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(11)

EP 0 690 141 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
28.10.1998 Bulletin 1998/44

(51) Int Cl.⁶: **C22C 38/42, C22C 38/48**

(21) Application number: **95109943.1**

(22) Date of filing: **26.06.1995**

(54) **Structural member made from an austenitic heat resistant steel excellent in elevated temperature strength**

Bauteil aus hitzebeständigem austenitischem Stahl mit ausgezeichneter Festigkeit bei hohen Temperaturen

Élément structurel en acier austénitique réfractaire présentant, une excellente résistance mécanique aux températures élevées

(84) Designated Contracting States:
DE FR GB SE

(30) Priority: **28.06.1994 JP 146438/94**

(43) Date of publication of application:
03.01.1996 Bulletin 1996/01

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(56) References cited:
AT-A- 278 886 BE-A- 853 481
DE-A- 2 314 661 GB-A- 1 574 101

- **PATENT ABSTRACTS OF JAPAN vol. 011 no. 361 (C-459), 25 November 1987 & JP-A-62 133048 (SUMITOMO METAL IND LTD) 16 June 1987,**
- **PATENT ABSTRACTS OF JAPAN vol. 018 no. 449 (M-1660), 22 August 1994 & JP-A-06 142980 (SUMITOMO METAL IND LTD; OTHERS: 01) 24 May 1994,**

EP 0 690 141 B1

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Description

FIELD OF THE INVENTION

5 This invention relates to a structural member of a boiler made of an austenitic heat resistant steel having high strength at elevated temperatures.

DESCRIPTION OF THE PRIOR ART

10 18-8 austenitic stainless steels, such as JIS (Japanese Industrial Standard) SUS 304H, SUS 316H, SUS 321H and SUS 347H have been used for structural members in boilers, chemical plants and other apparatus and installations which are operated in a high temperature environment. In recent years, these apparatus and installations have been required to operate in severer conditions and environments. Accordingly, the structural materials have been required to exhibit more improved physical and chemical properties as compared with the conventional 18-8 austenitic stainless steels which do not have sufficient strength at elevated temperatures for such uses.

15 In general, using both precipitation of carbonitrides and solid solution hardening by addition of considerable amounts of molybdenum and tungsten is effective for improving strength of austenitic stainless steel at high temperatures. However, in the case of adding large amounts of molybdenum and tungsten, the addition of large amounts of nickel is required in order to ensure a stable structure of austenitic phase. Nevertheless, nickel is extremely expensive, thus raising the steel production costs.

20 GB-A-1 574 101 discloses an austenitic stainless steel having acid resistance and corrosion resistance and having a low Mn content of 0.10-0.30 %.

It is an object of this invention to provide a structural member of a boiler made of a heat resistant austenitic stainless steel having superior strength at high temperatures and being able to withstand severe operating conditions at elevated temperatures, wherein the use of costly alloying elements is limited as much as possible.

25 One of the inventors of this invention, has already proposed nitrogen containing austenitic steels with excellent elevated temperature strength and stable microscopic structure (see Japanese Patent Public Disclosure, JPPD 62-133048). The steel contains some elements such as copper, boron and magnesium which are effective for improving the creep rupture strength. Furthermore, the use of silicon and aluminum contents is suppressed in the above-mentioned steel.

30 After having conducted further studies, the inventors discovered that in an austenitic stainless steel containing copper, niobium and nitrogen, an increase of creep rupture strength at a higher temperature range for long periods of time can be achieved by suppressing the manganese content to be not more than 0.5%.

35 SUMMARY OF THE INVENTION

The present invention has been made on the basis of the above-mentioned findings and relates to a structural member of a boiler made of a heat resistant austenitic stainless steel having high strength at elevated temperatures, consisting of, on the weight percent basis, 0.05 to 0.15 % carbon, not more than 0.5 % silicon, 0.05 to 0.50 % manganese, 17 to 25 % chromium, 7 to 20 % nickel, 2.0 to 4.5 % copper, 0.10 to 0.80 % niobium, 0.001 to 0.010 % boron, 0.05 to 0.25 % nitrogen, 0.003 to 0.030 % sol. aluminum, 0 to 0.015 % magnesium, optionally one or both of 0.3 to 2.0 % molybdenum and 0.5 to 4.0 % tungsten, and the balance being iron and incidental impurities.

