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HIGH TEMPERATURE ALLOYS

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Fig. 1

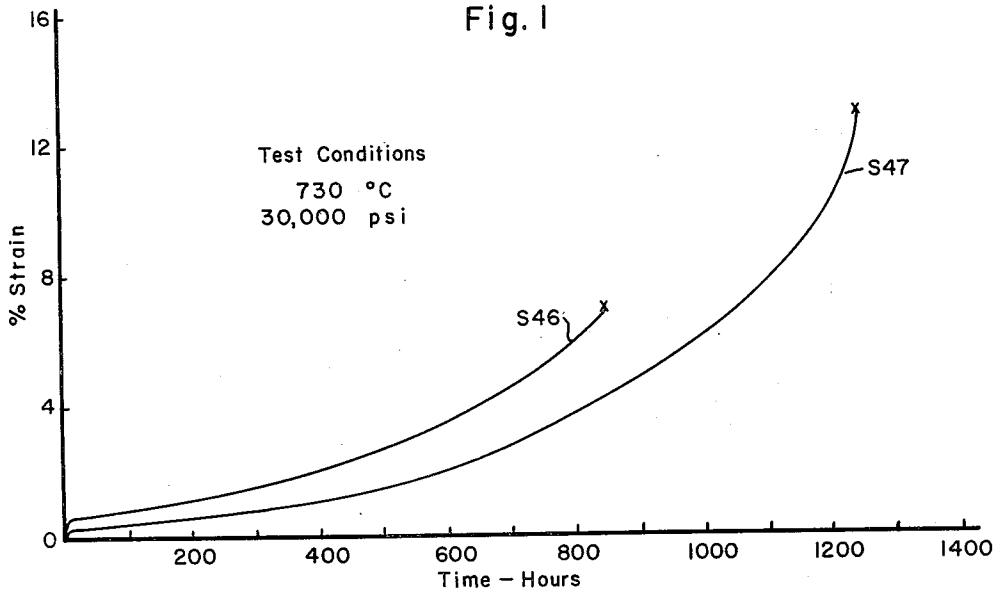
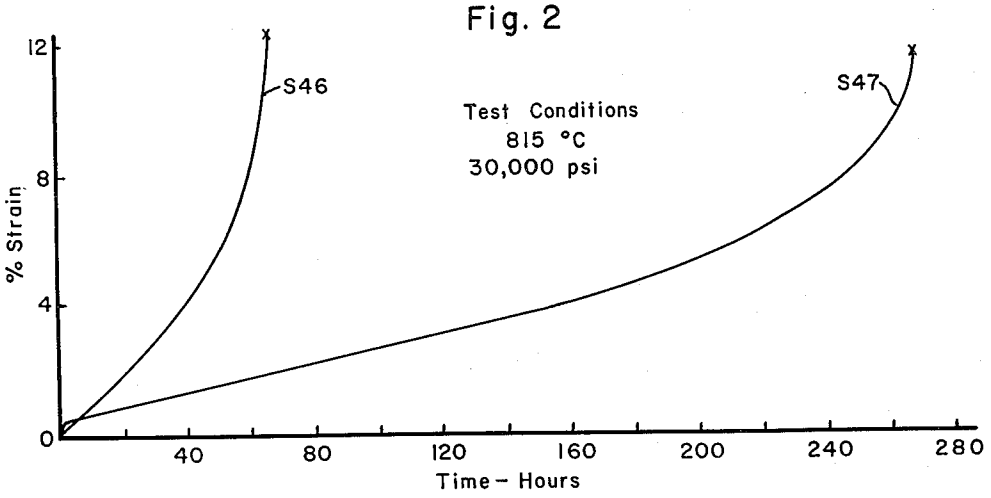


Fig. 2



WITNESSES

Leon J. Faza

H. M. Snyder

INVENTOR

Alexander W. Cochardt

BY

Frederick Sheppard

ATTORNEY

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HIGH TEMPERATURE ALLOYS

Alexander W. Cochardt, Wilkins Township, Allegheny County, Pa., assignor to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

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This invention relates to improved nickel-chromium-iron and cobalt-nickel-chromium base high temperature alloys, particularly suitable for use in the temperature range of from 650° C. to 870° C., and members, such as turbine blades, prepared therefrom.

