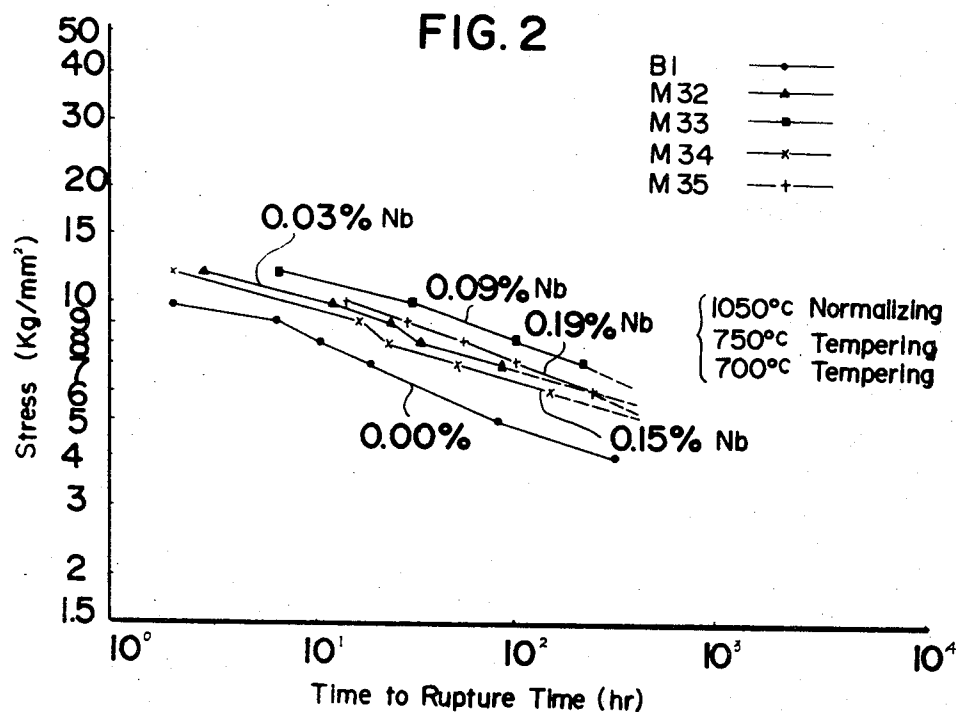
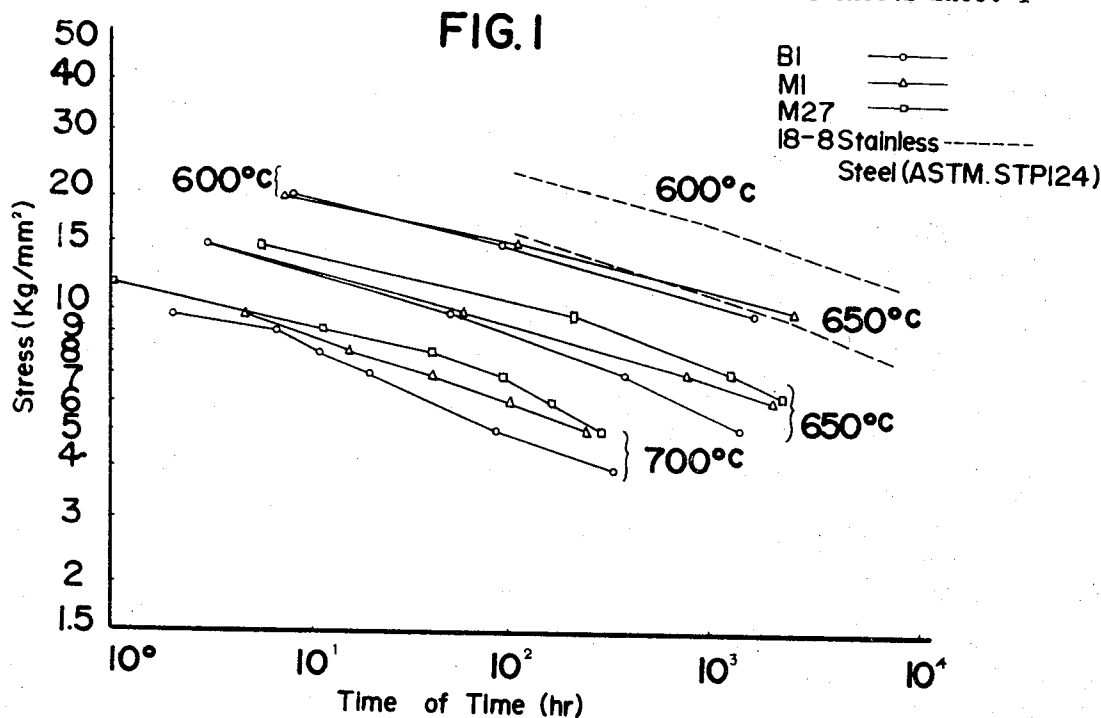