45 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the relationship between the manganese content and the creep rupture strength of the steel, and Figure 2 shows the creep rupture strength of the steels used in this invention as compared to that of the comparative steels having similar chemical compositions.

50 DETAILED DESCRIPTION OF THE INVENTION

Hereinafter the behavior and function of each alloying element will be described in more detail as well as the technical reason for defining the content of each alloying element, wherein percent (%) represents percent by weight.

55 Carbon;

Carbon is an element effective to ensure the necessary tensile strength and creep rupture strength of a heat resistant steel. However, more than 0.15% carbon only increases insoluble carbides in the solution treatment condition,

and cannot contribute to increasing the strength at high temperatures. Furthermore, more than 0.15% carbon decreases the toughness and other mechanical properties. The carbon content is therefore defined to be not more than 0.15%.

Although the carbon content of the steel which contains considerable amounts of nitrogen can be at a fairly low level, the lower limit of the carbon content is defined as 0.05% to obtain the above-mentioned effects.

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Silicon;

Silicon is usually used as a deoxidizing agent of the steel. Silicon is also effective to improve oxidation resistance of the steel. However, an excess of silicon is detrimental to weldability and hot workability of the steel. In the steel used in this invention which contains considerable amounts of nitrogen, excessive amounts of silicon accelerates precipitation of nitrides to reduce toughness while the steel is exposed to an aging or a creeping condition. The silicon content is therefore restricted to be not more than 0.5%; preferably to be not more than 0.3%, if higher toughness and ductility are required, more preferably the silicon content should be reduced to substantially nil or trace amounts.

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Manganese;

Manganese exhibits a deoxidizing effect of the steel as well as silicon, and is also effective to improve hot workability of the steel. Manganese is usually contained in ordinary austenitic stainless steel in amounts of about 1 to 2% so as to obtain said effects on the steel. However, in the steel used in this invention which contains considerable amounts of copper, nickel and nitrogen, creep rupture strength at elevated temperatures for long periods of time is remarkably increased by suppressing manganese content to be not more than 0.50%, because the lowering of the manganese content suppresses growth of copper phase and NbCrN complex nitride, both of which are finely precipitated in the steel matrix during creeping.

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Considering the creep rupture strength of the steel, there are no lower limits of the manganese content. However, in view of improving both the deoxidizing effect and the hot workability, the lower limit of the manganese content is restricted to 0.05%.

Chromium;

Chromium is an element to improve oxidation resistance and heat resistance at elevated temperatures. These properties are increased in accordance with the increase of the chromium content. If the chromium content is less than 17%, the above-mentioned effects will not be achieved. On the other hand, if the chromium content is more than 25%, the nickel content must be increased in order to make an austenitic structure stable, thus resulting in an increase of production costs. Therefore the chromium content is restricted to a range of 17 to 25%.

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Nickel;

Nickel is an indispensable component for ensuring a stable austenitic structure, but the optimum amount is determined by the amounts of ferrite forming elements, such as chromium, molybdenum, tungsten and niobium, and amounts of austenite forming elements, such as, carbon and nitrogen. If the nickel content is less than 7%, it becomes difficult to obtain a stable austenitic structure, whereas if the nickel content exceeds 20%, the production cost becomes too high. Accordingly, the nickel content is restricted to a range of 7 to 20%.

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Copper;

Copper precipitates as a fine metallic phase in the matrix of the steel and is uniformly dispersed therein while the steel is exposed to a creeping condition, contributing to the improvement of the creep rupture strength. In order to obtain the above-mentioned effect, the copper content should be not less than 2.0%. On the other hand, if the copper content exceeds 4.5%, the creep rupture ductility decreases and the workability of the steel becomes poor. The copper content is therefore defined to a range of 2.0 to 4.5%.

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Nitrogen;

Nitrogen, as well as carbon, is an element which effectively improves tensile strength and creep rupture strength of the steel.