Among the difficulties encountered in constructing gas and steam turbines that will operate successfully at temperatures in the range of 650° C. to 870° C., and higher, if possible, have been deficiencies in properties of commercially available alloys from which blades may be manufactured. The properties sought in a material for this application are high rupture stress, relatively long rupture time, and substantial rupture elongation, under reasonably expected loads, and in addition, corrosion resistance, notch ductility, ductility at low temperature, and workability sufficient to permit forging, swaging, and rolling. The alloys now in use are especially deficient in that rupture stress and rupture elongation of these materials are not sufficiently high, and further, they display a tendency toward notch-sensitivity.

It is therefore the object of this invention to provide a notch-ductile, wrought cobalt-nickel-chromium and iron-nickel-chromium base alloys having high rupture stress and good rupture elongation particularly at temperatures in a range from 650° C. to 870° C., in association with selected amounts of hafnium and other hardening additives.

It is another object of this invention to provide for members such as turbine blades prepared from a cobalt-nickel-chromium base alloy having high stress rupture properties and containing predetermined amounts of tungsten, molybdenum and titanium in association with selected amounts of hafnium.

It is a further object of this invention to provide a wrought nickel-chromium-iron base alloy having high stress rupture properties at elevated temperatures and containing predetermined amounts of titanium, columbium, and aluminum in association with selected amounts of hafnium.

Other objects of the invention will become apparent as the disclosure proceeds.

For a better understanding of the nature and objects of the invention reference should be had to the following detailed description and the drawings wherein:

FIGURE 1 is a graph showing the creep properties of two alloys subjected to a constant stress of 30,000 p.s.i. at 730° C. in which the strain is plotted against time; and,

FIG. 2 is a graph showing the creep properties for two alloys subjected to a constant stress of 30,000 p.s.i. at 815° C. in which strain is plotted against time.

The invention generally relates to nickel-chromium-iron and cobalt-nickel-chromium base alloys containing critical proportions of hafnium in the range of 0.01% to 1.5% which also include other alloying additives such as titanium, tungsten, columbium, aluminum, and molybdenum, and, which when appropriately heat treated, and aged, exhibit superior stress rupture properties and notch ductility particularly at temperatures in the range from 650° C. to 870° C. More specifically, one preferred alloy of the present invention comprises, by weight, from 27.7% to 32.5% nickel, 18% to 19.5% chromium, 7.25% to 8.75% tungsten, 3.5% to 4.5% molybdenum, 3% to 4% titanium, 0.1% to 1% hafnium, less than 2% iron, and the balance cobalt, except for incidental impurities and small amounts of additives.

Another preferred alloy in accordance with this invention comprises, by weight, from 14% to 16% chromium, from 5% to 9% iron, from 2.25% to 2.75% titanium, 0.7% to 1.2% columbium, 0.4% to 1% aluminum, 0.1% to 1.0% hafnium, and the balance, at least 70%, nickel, with incidental impurities and additives.

Small amounts of aditives such as boron in amounts of up to 0.1%, vanadium up to 0.4%, and manganese in amounts up to 1% or even more, may be present in the alloys to improve the forgeability and hot working properties, to improve the grain structure and for other benefits.

The alloy can be prepared by arc melting or in a vacuum induction furnace and the melt is cast into an ingot. The ingot can be forged at a temperature from 1035° C. to 1150° C. to produce a more homogeneous material and to yield the desired shape and size of billet or a final desired shaped member made as a turbine blade. The finally shaped member is solution treated at a temperature from 1000° C. to 1200° C. to put into solution the precipitation hardening constituents, quenched from this temperature in either oil or water, aged for an extended period at a temperature from 650° C. to 760° C., and lastly, cooled to ambient temperature.

The tungsten and molybdenum in the alloys function as solution hardeners. Titanium and aluminum function as precipitation hardeners. Chromium provides for corrosion resistance, while iron improves the creep properties of the alloys. Columbium, when present, tends to assure good high temperature properties, including better strength and ductility.

The superior high temperature performance of the alloys of this invention over alloys known to the art is primarily attributable to the addition of a critical amount of the element hafnium. It is believed that the beneficial effect of hafnium is due, in part, to the fact that hafnium compounds have an extremely high free energy of formation. For example, one such compound commonly found in the alloys of this invention is hafnium oxide which has a free energy of formation of —130 kcal./mole per oxygen atom at room temperature.