HIGH-TEMPERATURE ALLOY STEEL CONTAINING Cr AND Mo

Filed June 27, 1967

4 Sheets-Sheet 1



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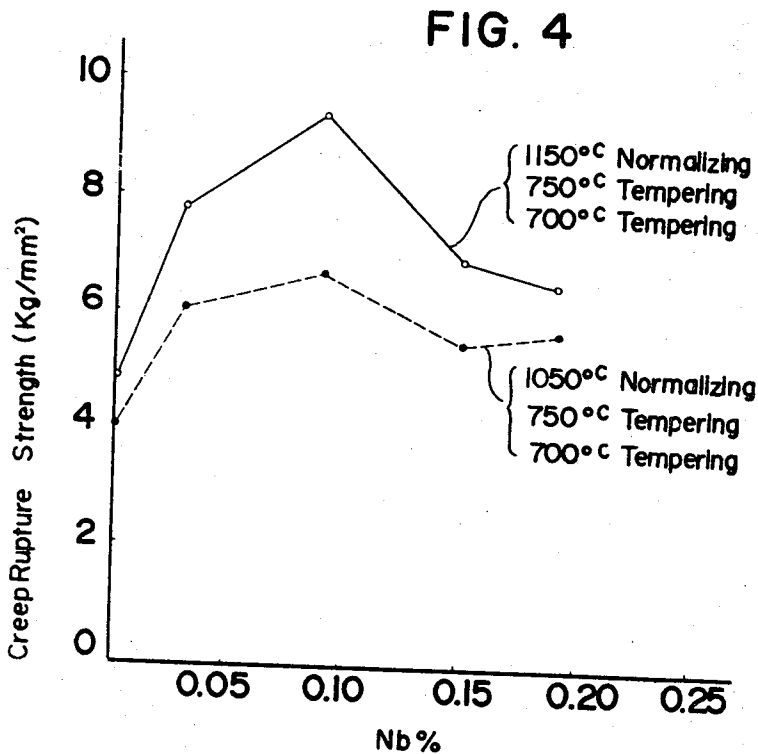
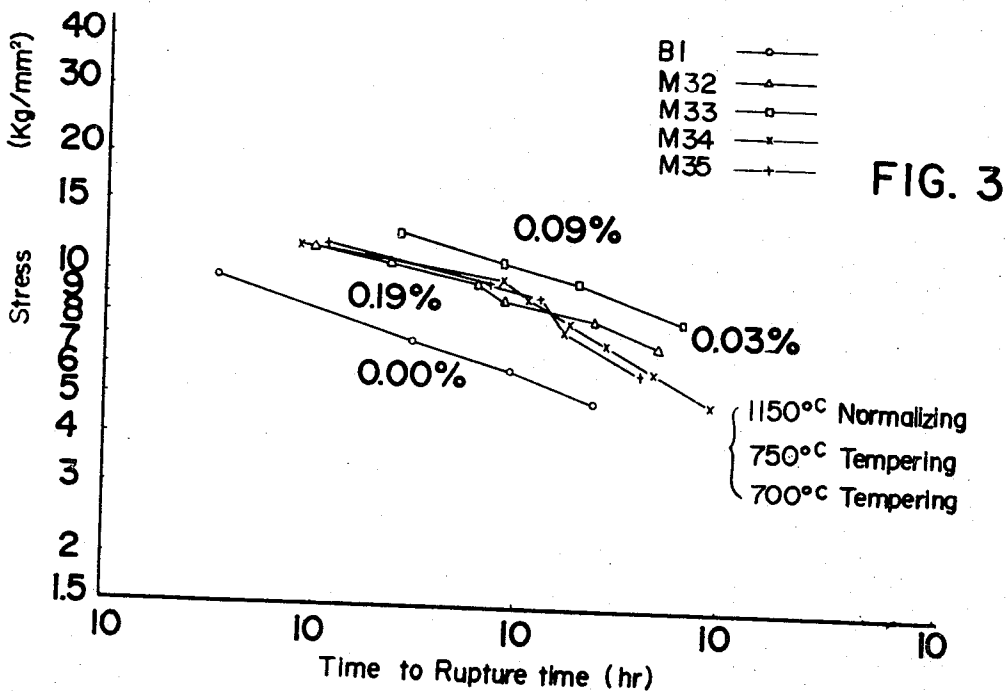
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HIGH-TEMPERATURE ALLOY STEEL CONTAINING Cr AND Mo