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Less than 0.05% nitrogen content cannot fully give the above-mentioned effect. Since nitrogen has larger solid-solubility as compared with carbon, a large amount of nitrogen can dissolve in the austenitic matrix by solution treatment. Reduction of toughness due to precipitation of nitrides after aging is relatively small. However, if the nitrogen content

exceeds 0.25%, toughness of the steel after aging is reduced. The nitrogen content is therefore restricted to a range of 0.05 to 0.25%.

Niobium;

5 Niobium is an element which improves the creep rupture strength of the steel due to precipitation and dispersion hardening of fine niobium carbonitride. If the niobium content is less than 0.10%, the above-mentioned effect is not fully achieved, whereas if the niobium content exceeds 0.80%, both weldability and workability become poor and the mechanical properties are diminished by an increase of insoluble carbonitrides, which are peculiar to the nitrogen containing steel. Accordingly the niobium content is restricted to a range of 0.10 to 0.80%.

Acid soluble aluminum (sol.aluminum);

15 Aluminum is added to a molten steel as a deoxidizing agent, and more than 0.003% sol.aluminum should be contained in the steel in order to achieve deoxidization. However, if the residual sol.aluminum content in the steel exceeds 0.030%, precipitation of σ phase or the other intermetallic compounds is promoted at an elevated temperature for long periods of time, resulting in a reduction of toughness. The content of sol.aluminum is therefore defined in a range of 0.003 to 0.030%, preferably 0.003 to 0.020%.

20 Boron;

Boron contributes to increase the creep rupture strength by strengthening of austenitic matrix due to precipitation and dispersion of fine carbonitride and by strengthening the grain boundary. If the boron content is less than 0.001%, the above-mentioned effect is not fully obtained, whereas if the boron content exceeds 0.01%, the weldability becomes poor. The boron content is therefore defined in a range of 0.001% to 0.010%.

25 In addition to the above-mentioned components, if necessary, molybdenum or tungsten or both of them may be added to the steel used in this invention. Also magnesium may be added to the steel, if needed. The technical reason for defining the content of each said optional element will hereinafter be described in detail.

30 Molybdenum and Tungsten;

These elements serve to improve elevated temperature strength of the steel. Less than 0.3% molybdenum or less than 0.5% tungsten cannot fully achieve this effect. On the other hand, excessive amounts of molybdenum and tungsten increase cost of the steel. Furthermore, when the molybdenum content and the tungsten content exceed 3.0% and 5% respectively, the strength at elevated temperatures is no more improved and the workability of the steel is diminished. For this reason, the molybdenum content and the tungsten content are restricted to ranges of 0.3 to 2.0% and 0.5 to 4.0%, respectively.

35 The reason for the upper limits of the molybdenum content and the tungsten content being lower than those disclosed in the above-mentioned JPPD 62-133048 (3.0% Mo and 5.0% W) is based on the fact that the manganese content, which is effective in order to improve the workability of the steel, is suppressed to a low level in the steel of this invention.

Magnesium;

45 Magnesium is effective to fully deoxidize the steel used in this invention which contains rather small amounts of manganese and aluminum. Magnesium also contributes to improve creep rupture strength. If the magnesium content is less than 0.001%, the above-mentioned effect is scarcely attained. On the other hand, when the magnesium content exceeds 0.015%, the weldability and the workability of the steel are diminished. Therefore, when the magnesium is added to the steel, it is preferable that the content is restricted to a range 0.001% to 0.015%.

50 EXAMPLE

Test specimens of a series of steel as used according to this invention (alloy Nos.1 to 22) listed in Table 1 and another series of comparative steel (alloy marks A to M) listed in Table 2 were prepared by vacuum melting, forging, cold-rolling and solution-treatment.

55 Each of these test specimens was subjected to a creep rupture test, and creep rupture strength at 750°C for 1000 hours was estimated.

The test results are set forth in Table 3, Figure 1 and Figure 2, respectively. Figure 1 shows the test results regarding

EP 0 690 141 B1

the test specimens (Nos. 1 to 6 in Table 3) and that of the test specimens (Marks A to E in Table 3), wherein the black dots denote magnesium containing steels (4 to 6 and C to E) and white dots denote magnesium free steels (1 to 3 and A and B).

