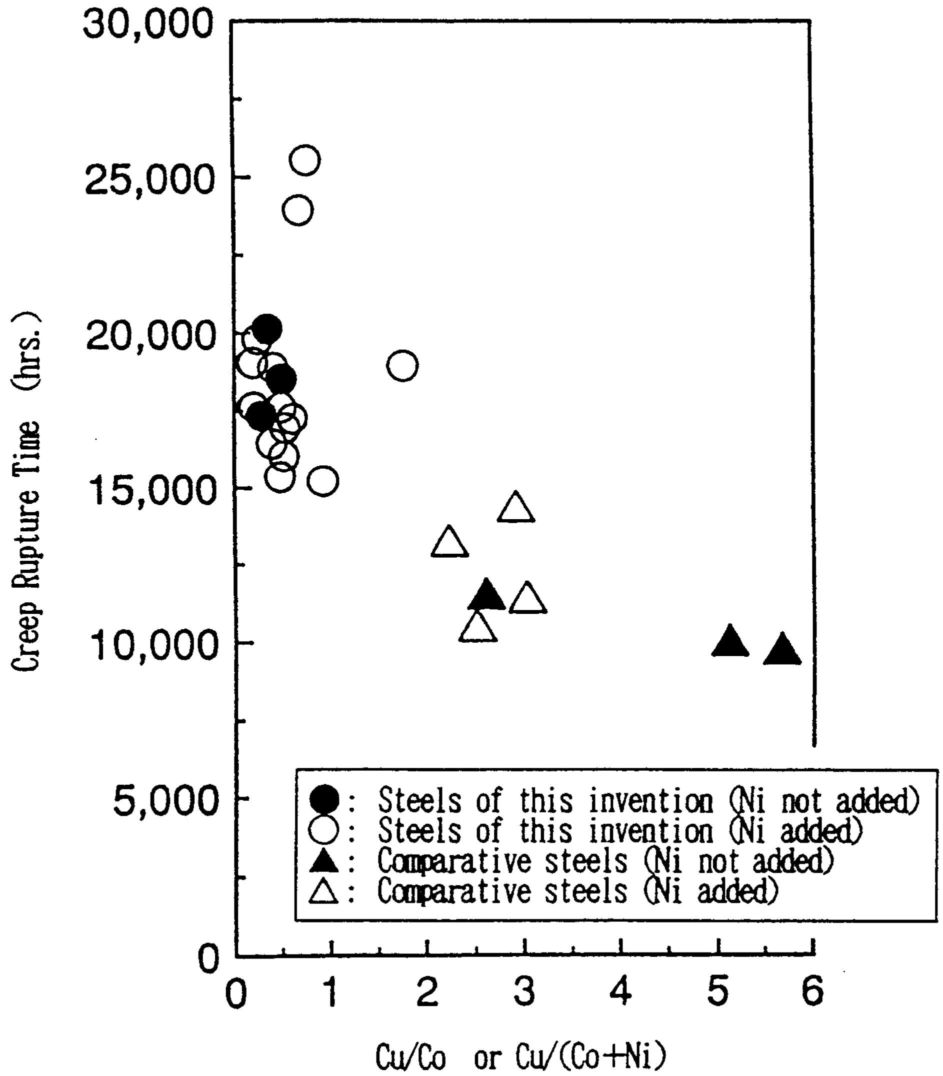
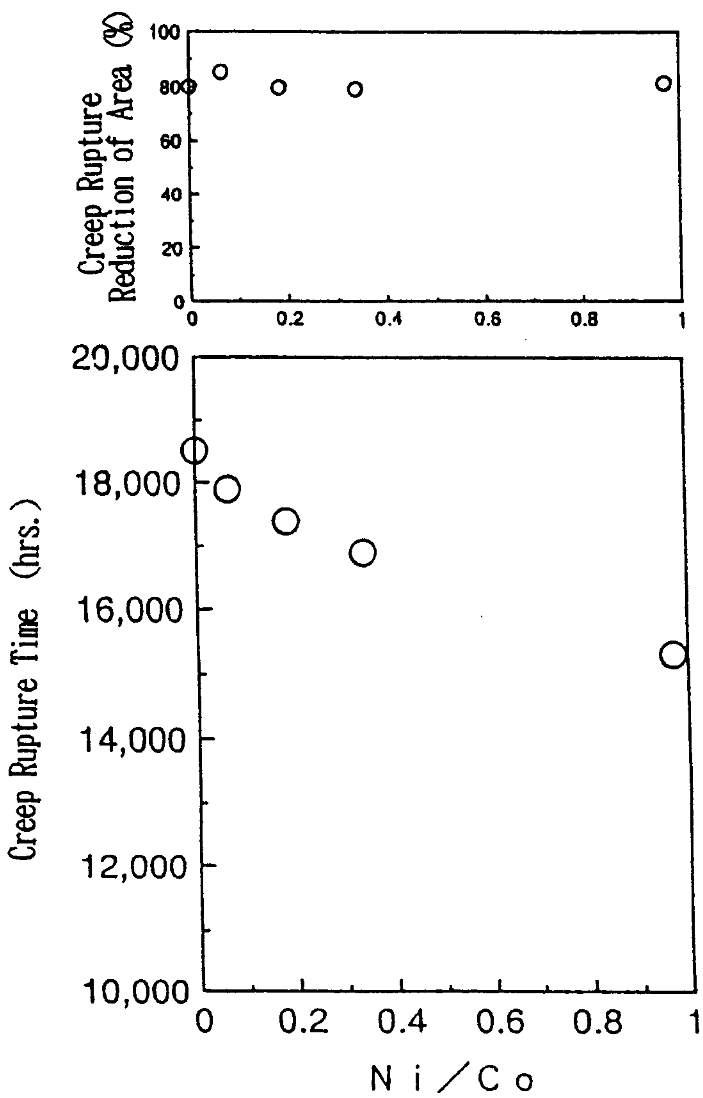