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4 Sheets-Sheet 2



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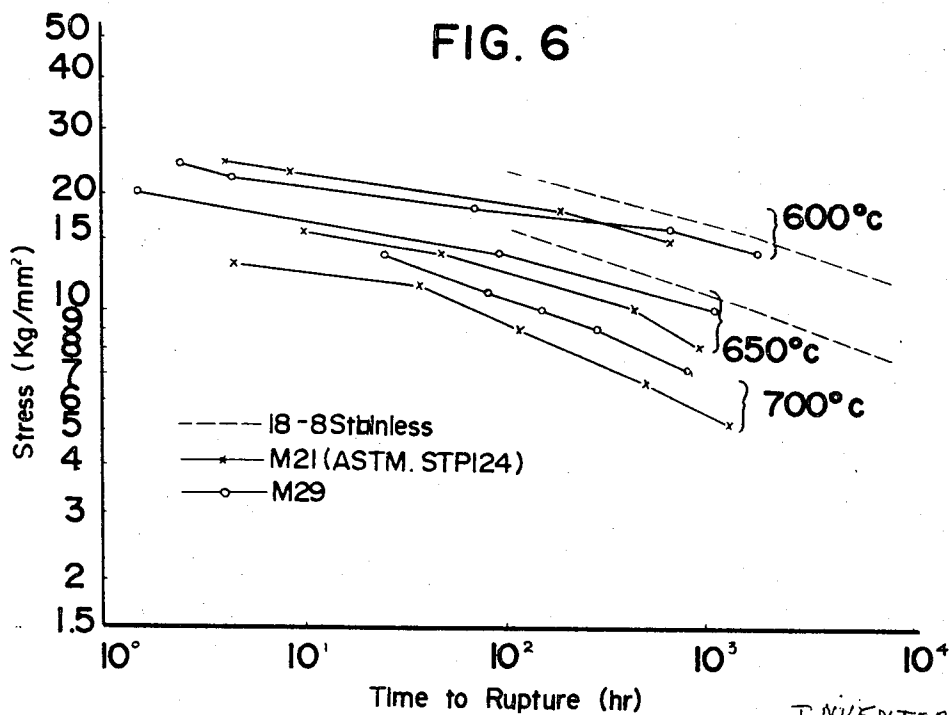
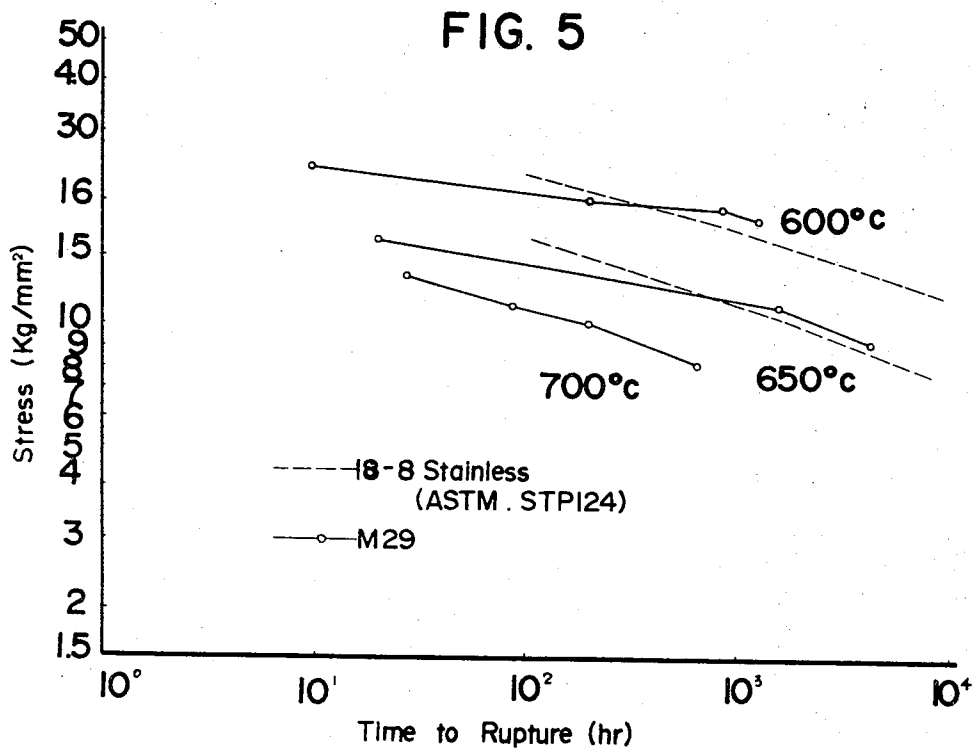
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HIGH-TEMPERATURE ALLOY STEEL CONTAINING Cr AND Mo