5 It is apparent from the test results that decreasing manganese content is very effective to improve the creep rupture strength, and particularly, that the creep rupture strength of the steels used in this invention with the controlled manganese content in the claimed range is distinctively improved as compared with that of the comparative steels with the manganese contents outside the claimed range.

10 Figure 2 shows the test results regarding the test specimens of Table 3 (Nos. 7, 9, 12, 16, 17, 19, 20 and 22, and Marks F to M), as classifying the alloy compositions into eight groups and comparing some of the steels used in this invention with the corresponding comparative steel. It is apparent from Figure 3 that the creep rupture strength is remarkably improved by controlling the manganese content in the range according to this invention in each steel group.

15 The creep rupture strength is improved by adding magnesium to the steel as shown in Figure 1. Furthermore, the creep rupture strength is improved by adding molybdenum (alloy No. 7), tungsten (alloy No. 9, 22), and magnesium plus tungsten (alloy No. 12) to the steel, as shown in Figure 2.

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Table 1
Chemical Composition (weight %, The Balance being Fe and impurities)

Alloy	No.	C	Si	Mn	Cr	Ni	Cu	N	Nb	B	sol.Al	Mg	Mo	W
Steels of This Invention	1	0.10	0.20	0.14	18.5	9.3	3.10	0.090	0.45	0.0035	0.015	-	-	-
	2	0.09	0.22	0.24	18.8	9.5	3.15	0.093	0.43	0.0035	0.011	-	-	-
	3	0.11	0.20	0.43	18.3	9.1	3.13	0.092	0.47	0.0040	0.010	-	-	-
	4	0.10	0.18	0.09	18.0	9.0	3.25	0.115	0.40	0.0033	0.016	0.010	-	-
	5	0.09	0.21	0.27	18.5	9.3	3.35	0.100	0.45	0.0038	0.010	0.009	-	-
	6	0.10	0.19	0.46	18.2	9.0	3.30	0.110	0.42	0.0040	0.010	0.011	-	-
	7	0.08	0.22	0.13	22.8	19.5	3.60	0.160	0.48	0.0035	0.009	-	0.83	-
	8	0.07	0.20	0.18	23.0	19.0	3.65	0.155	0.42	0.0041	0.015	-	1.86	-
	9	0.10	0.15	0.16	22.7	15.8	3.90	0.223	0.48	0.0038	0.018	-	-	1.60
	10	0.10	0.18	0.10	23.2	18.0	3.80	0.220	0.44	0.0033	0.010	-	-	3.54
	11	0.10	0.15	0.12	22.0	16.0	3.75	0.193	0.52	0.0038	0.010	-	0.83	0.75
	12	0.08	0.15	0.25	22.3	16.0	3.75	0.163	0.50	0.0030	0.008	0.008	-	1.58
	13	0.10	0.11	0.20	23.2	18.7	3.30	0.170	0.48	0.0050	0.010	0.010	-	2.50
	14	0.14	0.15	0.32	18.8	7.6	3.50	0.070	0.42	0.0035	0.013	-	-	-
	15	0.06	0.17	0.22	18.5	9.6	3.30	0.090	0.40	0.0085	0.010	-	-	-
	16	0.10	0.42	0.07	18.0	8.6	3.55	0.095	0.47	0.0040	0.011	-	-	-
	17	0.09	0.18	0.15	17.4	9.5	2.50	0.095	0.40	0.0020	0.020	-	-	-
	18	0.10	0.15	0.30	18.3	8.6	4.20	0.075	0.38	0.0025	0.012	-	-	-
	19	0.09	0.20	0.24	19.0	9.5	3.35	0.093	0.15	0.0040	0.010	-	-	-
	20	0.10	0.15	0.19	18.5	8.5	3.30	0.090	0.57	0.0030	0.015	-	-	-
	21	0.09	0.13	0.22	22.5	18.3	3.55	0.168	0.47	0.0038	0.008	-	-	1.58
	22	0.10	0.19	0.16	23.0	15.5	3.50	0.220	0.48	0.0040	0.013	-	-	1.75

Table 2
Chemical Composition (weight %, The Balance being Fe and impurities)