This free energy of formation of the oxide is higher than that with any other element presently used in high temperature alloys. Since the hafnium compounds thus formed are quite stable, even small hafnium additions will have a profound influence on the high temperature properties of the alloys. The presence of hafnium virtually precludes the formation of grain boundary films of nickel or cobalt sulfides, of nickel or cobalt oxides, or other harmful sulfides, oxides, nitrides, etc. The formation of these latter compounds at grain boundaries is often the cause of the brittleness in these alloys. The hafnium compounds that are formed; i.e., the hafnium sulfides, oxides, nitrides, etc., are not harmful to the alloy since they tend to assume a generally spherical form and are found dispersed throughout the grains rather than being concentrated along grain boundaries. It is believed

that there may be other reasons for the superior properties obtained by including hafnium in these alloys. In general, an addition of between .01% and 1.5% of hafnium will prove beneficial in alloys of the type under discussion. The preferred compositions include a hafnium content in the range from .1% to 1%.

To demonstrate the effectiveness of the hafnium additions in alloys known to the art, an alloy composition containing no hafnium and identified herein as S46, is compared with a hafnium-containing alloy, alloy S47. The hafnium-free alloy S46 is considered comparable with any other nickel or cobalt base alloy that has been developed to date for the applications mentioned above. The compositions of S46 and S47 are set forth in Table I.

TABLE I

[Compositions of alloys S46 and S47 in weight percent]

	Co	Ni	Cr	W	Mo	Ti	Hf	Fe and Impurities
S46	35	30	19	8	4	3.75	------	Bal.
S47	34.8	29.8	19	8	4	3.75	0.5	Bal.

A heat having the composition designated as alloy S46 was melted and cast into ingots. The ingots were forged from 1100° C. into bar stock having a diameter of 7/16 inch. The bar stock was then solution treated for one hour at 1180° C. and was quenched from that temperature. An ageing treatment followed which consisted of holding the bar stock at a temperature of 730° C. for twenty-four hours.

A heat of a hafnium-containing composition, designated as alloy S47 in Table I, was made and an ingot cast and processed in a manner identical to that described for alloy S46. It will be noted that S46 and S47 are essentially identical alloys except that S47 contains a small but critical amount of hafnium.

Specimens of the no-hafnium containing alloy S46 and the hafnium-containing alloy S47 were subjected to creep rupture tests at temperatures of 730° C. and 815° C. under a constant stress of 30,000 lbs. per square inch. The performance of these alloys can be compared by referring to FIGS. 1 and 2 where the test data are graphically set forth. It is noted that the addition of 0.5% hafnium greatly improves creep rupture properties. At 730° C. the rupture time is increased from 868 to 1246 hours and the rupture elongation from 7.2% to 13% by the hafnium addition to the alloy. At 815° C. the rupture time is increase from 67 to 268 hours by the hafnium addition, while the elongations are essentially equivalent.

The following table sets forth the composition of certain well-known commercial high temperature alloys:

TABLE II

	C	Mn	Si	Cr	Ni	Co	Mo	W	Cb	Ti	N	Fe	Other
Alloy A	.04	1.0	0.6	13.0	44.0	----------	6.0	----------	----------	2.5	------	Bal.	
Alloy B	0.1	1.0	1.0	15.5	78.0	----------	----------	----------	----------	0.65	------	2.0	Al 3.25.
Alloy C	0.1	1.0	------	16.0	44.0	29.5	3.0	----------	----------	2.5	------	1.5	Al 3.0.
Alloy D	0.04	0.50	0.40	15.0	73.0	----------	----------	----------	1.0	2.5	------	7.0	Al 0.7.
Alloy E	0.03	0.70	0.65	17.9	37.0	20.0	3.03	----------	----------	2.99	------	Bal.	Al 0.25.
Alloy F	0.36	1.54	0.59	21.08	20.8	20.54	3.0	2.18	0.98	------	0.11	Bal.	
Alloy G	.05	1.35	0.95	15.0	26.0	----------	1.75	----------	----------	2.0	------	Bal.	Al 20; V. 30.
Alloy H	0.35–0.45	1.0 max.	1.0 max.	18.50–20.50	19.0–21.0	42.0–44.0	3.50–4.00	3.50–4.00	3.50–4.00	------	------	Bal.	

