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Sasaki et al.

[11] **3,778,256**

[45] **Dec. 11, 1973**

[54] **HEAT-RESISTANT ALLOY FOR A COMBUSTION LINER OF A GAS TURBINE**

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[73] Assignee: **Hitachi, Ltd.,** Tokyo, Japan

[22] Filed: **Dec. 28, 1971**

[21] Appl. No.: **213,050**

[30] **Foreign Application Priority Data**

Dec. 28, 1970 Japan 45/119867

[52] **U.S. Cl.** .... **75/134 F,** 75/122, 75/171

[51] **Int. Cl.** **C22c 19/00,** C22c 31/00

[58] **Field of Search** .... 75/134 F, 122, 171, 75/128 A, 128 G, 128 T, 128 E

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Assistant Examiner—E. L. Weise
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[57] **ABSTRACT**

An alloy for a combustion liner of a gas turbine, characterized by comprising 0.03 to 0.10 weight percent of carbon, 0.3 to 1.0 weight percent of silicon, 0.50 to 3.00 weight percent of manganese, 43.0 to 50.0 weight percent of nickel, 22.0 to 30.0 weight percent of chromium, 0.10 to 0.50 weight percent of titanium, at least one of 0.005 to 0.20 weight percent of elements of cerium group in rare earth elements and 0.20 to 0.90 weight percent of niobium, and the balance iron and impurities accompanying thereto.

13 Claims, 10 Drawing Figures

FIG. 2

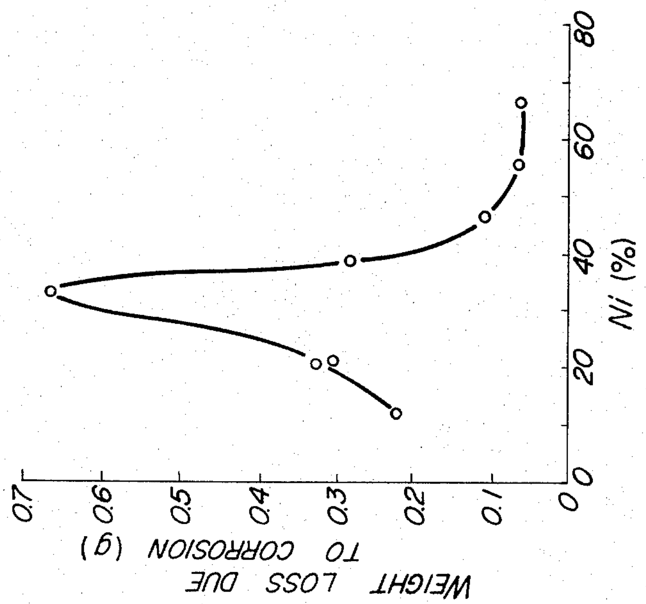

WEIGHT LOSS DUE TO CORROSION (g)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
Ni (%)

FIG. 1

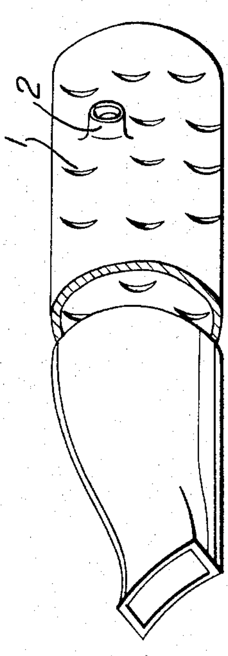
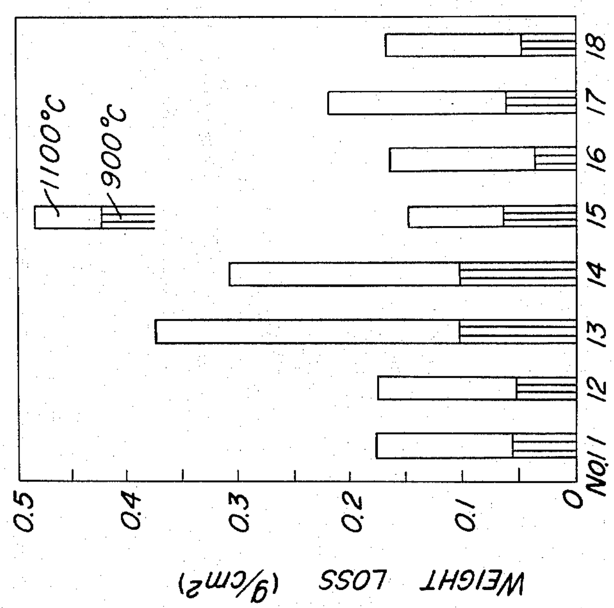
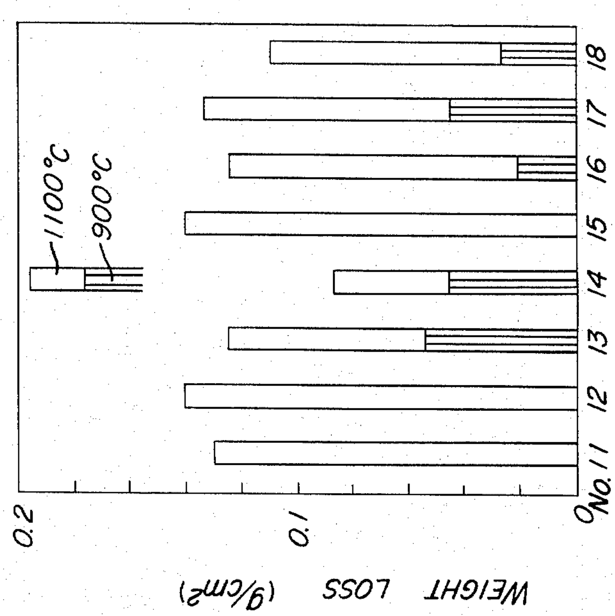