Alloy	C	Si	Mn	Cr	Ni	Cu	N	Nb	B	sol. Al	Mg	Mo	W
Na													
A	0.10	0.20	*0.59	18.5	9.3	3.10	0.090	0.45	0.0035	0.015	-	-	-
B	0.09	0.22	*0.86	18.8	9.5	3.15	0.093	0.43	0.0035	0.011	-	-	-
C	0.10	0.18	*0.63	18.0	9.0	3.25	0.115	0.40	0.0033	0.016	0.010	-	-
D	0.09	0.21	*0.88	18.5	9.3	3.35	0.100	0.45	0.0038	0.010	0.009	-	-
E	0.10	0.19	*1.14	18.2	9.0	3.30	0.110	0.42	0.0040	0.010	0.011	-	-
F	0.08	0.22	*0.78	22.8	19.5	3.60	0.160	0.48	0.0035	0.009	-	0.083	-
G	0.10	0.15	*0.85	22.7	15.8	3.90	0.223	0.48	0.0038	0.018	-	-	1.60
H	0.08	0.15	*0.95	22.3	16.0	3.75	0.163	0.50	0.0030	0.008	0.008	-	1.58
I	0.10	0.42	*0.70	18.0	8.6	3.55	0.095	0.47	0.0040	0.011	-	-	-
J	0.09	0.18	*0.65	17.4	9.5	2.50	0.095	0.40	0.0020	0.020	-	-	-
K	0.09	0.20	*0.73	19.0	9.5	3.35	0.093	0.15	0.0040	0.010	-	-	-
L	0.10	0.15	*0.63	18.5	8.5	3.30	0.090	0.57	0.0030	0.015	-	-	-
M	0.10	0.19	*1.08	23.0	15.5	3.50	0.220	0.48	0.0040	0.013	-	-	1.75

(Note) * : Outside of the Claimed Range of This Invention

Table 3

Alloy	Creep Rupture Strength at 750°C, 1000 hr (kgf/mm ²)*	Alloy	Creep Rupture Strength at 750°C, 1000 hr (kgf/mm ²)*
Steels of This Invention	1	Comparative steels	A
	2		B
	3		C
	4		D
	5		E
	6		F
	7		G
	8		H
	9		I
	10		J
	11		K
	12		L
	13		M
	14		
	15		
	16		
	17		
	18		
	19		
	20		
	21		
	22		

* 1 kgf/mm² ≅ 9.8 N/mm²

The resultant steel as used in this invention has excellent strength at elevated temperatures and exhibits improved creep rupture strength at higher temperatures for long periods of time. Since nitrogen replaces nickel, the resultant steel can be produced at low cost. The steel is suitable for use in the structural members for boilers, chemical plants and other installations which are operated in a high temperature environment.

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

Claims

1. A structural member of a boiler made of a heat resistant austenitic stainless steel having high strength at elevated temperatures, consisting of, on the weight percent basis, 0.05 to 0.15 % carbon, not more than 0.5 % silicon, 0.05 to 0.50% manganese, 17 to 25 % chromium, 7 to 20 % nickel, 2.0 to 4.5 % copper, 0.10 to 0.80 % niobium, 0.001 to 0.010 % boron, 0.05 to 0.25 % nitrogen, 0.003 to 0.030 % sol.aluminum, 0 to 0.015 % magnesium, optionally one or both of 0.3 to 2.0 % molybdenum and 0.5 to 4.0 % tungsten, and the balance being iron and incidental impurities.

Patentansprüche

1. Bauteil eines Boilers, hergestellt aus einem wärmebeständigen austenitischen nicht rostenden Stahl mit hoher Festigkeit bei erhöhten Temperaturen, der, auf Gewichtsprozentbasis besteht aus: 0,05 bis 0,15 % Kohlenstoff, nicht mehr als 0,5 % Silizium, 0,05 bis 0,50 % Mangan, 17 bis 25 % Chrom, 7 bis 20 % Nickel, 2,0 bis 4,5 % Kupfer, 0,10 bis 0,80 % Niob, 0,001 bis 0,010 % Bor, 0,05 bis 0,25 % Stickstoff, 0,003 bis 0,030 % sol.Aluminium, 0 bis

EP 0 690 141 B1

0,015 % Magnesium, wahlweise eines oder beide aus 0,3 bis 2,0 % Molybdän und 0,5 bis 4,0 % Wolfram, wobei der Rest Eisen und zufällige Verunreinigungen sind.