One of the above listed commercial alloys, alloy D, which is widely employed as blade material in industrial gas turbines, becomes relatively brittle after a moderate time of exposure to temperatures in the range 590° C.–760° C., and there have been instances in which its relatively low ductility has resulted in gas turbine blades cracking in service after relatively short exposure to elevated temperatures.

In comparing the test data obtained for alloy S47 with published data available for alloy D, it is noted that alloy S47 exhibits considerable more ductility than alloy D. For example, at a temperature of 730° C. and a rupture stress of 30,000 lbs. per square inch, the rupture elongation of alloy D is reported to be only 2%, while the elongation of S47 at the same stress and temperature is more than six times greater. At 650° C. the rupture elongation data obtained with alloy D is even less favorable. The poor rupture elongation of alloy D perhaps explains the high notch sensitivity observed at those temperatures. In contrast, specimens of S47 are uniformly found to be notch ductile. Notched sections of the specimens exhibited longer rupture times than the plain sections. At 815° C. alloy D becomes less brittle, however, it still compares unfavorably with alloy S47. When tested under the same conditions at 815° C., alloy D has a rupture time of 60 hours and a rupture elongation of only 6.1%, while alloy S47 has a rupture time of 268 hours and a rupture elongation of 11.7% (see Table III).

In Table III the stress rupture properties of the commercial high temperature alloys of Table II are listed for comparison with the same properties of alloy S47. The temperature of test is 815° C.

TABLE III

Alloy	Stress, p.s.i.	Rupture Time, Hours	Rupture Elongation, Percent
A	20,000	100	(1)
B	15,000	110	2
C	40,000	150	9
D	30,000	60	6.1
E	24,500	100	33
F	15,000	100	(1)
G	16,000	100	(1)
H	25,000	100	(1)
S47	30,000	268	11.7

[1] Rupture elongation not reported.

Study of Table III reveals that only one alloy, alloy C, has stress rupture properties at 815° C. that exceed the like properties of S47. Alloy D has the disadvantages previously discussed. All the other alloys listed have distinctly lower rupture stresses and rupture times. While alloy C has relatively good properties at 815° C., and thus superficially appears preferable to S47 for the contemplated applications, it is even more brittle and more notch sensitive than alloy D in the temperature range from 600° C. to 750° C. The notch sensitivity of alloy C is the reason that this alloy has not found application as a blade material in industrial gas turbines.

The alloys of Table II can be materially improved by adding hafnium thereto in accordance with the present invention.

While hafnium is a relatively expensive material, since only very small amounts are required to obtain the beneficial result, the total cost of each of the alloys would be increased to only a minor extent. Thus, from .01% up to 1.5%, and preferably from 0.1% to 1.0%, of hafnium can be added to alloys A to H of Table II with greatly improved ductility and creep rupture properties being obtained. In this connection, nickel-chromium-iron base alloys, essentially similar to alloy D of Table

II with the addition of hafnium, were prepared using the following basic alloy composition:

Element:	Percent
Chromium, min.	14.0–16.0
Iron	5.0–9.0
Titanium	2.25–2.75
Columbium	0.7–1.2
Aluminum	0.4–1.0
Manganese	0.3–1.0
Silicon, max.	0.5
Copper, max.	0.2
Carbon, max.	0.08
Sulfur	0.01
Nickel, Balance, min.	70
Hafnium	0.01–1.5

Hafnium was added in an amount in this basic alloy to produce a first alloy composition having 0.5% hafnium and a second alloy composition having 1.0% hafnium.

According to the present invention superior high temperature alloys have been obtained by adding to nickel-chromium-iron and cobalt-nickel-chromium base alloys an amount of hafnium in the range from .01% to 1.5%. The alloys exhibit notch ductility, good stress rupture properties, and good rupture elongation. This has been accomplished without unduly increasing the cost of the alloys.