1
2

FIG. 4



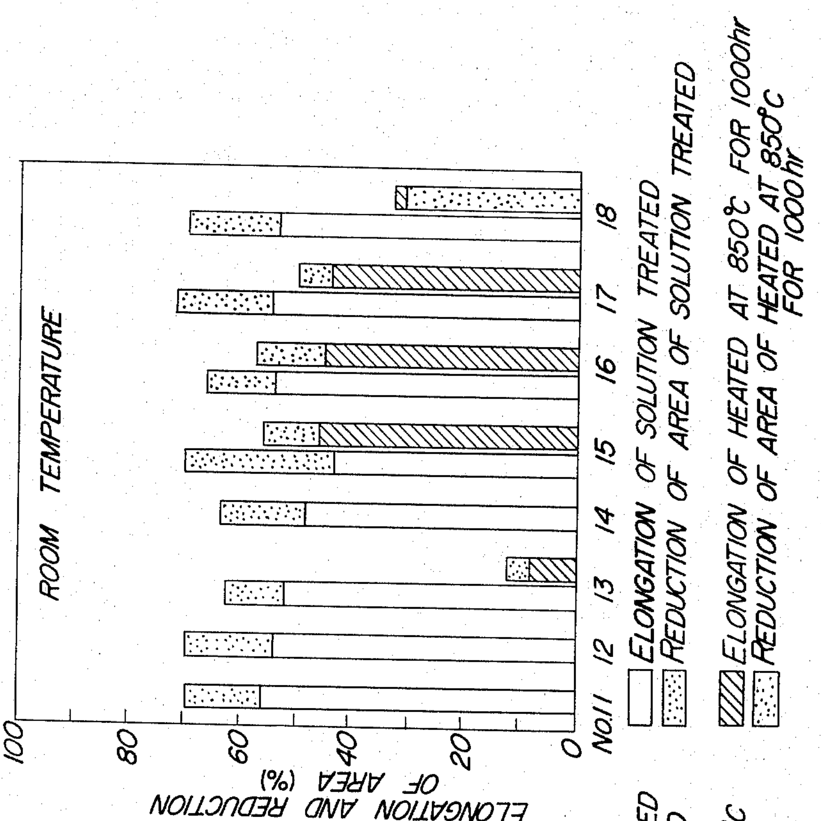
WEIGHT LOSS OF VARIOUS ALLOYS DUE TO 75% V_2O_5 + 25% Na_2SO_4 ATTACK