5 **Revendications**

1. Élément structural d'une chaudière fabriqué dans un acier inoxydable austénitique réfractaire qui possède une résistance mécanique importante aux températures élevées, qui est constitué, sur la base du pourcentage en poids, de 0,05 à 0,15% de carbone, de pas plus de 0,5% de silicium, de 0,05% à 0,50% de manganèse, de 17 à 25% de chrome, de 7 à 20% de nickel, de 2,0 à 4,5% de cuivre, de 0,10 à 0,80% de niobium, de 0,001 à 0,010% de bore, de 0,05 à 0,25% d'azote, de 0,003 à 0,030% d'aluminium sol., de O à 0,015% de magnésium, éventuellement d'un ou des deux éléments parmi 0,3 à 2,0% de molybdène et 0,5 à 4,0% de tungstène, et le complément étant du fer et des impuretés accidentelles.

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FIG. 1

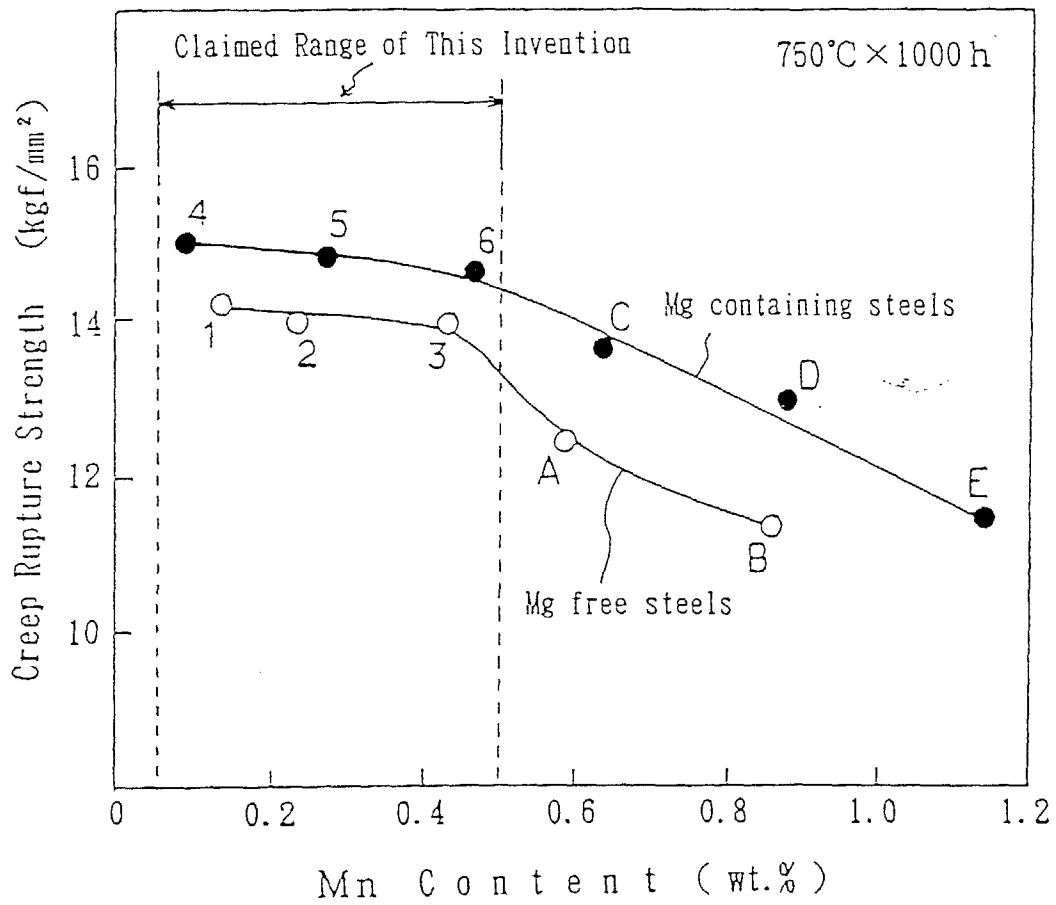


FIG. 2