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4 Sheets-Sheet 3



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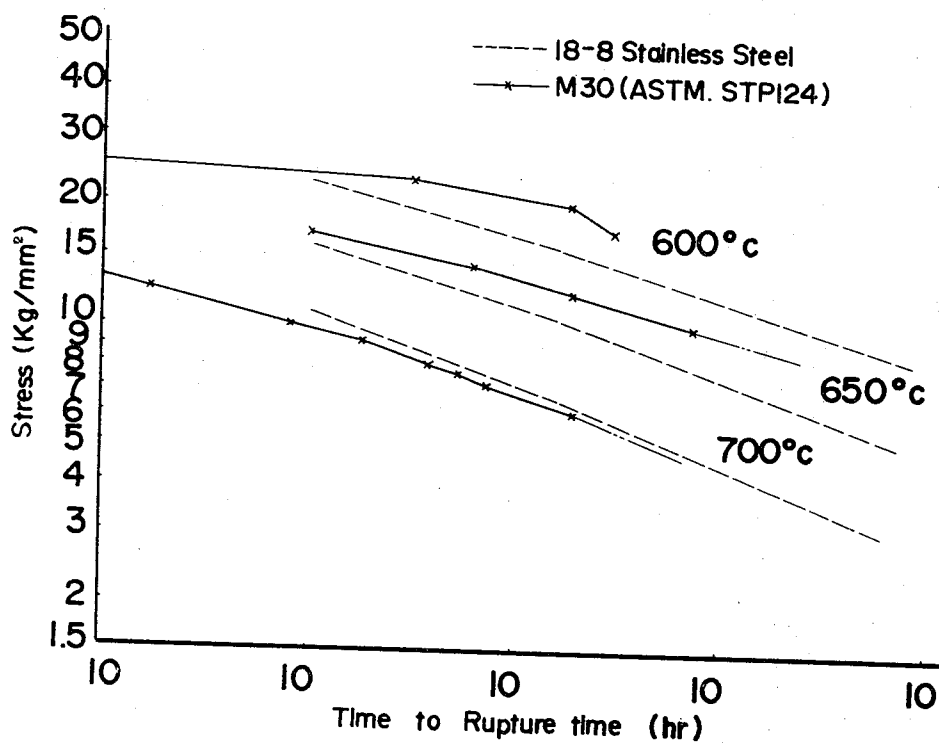
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HIGH-TEMPERATURE ALLOY STEEL CONTAINING Cr AND Mo

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4 Sheets-Sheet 4

FIG. 7



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HIGH-TEMPERATURE ALLOY STEEL
CONTAINING Cr AND Mo

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41/41,584

Int. Cl. C22c 39/14

U.S. Cl. 75—126

1 Claim

ABSTRACT OF THE DISCLOSURE

The disclosed alloy steel is a high-temperature high-strength alloy steel, the alloy steel being a ferritic high-temperature steel and inexpensive compared with an austenitic stainless steel still having the high-strength corresponding to the austenitic stainless steel in high temperature such as 600° to 650° C. The alloy steel has also an oxidation-resistant property in the above high temperature range. To accomplish the purpose described alloy steel it consists essentially of chromium 5 to 8%, and molybdenum 1% further adding vanadium, niobium and boron.

BACKGROUND OF THE INVENTION

This invention relates to a high-temperature alloy steel, and more particularly is directed to a high-temperature alloy steel which has high strength substantially equivalent to 18-8 stainless steel such as used for boiler tubes in high-temperature and which is still inexpensive.

Since a power generating efficiency in a generation plant using a steam turbine may be improved by utilizing higher temperature and pressure steam, the steam conditions used in a heat power station are inclined to develop to higher temperature and pressure. However, inasmuch as an expensive austenitic stainless steel has been used in high-temperature and high-pressure portions of the generation set, the power unit has not been economical in settlement, operation, etc.