FIG. 3



WEIGHT LOSS OF VARIOUS ALLOYS DUE TO 100% V_2O_5 ATTACK

FIG. 6



TENSILE PROPERTIES OF VARIOUS ALLOYS AT ROOM TEMPERATURE

FIG. 5

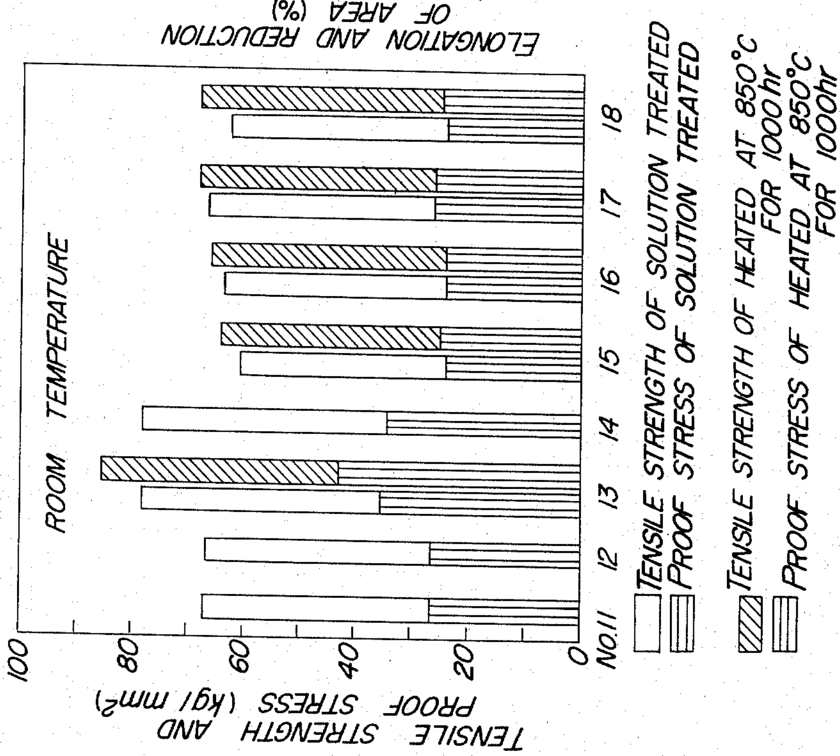


FIG. 8

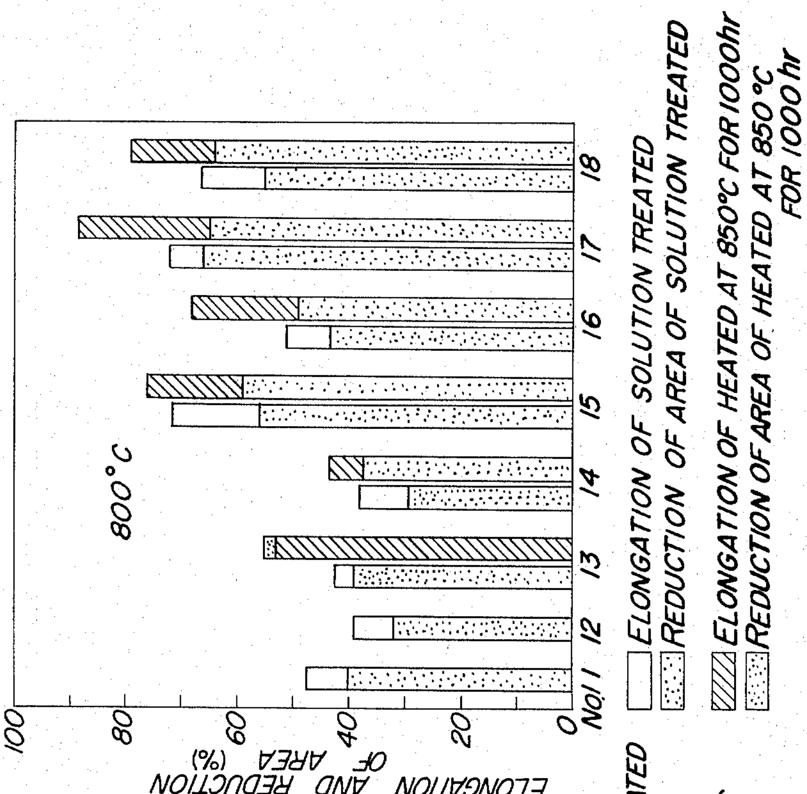
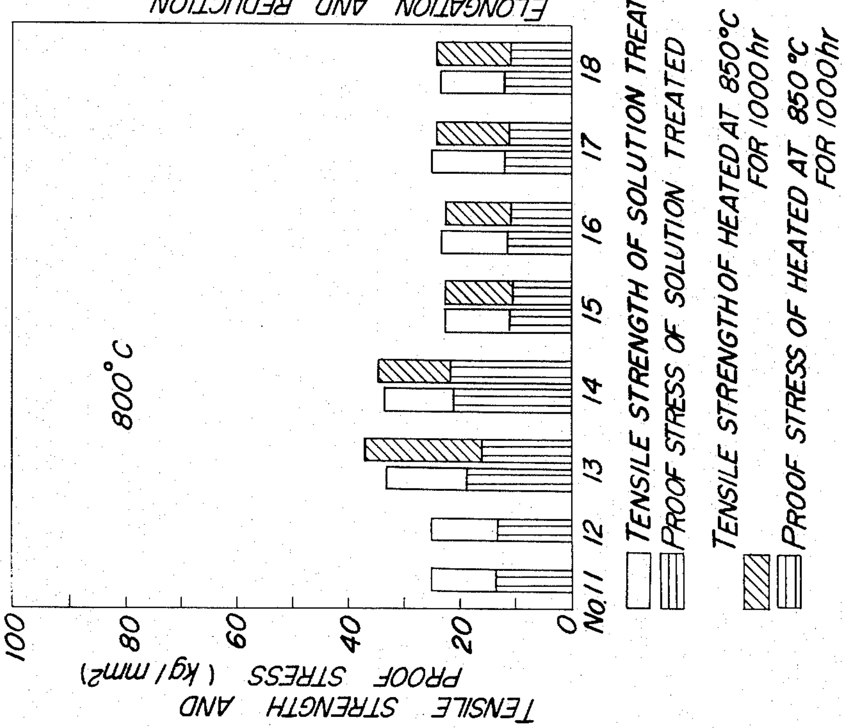
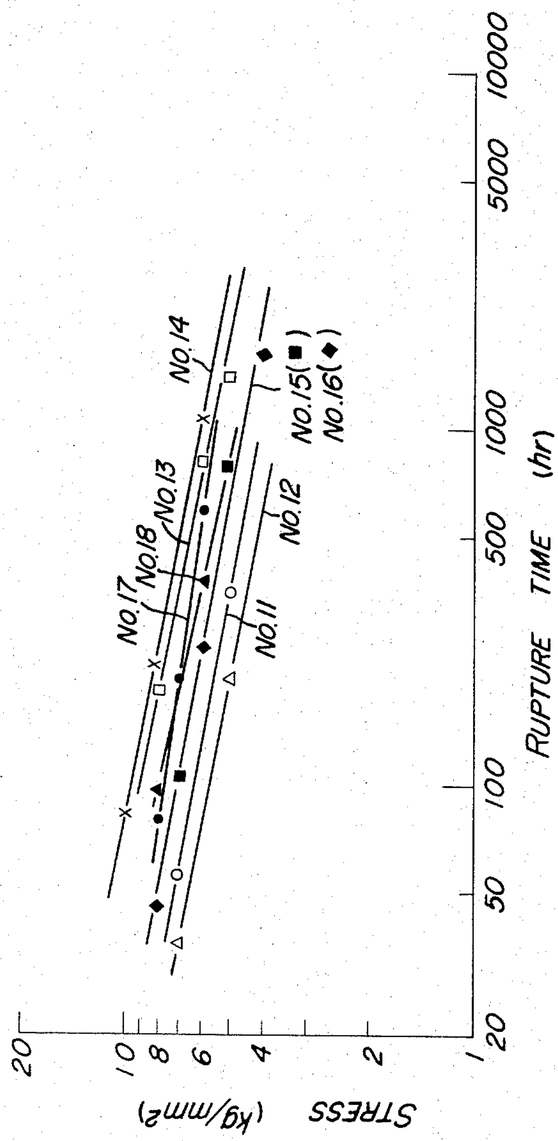