While considerable emphasis has been placed upon the properties of the alloys of this invention at elevated temperatures in the range of from 650° C. to 870° C., it will be understood that the properties are excellent for use at other temperatures, such as at room temperature and at intermediate temperatures. Also, other members than turbine blades may be manufactured from the alloys. Thus, tools and dies, and members subjected to hard usage may be made from these alloys.

It will be understood that the specific heat treatment described in the example in the above specification may be varied to suit the particular application contemplated. In general, the above specification is exemplary rather than limiting.

I claim as my invention:

1. A notch-ductile alloy having good stress rupture properties under load in a temperature range of from 650° C. to 870° C., comprising, by weight, 27.7% to 32.5% nickel, 18% to 19.5% chromium, 7.25% to 8.75% tungsten, 3.5% to 4.5% molybdenum, 3% to 4% titanium, .01% to 1.5% hafnium, less than 2% iron, and the balance cobalt except for incidental impurities amounting to not more than 1%.

2. An alloy having notch ductility and good stress rupture properties under load in a temperature range of from 650° C. to 870° C. comprising, by weight, 27.7% to 32.5% nickel, 18% to 19.5% chromium, 7.25% to 8.75% tungsten, 3.5% to 4.5% molybdenum, 3% to 4% titanium, 0.1% to 1% hafnium, less than 2% iron, and the balance cobalt except for incidental impurities amounting to not more than 1%.

3. A high temperature alloy suitable for load-bearing applications at elevated temperatures comprised, by weight, of at least 14% to 16% chromium, 5.0% to 9.0% iron, 2.25% to 2.75% titanium, 0.7% to 1.2% columbium, 0.4% to 1.0% aluminum, 0.01% to 1.5% hafnium, and the balance nickel in amount not less than 70% of the total with minor additives and impurities not exceeding 2%.

4. A wrought alloy having good ductility and stress rupture properties when loaded at elevated temperatures comprising, by weight, at least 14% to 16% chromium, from 5% to 9% iron, from 2.25% to 2.75% titanium, from 0.7% to 1.2% columbium, from 0.4% to 1% aluminum, from .1% to 1% hafnium, and the balance nickel with minor additives and impurities not exceeding 2%, said nickel comprising at least 70% by weight of the alloy.

5. A wrought alloy suitable for use under load in a temperature range of from 650° C. to 870° C. comprising, by weight, 29.8% nickel, 19% chromium, 8% tungsten, 4% molybdenum, 3.75% titanium, 0.5% hafnium, and the balance cobalt except for incidental impurities not exceeding 1%.

6. A wrought member suitable for use as a turbine blade having high creep strength and notch ductility at temperatures of from 650° C. to 870° C., comprising an alloy composed of, by weight, from 27.7% to 32.5% nickel, from 18% to 19.5% chromium, from 7.25% to 8.75% tungsten, from 3.5% to 4.5% molybdenum, from 3% to 4% titanium, from 0.1% to 1% hafnium, less than 2% iron, and the balance cobalt except for incidental impurities not exceeding 1%.

7. In a process for producing a wrought member suitable for use as a turbine blade for service at temperatures of from 650° C. to 870° C., the wrought member comprising an alloy composed of, by weight, 29.8% nickel, 19% chromium, 8% tungsten, 4% molybdenum, 3.75% titanium, 0.5% hafnium, and the balance cobalt except for incidental impurities not exceeding 1%, the steps of, (1) solution treating said wrought member at a temperature over 1090° C., and (2), aging said member at from 650° C. to 760° C. for about 24 hours, said alloy as treated characterized in exhibiting at a constant stress of 30,000 p.s.i. and at a temperature of 815° C. a rupture time in excess of 200 hours.

8. A wrought member suitable for use as a turbine blade having high creep strength and notch ductility at elevated temperatures, comprising a nickel-chromium-iron base alloy composed of, by weight, at least 14% to 16% chromium, 5% to 9% iron, 2.25% to 2.75% titanium, 0.7% to 1.2% columbium, 0.4% to 1% aluminum, 0.1% to 1% hafnium, and the balance, amounting to at least 70%, nickel, except for impurities not exceeding 2%.

References Cited in the file of this patent

UNITED STATES PATENTS

2,304,353	Griffiths et al.	Dec. 8, 1942
2,570,193	Bieber et al.	Oct. 9, 1951