Heretofore, instead of the aforementioned expensive austenitic stainless steel, ferritic high-temperature alloy steels such as one consisting essentially of the following elements in the following weight percentages:

Chromium	8
Molybdenum	3
Titanium	0.5

the balance being substantially all iron, and the other consisting essentially of the following elements in the following weight percentages:

Chromium	9-10
Molybdenum	2
Vanadium	0.3
Columbium	0.4-0.5
Cobalt	2
Carbon	0.1

the balance being substantially all iron have been publicly well known and used. Since the former alloy steel composition contains titanium, there has been a difficulty for the production due to the requirement for a vacuum melting or dissolution. And the latter alloy steel composition has had a difficulty or disadvantage in its property. As was described hereinbefore, such high-temperature alloy steels have heretofore normally more than two percentages of molybdenum which causes the steel to be expensive.

As was described hereinbefore, the ferritic alloy steel for a boiler tube generally used recently is of so-called

chromium molybdenum steel alloyed by chromium and molybdenum to iron, its high-strength in high temperature mainly depending upon the precipitation of the carbide of chromium and molybdenum. However, since the forming capability of carbide of chromium and molybdenum is weak, long operation in high temperature enables carbide flocculation so that the strengthening of the alloy steel is not improved.

SUMMARY OF THE INVENTION

This invention eliminates the aforementioned difficulties and disadvantages of the conventional high-temperature alloy steels and provides a novel and improved high-temperature ferritic alloy steel which has high strength substantially corresponding to the expensive austenitic stainless steel in high temperature.

In accordance with the present invention there is provided a high-temperature and high-strength alloy steel consisting essentially of the following elements in about the following weight percentages:

Chromium	5-8
Molybdenum	1

the balance being substantially iron, there being added vanadium, niobium and boron. Such an alloy steel is provided to be good oxidation-resistant in high temperature range such as 600° to 650° C. and still inexpensive, and yet to be of high-strength ferritic alloy steel equivalent to an austenitic stainless steel in high temperature.

According to the present invention molybdenum used normally as strengthening elements for solid solution of the ferritic high temperature alloy steel is adapted to be included by more or less one percentage in weight, and vanadium and niobium of carbide forming elements being added a little amount thereto in order to improve further its high strength in high temperature, boron being added so as to increase stability of these carbide in high temperature and at least 5 to 8 weight percentages of chromium being added to maintain oxidation-resistant in high temperature. Such adding elements are equilibrated, in consideration with its workability in high temperature, in the range of not producing ferrite during hot working.

A high-temperature high-strength alloy steel in accordance with the present invention as one preferred typical representative consists essentially of the following elements in about the following weight percentages:

Carbon	0.03-0.15
Silicon	0-1
Manganese	0.3-1.2
Chromium	5.0-8.0
Molybdenum	0.5-1.5
Vanadium	0-0.3
Niobium	0.03-0.15
Boron	0.001-0.012

and also consists essentially of the following elements in approximately the following weight percentages as the composition existing normally on the production of the alloy steel:

Nickel	0-1.0
Nitrogen	0-0.04
Phosphorus	0-0.035
Sulphur	0-0.035
Cobalt	0-0.25
Aluminum	0-0.05
Titanium	0-0.04
Tungsten	0-0.25
Tin	0-0.04

the balance being substantially iron and the other impurities.

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It is one advantage of the present invention that 5–8 weight percentages of chromium is added to the alloy steel in order to maintain sufficient oxidation-resistant property in the high-temperature range 600° to 650° and 0.5–1.5 weight percentages of molybdenum is added thereto to improve high-strength in high temperature.

Yet another advantage of the present invention is seen in that high-strength in high temperature is maintained in adding further vanadium and niobium to the alloy steel being of strong forming capability for carbide, and borons added thereto so as to increase stability of carbide in high temperature corresponding to expensive austenitic stainless steel is produced inexpensively.

As regards this aspect of the present invention, it is preferred that the alloy steel contains 0.03–0.15% of carbon inasmuch as its strength in high temperature is not strong for carbon contents below about 0.03% and the workability is low above approximately 0.15%.

It is also preferable that the steel includes below 1% of silicon and 0.3–1.2% manganese as deoxidizers since over 1.0% of silicon and 1.2% of manganese effects insufficient hot workability.

It is preferred that the steel is inclusive of 5–8% in weight of chromium in order to maintain sufficient oxidation-resistant property in high temperature range 600°–650° C. since low workability for over 8% contents and low oxidation-resistant for below 5% contents are held.

It is yet preferable that the steel contains 0.5–1.5% of molybdenum as strengthening element for solid solution thereof so as to improve high-strength in high-temperature, since its strength decreases for below 0.5% content and no use effects for over 1.5% contents.