FIG. 7



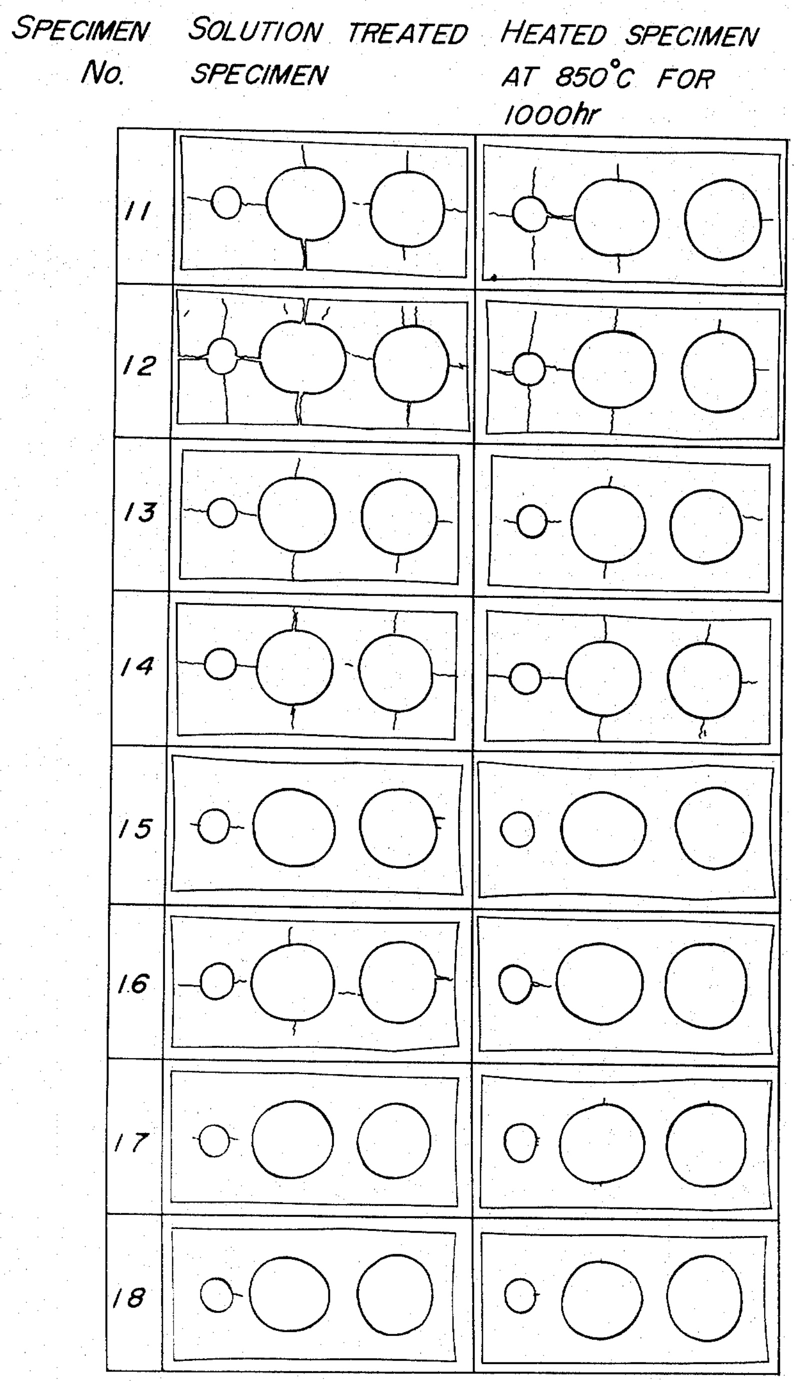
TENSILE PROPERTIES OF VARIOUS ALLOYS AT 800°C

FIG. 9



CREEP RUPTURE PROPERTIES OF VARIOUS ALLOYS AT 800°C

FIG. 10


SPECIMEN No.
SOLUTION TREATED SPECIMEN
HEATED SPECIMEN AT 850°C FOR 1000hr
11
12
13
14
15
16
17
18

HEAT-RESISTANT ALLOY FOR A COMBUSTION LINER OF A GAS TURBINE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an alloy which is intended to be used for forming a combustion liner of a gas turbine.

2. Description of the Prior Art

A combustion liner of a gas turbine is usually formed by shaping alloy sheets having thickness of 1 to 4 mm to a cylindrical form, pressing one end of the cylinder to form a tapered shape, then welding the sheets, and forming louvers for allowing air into the combustion liner and holes for mounting cross fire tubes. The number of the louvers is determined in accordance with the dimension of the combustion liner.

In the combustion liner of gas turbine, there is passed combustion gas of 1,000° to 1,700°C, so that in order to prevent the combustion liner from being molten by the high temperature to which it is exposed, the outer surface of the combustion liner is air-cooled and at the same time air is allowed to flow into the combustion liner. Thus, the temperature to which the combustion liner is usually heated is limited to 600° to 850°C.