30,000
25,000
20,000
15,000
10,000
5,000
0
Creep Rupture Time (hrs.)
0
1
2
3
4
5
6
Cu/Co or Cu/(Co+Ni)
●: Steels of this invention (Ni not added)
○: Steels of this invention (Ni added)
▲: Comparative steels (Ni not added)
△: Comparative steels (Ni added)

Fig-3


Creep Rupture
Reduction of Area (%)
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
Creep Rupture Time (hrs.)
20,000
18,000
16,000
14,000
12,000
10,000
0
0.2
0.4
0.6
0.8
1
Ni/Co

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 5892

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO-A-94 08063 (BUCK R.) *Claims 1-4; Example II, pages 21 and 22*	1,2	C22C38/30 C22C38/32
A	EP-A-0 411 931 (CARPENTER TECHNOLOGY CORPORATION) *Claims 1-13*	1,2	
A	GB-A-678 616 (ALLOY RESEARCH CORP.) * the whole document *	1,2	
X	PATENT ABSTRACTS OF JAPAN vol. 18, no. 128 (C-1174) 2 March 1994 & JP-A-05 311 342 (NIPPON STEEL CORP.) 22 November 1993 * abstract *	1,2	
X	PATENT ABSTRACTS OF JAPAN vol. 18, no. 128 (C-1174) 2 March 1994 & JP-A-05 311 345 (NIPPON STEEL CORP.) 22 November 1993 * abstract *	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Y	PATENT ABSTRACTS OF JAPAN vol. 18, no. 128 (C-1174) 2 March 1994 & JP-A-05 311 344 (NIPPON STEEL CORP.) 22 November 1993 * abstract *	1	C22C
Y	PATENT ABSTRACTS OF JAPAN vol. 18, no. 128 (C-1174) 2 March 1994 & JP-A-05 311 346 (NIPPON STEEL CORP.) 22 November 1993 * abstract *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 February 1995	Lippens, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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