It is still preferred that the steel contains below 0.3% of vanadium and 0.03–0.15% of niobium which are strong in forming capability for carbide and prevent strength in high temperature from being lower since flocculation thereof develops over 0.3% of vanadium and its strength lowers and price increases to effect no advantage for over 0.15% of niobium content, and no effect occurs for below 0.03% niobium content.

It is still preferable that the steel contains 0.001–0.012% of boron which increases stability of carbide in high temperature to stabilize its structure since no effectiveness for below 0.001% content and its workability deteriorates for over 0.012% content.

Other objects and advantages of the present invention will further become apparent hereinafter, and from the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical chart in which is plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding vanadium to the strength in high temperature of 7% chromium, 1% molybdenum alloy steel compared with 18–8 stainless steel;

FIGS. 2 and 3 are graphical charts in which are plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding niobium to the strength in high temperature of 7% chromium, 1% molybdenum alloy steel;

FIG. 4 is a graphical chart in which is plotted the relationship between creep rupture strength and content of niobium, plotted as abscissae against the influence of adding niobium to the creep rupture strength of the alloy steel;

FIG. 5 is a graphical chart in which is plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding niobium to the strength in high temperature of the alloy steel compared with 18–8 stainless steel;

FIG. 6 is a graphical chart in which is plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding niobium and vanadium to the strength in high temperature of the steel compared with 18–8 stainless steel;

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FIG. 7 is a graphical chart in which is plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding niobium, vanadium, and boron to the strength in high temperature of the steel compared with 18–8 stainless steel.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Now the present invention will be hereinafter illustrated and described by way of examples as alloy steels adding forming elements for carbide. In such examples strength in high temperature is shown as results of creep rupture test.

EXAMPLE 1

Adding mere vanadium to 5–8 chromium, 1% molybdenum alloy steel.

In such kinds of ferritic high-temperature alloy steels 0.2–0.4% in weight of vanadium is added so that creep rupture strength in high temperature is seemed to be increased extremely. As to three kinds of steels shown in the following Table 1 the influence caused by adding vanadium thereto was tested.

TABLE 1

Steel	C, percent	Si, percent	Mn, percent	Cr, percent	Mo, percent	V, percent
B1.....	0.11	0.37	0.29	6.94	0.97	0.24
M1.....	0.11	0.40	0.36	7.04	0.96	0.24
M27.....	0.12	0.48	0.59	7.40	1.00	0.44

In order to improve the characteristic values of these kinds of steels the following heat treatment worked. That is, in order to dissolve vanadium carbide into the austenite, the alloy steel is normalized at temperature 1050° C., and heated thereafter at temperature 750° C. to precipitate vanadium carbide. However, in such a state its hardness was HV250 which was still higher, accordingly reheated at 700° C. which lowered its hardness in the order of HV200.

Referring now to FIG. 1, a graphical chart as results of creep rupture tests at temperature 600°, 650° and 700° C., respectively in which is plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding vanadium to the strength in high temperature of the alloy steel which was heat treated as aforesaid compared with 18–8 stainless steel, it will be seen as to the following matters from also the test data of the above indicated Table 1.

(a) Even if 0.2–0.4% in weight of vanadium is added to austenitic stainless steel it is not effected in creep rupture strength.

(b) Adding of the vanadium improves the strength in high temperature below 650° C. for long time.

(c) Even though the adding amount of the vanadium thereto is increased from 0.2 to 0.4% in weight, since the strength in the long time is not affected, it will be preferable that at the economic standpoint the vanadium is added thereto in the order of 0.2 weight percentage, and yet such a steel indicates no change of its creep rupture strength even if its austenizing temperature thereof is increased further to 1150° C.

EXAMPLE 2

Adding mere niobium to 5–8% chromium, 1% molybdenum steel.

Normally adding amount of niobium to ferritic high-temperature steel is 0.2–0.5 weight percentage. However, it has been found that as results of experiments by decreasing the adding amount thereof to 0.03–0.15% the strength can be increased further. The example as results of the aforementioned experiments is illustrated in the following Table 2.

TABLE 2

Steel	C, percent	Si, percent	Mn, percent	Cr, percent	Mo, percent	Nb, percent
B1.....	0.11	0.37	0.29	6.94	0.97	-----
M32.....	0.13	0.55	0.66	7.13	1.09	0.03
M33.....	0.12	0.48	0.56	7.09	0.97	0.09
M34.....	0.12	0.57	0.62	7.14	0.05	0.15
M35.....	0.13	0.53	0.58	7.00	0.01	0.19

The purpose for adding niobium to such ferritic high-temperature steel is that niobium carbide is uniformly dispersed in the material so as to maintain its strength in high temperature. The problem as to its precipitated structure is as follows:

(a) Normalizing temperature for melting once niobium carbide in the material.