As described above, in manufacturing the combustion liner, the material must be subjected to bending and welding and, in use, it is brought into contact with a high temperature combustion gas and air. Therefore, the material for forming the combustion liner must have superior characteristics in respect of formability, weldability, heat resistant characteristics and oxidation resistant characteristics at a high temperature. Further, since the combustion liner is subjected to sudden temperature change during each starting and stopping of the gas turbine engine, the material must have a substantial resistance to thermal shock. Further, the material must also have a superior ductility and a substantial resistance against becoming brittle after heating. These factors are all essential and particularly the high temperature corrosion resistant characteristics and the thermal shock resistant characteristics are important in determining the life of the combustion liner.

Conventionally, a combustion liner for a gas turbine has been made of a heat resistant steel in accordance with the AISI specification 309 (a heat resistant steel including 22 weight percent of chromium and 12 weight percent of nickel) or 310 (a heat resistant steel including 25 weight percent of chromium and 20 weight percent of nickel). However, recently, a cheap heavy oil has been used as a fuel of the gas turbine engine, the aforementioned steel is subjected to a problem of high temperature corrosion due to the influence of corrosive V_2O_5 which is produced when the heavy oil is burnt. Further, when the material is subjected to a high temperature for a prolonged time, brittle sigma phases and carbides precipitate and make the material brittle.

For these reasons, there has been developed alloys which have a substantial resistance to the corrosive gas produced by a combustion of heavy oil. They include a heat resistant alloy including 25 weight percent of chromium, 45 weight percent of nickel, 3 weight percent of cobalt, 3 weight percent of molybdenum, and 3 weight percent of tungsten, and a heat resistant alloy including 22 weight percent of chromium, 47 weight percent of nickel, 1.5 weight percent of cobalt, 9 weight percent of molybdenum and 0.6 weight percent of tungsten. These alloys are now in use for the combustion liner of a gas turbine. However, these alloys have less resistance against a thermal shock and have been found disadvantageous in that cracks are produced at the ends of louvers when the combustion liner is subjected to repeated sudden temperature changes. Further, these alloys are expensive since they include high percentages of molybdenum and tungsten and, moreover, they have hard matrix and include carbide and intermetallic compound. Therefore, they become brittle after a relatively short use.

SUMMARY OF THE INVENTION

Objects of the Invention

A primary object of the present invention is to provide a novel alloy for a combustion liner of a gas turbine.

Another object of the present invention is to provide an alloy for a combustion liner for a gas turbine which is resistant to a corrosive gas produced by the combustion of heavy oil as well as to a thermal shock.

A further object of the present invention is to provide an alloy for a combustion liner of a gas turbine which also has a substantial resistance to a sulfurized corrosion.

A further object of the present invention is to provide an alloy for a combustion liner of a gas turbine which is less expensive as compared with a heat resistant alloy including 25 weight percent of chromium, 45 weight percent of nickel, 3 weight percent of cobalt, 3 weight percent of molybdenum, and 3 weight percent of tungsten, or a heat resistant alloy including 22 weight percent of chromium, 47 weight percent of nickel, 1.5 weight percent of cobalt, 9 weight percent of molybdenum and 0.6 weight percent of tungsten.

Statement of the Invention

According to the present invention, there is provided an alloy including 0.03 to 0.10 weight percent of carbon, 0.30 to 1.00 weight percent of silicon, 0.50 to 3.00 weight percent of manganese, 43.0 to 50.0 weight percent of nickel, 22.0 to 30.0 weight percent of chromium, 0.10 to 0.50 weight percent of titanium, at least one of 0.005 to 0.20 weight percent of elements of cerium group in rare earth metals and 0.20 to 0.90 weight percent of niobium, and the balance iron and impurities accompanying thereto.

The alloy in accordance with the present invention has been developed to obtain superior formability, weldability, high temperature corrosion resistant characteristics, high temperature oxidation resistant characteristics, thermal shock resistance, ductility and resistance against becoming brittle after heating, which are required for an combustion liner of a gas turbine, and particularly to improve high temperature corrosion resistant characteristics and thermal shock resistance.

The present invention has been achieved by noting that, in a heat resistant alloy mainly including nickel and chromium, the high temperature corrosion resistant characteristics is substantially affected by the amount of the nickel content and that it is possible to improve the thermal shock resistance by adding titanium together with elements of cerium group in rare earth metals and/or niobium. Thus, the present invention is characterized by the fact that the nickel-chromium type heat resistant alloy including more than 43.0 weight percent of nickel further includes titanium and elements of cerium groups in rare earth metals and/or niobium.

According to the present invention, the amounts of the components have been determined from the following reasons.

The amount of the carbon content should be small in order to obtain a good ductility but from the viewpoint of strength the carbon should be contained as much as possible. Therefore, in order to have the both requirements suitably met, the amount of carbon content is determined to 0.03 to 0.10 weight percent.

The raw material usually includes at least 0.03 percent carbon and, in order to have the carbon content less than this value, a material of higher purity must be used or particular melting process must be employed. Therefore, the manufacturing cost is increased. Further, less carbon content decreases the strength of the alloy. For these reasons, the minimum value of the carbon content is determined to 0.03 percent.

If the carbon content is more than 0.10 percent, the ductility is reduced and cracks may be produced during forming. Further, much carbides precipitate during a use at high temperature causing a brittleness of the material.

The silicon content is added as a deoxidizing agent. If the content is less than 0.30 percent, a sufficient deoxidizing effect cannot be obtained, but if the content is more than 1.0 percent, it will adversely affect on the ductility and enhances precipitation of sigma phases at a high temperature.

Manganese is added for the purpose of deoxidization and desulfurization. If the content is less than 0.50 percent, a sufficient effect cannot be obtained, but if it exceeds 3.0 percent, the oxidation resistant characteristics of the alloy is deteriorated and precipitation of sigma phases is enhanced. Therefore, the content is determined between 0.30 to 3.0 percent.

Chromium is essential for improving the high temperature corrosion resistant characteristics against for example V_2O_5. This content is determined to 22.0 to 30.0 percent in view of the fact that it is not effective to provide a sufficient oxidation resistant characteristics and high temperature corrosion resistant characteristics if the amount of the content is less than 22.0 percent, but has an adverse effect on the formability and enhances the precipitation of the sigma phases if the content exceeds 30.0 percent.

Nickel serves to stabilize the austenite structure, to prevent the precipitation of sigma phases even under a prolonged period of heating and to improve the oxidation resistant characteristics and the high temperature corrosion resistant characteristics against V_2O_5. However, the content must be more than 43.0 percent. Otherwise, a sufficient high temperature corrosion resistant characteristics cannot be obtained.

The corrosion resistance against V_2O_5 can be improved by increasing the nickel content, however, the increased nickel content reduces the resistance against the corrosion by SO_2 gas which may be encountered when heavy oil is used as fuel. Moreover, an increased amount of nickel will correspondingly increase the cost of the alloy. Therefore, the upper limit of the nickel content is determined to 50.0 percent.

Titanium is effective to provide a deoxidization effect and to improve a creep rupture strength by precipitation of fine carbides. However, if the content is less than 0.10 percent, it is not so effective but, if it exceeds 0.50 percent, the amount of inclusions increase and much carbides precipitate resulting in a brittle structure. Therefore, the content is determined within the range of 0.10 to 0.50 percent.

The elements of cerium group in rare earth metals has a high deoxidizing and desulphurizing power, and by adding them, the oxygen and the sulphur content in an alloy can be reduced to provide an increased ductility at a high temperature and an increased resistance against thermal shock. However, if the content is less than 0.005 weight percent, it is not possible to obtain a sufficient deoxidizing and desulphurizing effect and may result in an insufficient ductility under a high temperature and an insufficient resistance to thermal shock. On the other hand, if the content is more than 0.20 weight percent, the elements may be produced as inclusions to make the alloy brittle. The elements of cerium group includes lanthanum, cerium, praseodymium, neodymium and samarium, among which a mixture of lanthanum, cerium and neodymium is available in market as "Mishmetal" with a cheap price, so that it is advisable to use the mixture. Since the elements of cerium group are easily oxidized, it is advisable to add these elements into a molten pool of alloy at the end of melting process, preferably after the titanium is added and oxygen content is reduced due to the deoxidization effect of the titanium.

Niobium is precipitated in the form of carbides and improves the high temperature strength of the alloy. Further, it has a deoxidizing effect and is effective to reduce the oxygen content in the steel and improve the ductility at a high temperature. If the niobium content is less than 0.20 weight percent, the effect is insufficient while, if it exceeds 0.90 weight percent, precipitation and coagulation of carbides are promoted at a high temperature with the result that the creep rupture strength is reduced and the ductility and toughness at the room temperature are decreased after a prolonged period of heating. It is favourable to control the content of niobium in the range of 0.40–0.70 weight percent.

Either of the elements of cerium group in rare earth metals and the niobium should be added together with titanium. Otherwise, the addition of for example titanium only will not be effective to improve a high temperature ductility. It has been found that, if the elements of cerium group in rare earth metals and/or niobium is added in addition to the titanium, a remarkable effect can be attained than in a case when either one of the elements is separated added. A continued investigation revealed that the alloy of the present invention provides the most excellent characteristics when it includes titanium and niobium in combination. Since the high temperature ductility and the resistance to thermal shock are dependent on the amount of oxygen in the alloy, an alloy containing less than 0.010 weight percent of oxygen provides a preferred characteristics.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a combustion liner of a gas turbine which may be formed from the alloy in accordance with the present invention;

FIG. 2 is a diagram showing the relation between the weight loss due to corrosion as measured through a V_2O_5 corrosion test and the amount of nickel content in the sample;

FIG. 3 is a diagram showing the results of V_2O_5 corrosion tests performed on the specimens Nos. **11** through **18**;

FIG. 4 is a diagram showing the results of 75 weight percent V_2O_5 and 25 weight percent Na_2SO_4 corrosion tests;

FIG. 5 is a diagram showing the tensile strength and the proof stress of the specimens **11** through **18** as measured at the room temperature;

FIG. 6 is a diagram showing the elongation and the reduction of area of the same specimens as measured at the room temperature;

FIG. 7 is a diagram showing the tensile strength and the proof stress of the specimens **11** through **18** as measured at 800°C;

FIG. 8 is a diagram showing the elongation and the reduction of area as measured by the same tests;

FIG. 9 is a diagram showing the results of creep rupture tests performed at 800°C; and

FIG. 10 is a picture showing the results of the thermal shock tests performed on the specimens **11** through **18**.

EXAMPLES

FIG. 1 shows a general form of a combustion liner for a gas turbine. The combustion liner is formed by shaping sheets to a cylindrical form, making louvers and holes for mounting cross-fire tubes, pressing one end to form a tapered shape and thereafter welding a seamed joint of these shaped sheets. In the drawing, the reference numeral (**1**) designates the louver, and (**2**) the hole for mounting the cross-fire tube.

The alloy for making the combustion liner is required to have superior formability, weldability, high temperature oxidation resistant property, high temperature corrosion resistant property, thermal shock resistance, ductility, and resistance against becoming brittle after heating. Among the properties, the formability, weldability and the high temperature oxidation resistant property have been sufficiently attained by conventional heat resistant alloys containing high amount of nickel and chromium. In view of the fact, tests have been performed for the purpose of knowing the high temperature corrosion resistant propety.