(b) Lowering of its strength in case that it is exposed at high temperature for long time.

The example as to the aforementioned two points is illustrated in FIGS. 2 through 4. Relative to the above point (a) in order to obtain long time stability of the material at temperature range 600° to 650° C. tests were done under the condition above its temperature (700° C.). This is the condition for increasing the dispersion of elements in the steel.

Referring now to FIGS. 2 and 3, which show graphical charts in which are plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding niobium to the strength in high temperature of 7% chromium, 1% molybdenum alloy steel, it will be seen that by adding small amount of niobium its strength in high temperature is extremely improved.

Referring now to FIG. 4, which shows a graphical chart in which is plotted the relationship between creep rupture

strength and content of niobium, plotted as abscissae against the influence of adding niobium to the creep rupture strength of 7% chromium, 1% molybdenum alloy steel, it will be seen that the maximum effect occurs to the steel by adding thereto 0.09 weight percentage. Also, in order to obtain good strength in high temperature by adding niobium thereto, it has been found that normalizing it at temperatures 1050°–1150° C. is required.

In FIG. 5, which is a graphical chart in which is plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding niobium to the strength in high temperature of 7% chromium, 1% molybdenum alloy steel compared with 18–8 stainless steel, the example that specimen having the aforesaid composition for effecting the maximum of niobium content is compared with 18–8 stainless steel at strength in high temperatures 600°–650° C., is shown. It will be seen that therefor even if mere niobium is added thereto the strength equivalent to 18–8 stainless steel may be obtained, however, due to its small amount of content range it is difficult to do it into industrialization.

EXAMPLE 3

As to the effectiveness by adding both niobium and vanadium.

In Table 3 shown in the following, the example that both vanadium and niobium are added in the most proper amount to 5–8% chromium, 1% molybdenum alloy steel is illustrated.

TABLE 3

Steel:	C, percent	Si, percent	Mn, percent	Cr, percent	Mo, percent	V, percent	Nb, percent
M21.....	0.12	0.51	0.60	7.14	1.06	0.28	0.13
M29.....	0.08	0.36	0.35	6.97	1.00	0.27	0.14

Referring now to FIG. 6, which shows a graphical chart in which is plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding niobium and vanadium to the strength in high temperature of 7% chromium, 1% molybdenum alloy steel compared with 18–8 stainless steel, the example is shown that after the aforementioned steel was normalized at temperature 1150° C., was tempered at 750° C., and heat treated to be again tempered at 700° C., creep rupture tests were done. It will be seen that from the graphical chart in FIG. 6 in case both niobium and vanadium being added it indicates no change in strength in high temperature compared with the case adding mere niobium.

EXAMPLE 4

As to the effectiveness by adding niobium, vanadium and boron.

The further characteristic of the present invention is to add boron to the steel described in the above Example 3. The adding amount is of 0.001–0.012 weight percentage. This boron has no effect to the strength in high temperature of the steel by mere adding only boron, however, the strength in high temperature is extremely improved by adding that in case existing therein forming elements for carbide as will be hereinafter described.

TABLE 4

Steel	C, percent	Si, percent	Mn, percent	Cr, percent	Mo, percent	V, percent	Nb, percent	B, percent
M30.....	0.13	0.43	0.57	7.04	0.94	0.27	0.08	0.0080

Referring now to FIG. 7, which shows a graphical chart in which is plotted the relationship between weight and rupture time, plotted as abscissae against the influence of adding niobium, vanadium and boron to the strength in high temperature of 7% chromium, 1% molybdenum alloy steel compared with 18–8 stainless steel, the result is illustrated which after the steel consisting of the above table composition was normalized at temperature 1150° C., and was tempered at 750° and 700° C. in two steps, creep rupture tests were done at temperature 600°, 650° and 700° C., respectively.

It is seen that the strength at temperature 700° C. is somewhat lower than 18–8 stainless steel but that at 650° and 600° C. is extremely higher than that, and yet the strength at high temperature for long time is seemed to be higher. In the following Table 5, for the reference, at temperature 600° and 625° C. calculated by Larson and Miller method of rupture strength for long time test from the actual test value at 650° C. and that of 18–8 stainless steel are shown.

TABLE 5.—RUPTURE STRENGTH FOR TIME 10⁵ HOURS

Steel	600° C.	625° C.	650° C.
M30.....	10.7 kg./mm. ²	8.6 kg./mm. ²	-----
18–8, stainless steel.....	8.5 kg./mm. ²	6.5 kg./mm. ²	5.0 kg./mm. ²

¹ By ASTM. STP. 124.

From the aforementioned matters, it will be clearly understood that the high-temperature alloy steel in accordance with the present invention has the strength in high temperature range 600°–650° C. sufficiently equivalent to that of 18–8 stainless steel.

Also, in order to obtain sufficient characteristic of the material, after the chemical compositions of niobium, vanadium and boron are equilibrated specific heat treatment is required to work. That is, as one step it must be normalized at sufficient high temperature range 1050°–1150° C. for sufficiently dissolving such carbide elements to austenitic structure, as next step so as to precipitate the carbide it is tempered at 750° C. for thirty minutes to two hours thereafter cooling it, further in order to improve the workability at room temperature it is reheated at 700° C. for fifteen to thirty minutes. After these heat treatments completed in actual process, its hardness was approximately HV200 and cold workability such as pressing, bending, etc. was good.

The alloy steel in accordance with the present invention needs to contain 0.03–0.15% of carbon in weight since its strength in high temperature is not strong for carbon contents below about 0.03% and the workability is low above approximately 0.15%. It requires to include up to 1% of silicon and 0.3–1.2% manganese as deoxidizers as over 1.0% of silicon and 1.2% of manganese makes only high cost without any advantages and up to 0.3% of manganese effects insufficient hot workability. It is required to be inclusive of 5–8% in weight of chromium in order to maintain sufficient oxidation-resistant property in high temperature range 600°–650° C. since low workability for over 8% contents and low oxidation-resistant for below 5% contents are existing. It must also contain 0.5–1.5% of molybdenum as strengthening element for solid solution thereof so as to improve high-strength in high temperature, since its strength decreases for below 0.5% content and no use effects for over 1.5% contents. It is also required to contain up to 0.3% of vanadium and 0.03–0.15% of niobium which are strong in forming capability for carbide and prevent strength in high temperature from being lower since flocculation thereof develops over 0.3% of vanadium and its strength lowers and price increases to effect no advantage for

0.15% of niobium content, and no effect occurs for 0.03% niobium content. It is further needed to include 0.001–0.012% of boron which increases stability of carbide in high temperature to stabilize its structure since no effectiveness for below 0.001% content and its workability deteriorates for over 0.012% content.

Thus, the high-temperature alloy steel in accordance with the present invention provides economic advantages and high strength in high temperature from that 5–8 weight percentages of chromium is added to the alloy steel in order to maintain sufficient oxidation-resistant property in the high-temperature range 600°–650° C. and 0.5–1.5 weight percentages of molybdenum is added thereto to improve high-strength in high temperature, and from that further vanadium and niobium to the alloy steel being of strong forming capability for carbide in high temperature so that the alloy steel having high strength in high temperature corresponding to expensive austenitic stainless steel is produced inexpensively.

What is claimed is:

1. A high-temperature alloy steel consisting essentially of the following elements in the following weight percentages:

Carbon	0.03–0.15
Silicon	0–1
Manganese	0.3–1.2
Chromium	5.0–8.0
Molybdenum	0.5–1.5
Vanadium	0–0.3
Niobium	0.03–0.15
Boron	0.001–0.012

the balance being iron and the other impurities.

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HYLAND BIZOT, Primary Examiner

UNITED STATES PATENT OFFICE

Certificate

Patent No. 3,539,338

Patented November 10, 1970

Tohru Mimino, Kazuhisa Kinoshita, Keisuke Hattori, and Akiyoshi Matsushita

Application having been made by Tohru Mimino, Kazuhisa Kinoshita, Keisuke Hattori, and Akiyoshi Matsushita, the inventors named in the patent above identified, and Nippon Kokan Kabushiki Kaisha, Tokyo, Japan, the assignee, for the issuance of a certificate under the provisions of Title 35, Section 256, of the United States Code, deleting the name of Akiyoshi Matsushita as a joint inventor, and a showing and proof of facts satisfying the requirements of the said section having been submitted, it is this 6th day of February 1973, certified that the name of the said Akiyoshi Matsushita is hereby deleted from the said patent as a joint inventor with the said Tohru Mimino, Kazuhisa Kinoshita, and Keisuke Hattori.

FRED W. SHERLING,
Associate Solicitor.