Table 1 shows the compositions of materials used for the tests. These materials were melted, casted, forged and heat treated at 1100°C for 1 hour then cooled in water and cut to specimens of 5 × 8 × 5 mm. The corrosion weight loss was measured by sprinkling 0.1 g of V_2O_5 on each of the specimens and heating at 1200°C for 100 hours in a heating pot.

TABLE 1

SAMPLE No.	CONTENTS (weight percent) C	Si	Mn	Ni	Cr
1	0.20	1.00	1.91	13.68	27.00
2	0.07	1.17	1.50	20.38	24.70
3	(0.07)	(0.5)	(1)	20.85	26.60
4	(0.07)	(0.5)	(1)	32.90	28.60
5	0.08	0.65	1.10	38.50	28.50
6	0.10	0.52	1.14	46.10	30.90
7	(0.07)	(0.5)	(1)	55.60	31.40
8	(0.07)	(0.5)	(1)	66.70	30.70

Note: The values in the parentheses show intended amounts. The balance is iron and impurities.

FIG. 2 shows the results of V_2O_5 corrosion tests. In the drawing, it should be noted that the weight loss due to corrosion widely varies in accordance with the amount of nickel content. More specifically, the weight loss increases as the nickel content increases when the amount of nickel is less than 33 weight percent. However, when the nickel content exceeds 33 weight percent, the weight loss remarkably decreases. A remarkable change in the weight loss is seen at a point corresponding to a nickel content of 43.0 weight percent. For this reason, the nickel content must be more than 43.0 weight percent in order to obtain an excellent high temperature corrosion resistant property.

Next, samples as shown in Table 2 were prepared to perform tests for determining the properties required for a combustion liner of a gas turbine.

TABLE 2.—CHEMICAL COMPOSITION OF ALLOYS

No.	(wt %) C	Si	Mn	Ni	Cr	Mo	W	Co	Nb	Ti	(ppm) La	Ce	N	O	H
11	0.05	0.98	1.49	44.22	26.71		2.35						255	212	2.5
12	.06	.95	1.47	44.80	27.04		2.41				220	122	187	219	1.2
13	.08	1.37	1.49	45.03	28.19	3.20	4.14	2.98					165	135	.9
14	.09	.58	.68	47.84	21.59	8.36	.79	1.57					214	97	.6
15	.05	1.02	1.53	44.22	27.12					0.21	110	123	165	137	Trace
16	.06	.69	1.58	44.11	26.59				0.28	.12	390	880	243	112	1.2
17	.07	1.20	1.52	46.21	28.43				.40	.46			222	92	1.9
18	.07	.82	1.59	47.98	26.49				.90	.19			247	77	.6

Note:
1. The balance is iron and impurities.
2. Specimens of the prior alloy are indicated by Nos. 11–14.

The specimens all included more than 43.0 weight percent of nickel as well as additional elements for improving the properties of the alloy. Specimens were prepared by melting the material in the air, heating at 1150°C for 1 hour after forging, and cooling in water.

The above V_2O_5 corrosion tests were performed by sprinkling 0.1 g of V_2O_5 on each specimen of 5 × 8 × 50 mm and heating at 900°C and 1100°C for 100 hours. After the heating, corrosion weight loss was measured. The results are shown in FIG. **3.** When heated at 900°C, the weight loss was the smallest in the sample No. **16** which included all of the titanium, niobium and the elements of cerium groups in rare earth metals. The weight loss increases in the order of the samples **18** and **17** which included titanium and niobium and the samples **14** and **13** which included molybdenum, tungsten and cobalt. When heated at 110°C, the weight loss was less than 0.14 g/cm^2 in each of the samples.

The corrosion tests using a mixture of V_2O_5 and Na_2SO_4 were performed by sprinkling a mixture of 75 weight percent of V_2O_5 and 25 weight percent of Na_2SO_4 on each specimen of 5 × 8 × 50 mm in dimension. The specimens were heated at 900°C or 1100°C for 100 hours and, thereafter, weight loss due to the corrosion was measured. The results are shown in FIG. **4.** When heated either at 900°C or at 1100°C, the specimens **13** and **14** which contained molybdenum and tungsten had remarkably greater weight loss as compared with other samples. This fact means that the alloy containing both of molybdenum and tungsten is easily corroded by SO_2 gas separated from Na_2SO_4. Therefore, these alloys are not suitable for use of heavy oil as fuel.

FIGS. **5** and **6** show results of tensile tests performed at the room temperature. The tests were performed on specimens which were processed by solution treatment and other specimens which were heated at 850°C for 1000 hours after solution treatment. The latter specimens were tested in order to know the properties of the alloy after it was exposed to an actual operating condition of a gas turbine engine under which the combustion liner was subjected to a temperature of 600° to 850°C and large amounts of carbides might precipitate therein. In order that the material is not made brittle when used at a high temperature, it is essential that the material shows an excellent property in respect of elongation and reduction of area. The strength should be as high as possible, but it is not an essential factor. FIG. **5** shows tensile strength and proof stress, and FIG. **6** shows elongation and reduction of area. The specimens that were processed by solution treatment but not heated showed high tensile strength and proof stress as well as sufficient elongation and reduction of area. On the other hand, with respect to the specimens that were heated after solution treatment, it should be noted that, although the specimens **15** to **17** showed satisfactory properties, the specimen **13** showed poor elongation and reduction of area.

Tension tests should preferably performed at a temperature to which the combustion liner of the gas turbine is heated during operation. Otherwise, it would not be possible to obtain practical data. In view of the above, the inventors performed tension tests at 800°C. The tensile strength and the proof stress obtained through the tests are shown in FIG. **7**, while elongation and reduction of area are shown in FIG. **8.**

These tests revealed that the data on elongation and reduction of area obtained by the tests performed at the room temperature cannot be applied to the operating condition. As apparent from FIG. **8,** the specimens **15** through **18** which embodied the present invention showed better elongation and reduction of area properties than that of specimens **11** through **14** in both states of solution treated and after heated.

A combustion liner of a gas turbine is not subjected to a substantial stress because the internal pressure thereof is relatively low. However, since it is used at an elevated temperature for a long period, creep rupture tests were performed. FIG. **9** shows the results of the creep rupture tests. From FIG. **9,** it should be noted that the specimens **15** through **18** have creep rupture strength slightly inferior to that of the specimens **13** and **14** which contain cobalt, tungsten and molybdenum, but superior to that of the specimens **11** and **12.** As described above, the combustion liner of gas turbine is not subjected to a substantial stress, so that the creep rupture strength of this order is satisfactory for use in a combustion liner of a gas turbine.

As a result of a creep rupture test, it was found that the values of creep rupture elongation of specimens formed of the prior alloy which are indicated by Nos. **11, 12, 13** and **14** are 10–24 percent, 8–10 percent, 13–20 percent and 19–22 percent, respectively. Further, it is found that the values of creep rupture elongations of specimens Nos. **15, 16, 17** and **18** of the alloy according to the present invention are 29–49 percent, 18–29 percent, 38–52 percent and 28–43 percent, respectively. It will be understood by a comparison of these values that the values of the rupture elongation of the specimens of the alloy according to the present invention are considerably greater than that of the prior alloy. This means that a crack is not almost produced in the combustion liner of the gas turbine during an operation of the gas turbine even if the combustion liner made of the alloy according to the present invention is used in the gas turbine.

Finally, the inventors tested the resistance to thermal shock which is one of the most essential properties of an alloy for use in a combustion liner of a gas turbine. Specimens of 5 × 20 × 9 mm were prepared and two 5 mmφ holes and a 2 mm hole were drilled in the specimens. These specimens were alternately moved into the water vessel and the electric furnace. One cycle of operation was constituted by placing each specimen in the water vessel for six seconds and thereafter moving it into the furnace heated to 800°C and holding it therein for 5 minutes and 54 seconds. After 400 cycles, the specimens were taken out and investigated for existence of cracks on the longitudinal sectional plane at centre of thickness. The results are shown in FIG. **10** in which it should be noted that the specimens of the alloys in accordance with the present invention showed a few fine cracks while the specimens **11, 12, 13** and **14** showed remarkable cracks. It will be apparent from the above result that the thermal shock resistance of the alloy of the present invention is very excellent.

From the above descriptions, it will be clear that the alloy in accordance with the present invention which contains titanium and niobium and/or elements of cerium group in rare earth metals in combination has a superior properties as an alloy for a combustion liner of a gas turbine.

We claim:

1. An alloy consisting essentially of 0.03 to 0.10 weight per cent of carbon, 0.30 to 1.00 weight per cent of silicon, 0.50 to 3.00 weight per cent of manganese, 43.0 to 50.0 weight per cent of nickel, 22.0 to 30.0 weight percent of chromium, 0.10 to 0.50 weight per cent of titanium, 0.20 to 0.90 weight per cent of niobium and the balance iron and impurities accompanying therewith and possessing high ductility.

2. An alloy according to claim **1,** wherein said alloy has been subject to forging.

3. An alloy in accordance with claim **2,** wherein the niobium is present in an amount of from 0.40 to 0.70 weight percent.

4. An alloy in accordance with claim **2** which contains less than 0.010 weight percent of oxygen.

5. An alloy in accordance with claim **1,** wherein the niobium is present in an amount of from 0.40 to 0.70 weight percent.

6. An alloy in accordance with claim **1** which contains less than 0.010 weight percent of oxygen.

7. An alloy consisting essentially of 0.03 to 0.10 weight per cent of carbon, 0.30 to 1.00 weight per cent of silicon, 0.50 to 3.00 weight per cent of manganese, 43.0 to 50.0 weight percent of nickel, 22.0 to 30.0 weight per cent of chromium, 0.10 to 0.50 weight per cent of titanium, 0.20 to 0.90 weight per cent of niobium, 0.005 to 0.20 weight per cent of at least one element selected from a cerium group in rare earth metals, and the balance iron and impurities accompanying therewith and possessing high ductility.

8. An alloy in accordance with claim **7** which contains 0.20 to 0.90 weight percent of niobium, and 0.005 to 0.20 weight percent of at least one element selected from cerium group in rare earth metals.

9. An alloy in accordance with claim **8** which contains less than 0.010 weight percent of oxygen.

10. An alloy in accordance with claim **7** which contains 0.40 to 0.70 weight percent of niobium, and 0.03 to 0.17 weight percent of at least one element selected from cerium group in rare earth metals.

11. An alloy in accordance with claim **10** which contains less than 0.010 weight percent of oxygen.

12. An alloy in accordance with claim **7**, wherein the element of the cerium group is selected from the group consisting of lanthanum, cerium, praseodymium, neodymium and samarium.

13. An alloy in accordance with claim **7**, wherein the cerium group elements are a mixture of lanthanum, cerium and neodymium.

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