

1

2,977,222

HEAT-RESISTING NICKEL BASE ALLOYS

Clarence George Bieber, Bayonne, N.J., assignor to The International Nickel Company, Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Aug. 22, 1955, Ser. No. 529,926

27 Claims. (Cl. 75—171)

The present invention relates to special high temperature, heat and stress resisting thermal members which are subjected in use under stress at elevated temperatures to destructive actions of various media, especially to the corrosive action of such media as oxidizing, neutral and reducing atmospheres containing harmful constituents, and to special heat resisting, columbium-free and tungsten-free, nickel-chromium alloys suitable for use as such thermal members.

Heretofore, the art has endeavored to produce satisfactory high temperature alloys for use as heat and stress resisting thermal members in such heat engines as gas turbines, jet engines and the like. While many alloys have been proposed, continual demands by industry for heat engines with higher speed and power capacity have placed more rigorous requirements on thermal members of heat engines, including the requirement that thermal members withstand higher and higher operating temperatures under higher and higher stresses. In addition, such heat and stress resisting thermal members must possess, among other things, resistance to creep and resistance to corrosion, erosion, oxidation and pitting at elevated temperatures as well as being capable of resisting destructive actions of operating media. Under operating conditions, thermal members of gas turbines and jet engines are subjected to various types of stresses, including not only steady or static stresses but also fluctuating or alternating dynamic stresses which complicate the problem of providing satisfactory alloys for use as thermal members, for example, turbine blades, valves and valve parts, and other component parts of heat engines and the like.

In evaluating alloys for high temperature properties, stress rupture tests at elevated temperatures are usually relied upon. Such a test can comprise subjecting a test specimen of the alloy to a rupture test at a temperature of 1500° F. under a given stress. The time it takes the specimen to rupture, i.e., its rupture life, under the foregoing conditions is employed to evaluate its behavior under stress in service. It has been proposed that cast alloys be employed in a number of instances but it has been found that the cast alloys had the disadvantage of varying widely in fatigue and creep properties among different castings of the same alloy. Furthermore, certain types of boron-hardened cast alloys were proposed for use as blade material but were found not completely

2

satisfactory, particularly because the alloys were usually glass brittle at room temperature and were highly sensitive to breakage in handling and also very sensitive to thermal shock. For these and a number of other reasons, it became necessary to employ thermal members made of wrought alloys in many applications. In searching for satisfactory wrought alloys, for example, alloys having a high rupture life at higher and higher temperatures, the art found that it was necessary to incorporate in the alloy very substantial amounts of certain special alloying elements. Under existing world conditions, the art became more cognizant of the fact that a shortage existed in certain important alloying elements and this led to the classification of these scarce alloying elements as "strategic elements." Columbium is considered the most strategic alloying element. The other important strategic but less scarce alloying elements are tungsten and cobalt. While still other alloying elements might be deemed strategic elements, these other elements are much more plentiful and much less strategic. The term "strategic elements," as employed herein, refers to the highly strategic elements columbium, tungsten and/or cobalt. In the search for wrought alloys of exceptionally high properties at elevated temperatures, it was found that the more satisfactory wrought alloys usually contained two or even all three of the aforementioned strategic elements in substantial amounts. Many of these more satisfactory wrought alloys required the presence of the particularly strategic element columbium in an amount which created a potential demand for columbium far exceeding the available supply. A number of alloys required the use of columbium and/or tungsten in combination with cobalt. In view of the situation requiring the minimum use of strategic elements, the art was placed under pressure to provide wrought alloys having a high fracture life of at least about 150 hours when tested at the relatively high temperature of about 1500° F. under the high stress for this temperature of about 30,000 pounds per square inch (p.s.i.) and being suitable for use as thermal members, for example, in jet engines, which must withstand high stresses at temperatures of the order of 1300° F. to 1700° F., particularly temperatures of the order of 1500° F. to 1700° F., such as are encountered when a plane is operated under conditions requiring high speed and/or power. Although many attempts were made to overcome the foregoing difficulties and other difficulties and disadvantages, none, as far as I am aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that the problem confronting the art of providing a high temperature, heat and stress resisting thermal member having a high level of high all-around properties can be solved by employing a special heat resisting, columbium-free, tungsten-free, nickel-chromium alloy containing a combination of elements within special ranges and capable of being fabricated into wrought form by hot working and cold working operations.

It is an object of the present invention to provide an improved alloy having improved high temperature prop-

erties and not requiring the presence of a plurality of strategic alloying elements and particularly not requiring the presence of the extremely strategic alloying element columbium.

Another object of the invention is to provide improved heat-treatable, nickel-chromium, high temperature, heat and stress resisting, wrought thermal members suitable for use in jet engines, gas turbines and the like.

The invention also contemplates providing improved heat treated, nickel-chromium, high temperature, heat and stress resisting, wrought thermal members characterized by resistance to the destructive actions of various operating media at high temperatures.

It is a further object of the invention to provide an improved heat and stress resisting, high temperature, nickel-chromium alloy which, in a heat treated, wrought condition, neither requires the presence of the highly strategic alloying element columbium nor the presence of a plurality of strategic elements to achieve a high rupture life of at least about 600 hours, and even 1000 or 1500 hours or more, under a stress of about 30,000 p.s.i. at 1500° F., and a rupture life of at least about 100 hours, and often at least 200 or even 250 hours or more, under a stress of about 25,000 p.s.i. at 1600° F.

It is still another object of the invention to provide a columbium-free, tungsten-free, heat resisting, wrought nickel-chromium alloy which is characterized by a level of high temperature properties in a heat treated condition comparable to or even better than the properties of other wrought alloys containing columbium or a plurality of strategic elements.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention provides a novel high temperature, heat and stress resisting thermal member especially adapted for use in heat engines and the like, e.g., jet engines, gas turbines, turbo-superchargers and exhaust gas power-recovery turbines, which is made of a special nickel-chromium-molybdenum-aluminum-titanium alloy, which does not require the presence of either of the strategic elements columbium and tungsten and which possesses commercial hot- and cold-workable properties enabling its fabrication into wrought members. The alloys within the scope of the present invention broadly comprise about 5% to 18% or 20% chromium, about 1% to 10% molybdenum, up to about 40% cobalt, about 0.05% to 0.35% carbon and an aluminum plus titanium content of about 3.5% to 8.5% with the ratio of aluminum to titanium being between about 0.5:1 and about 3:1, not more than about 5% iron and with the balance being essentially nickel. By varying the composition of the alloy within the aforesaid ranges, it is possible to obtain various combinations of properties in castings and/or heat treated wrought products. Thus, with a chromium content within the range of about 5% to about 9% and an aluminum plus titanium content of about 5.5% to about 8.5% and less than 10% cobalt, a high level rupture life, especially at high temperatures of the order of 1700° F. to 1800° F., is generally obtained without using large amounts of cobalt. However, by employing larger amounts of cobalt from about 10% to 40%, improved notched strength at temperatures of the order of about 1350° F. is obtained. In order to provide optimum high temperature strength, including high rupture life at temperatures on the order of about 1500° F., 1600° F. or higher, the alloys contemplated in accordance with the invention may contain minor amounts of boron and zirconium with the boron content ranging from a few ten thousandths of a percent up to about 0.009%, e.g., 0.0002% to 0.009%, and with the zirconium content being within the range of about 0.01% to about 0.25%. No further improvement in high tem-

perature properties is found in wrought alloys when the boron and zirconium are increased above the foregoing amounts and it is found that the forging temperature range is undesirably restricted. The balance of the alloy is nickel and the nickel plus cobalt content is usually about 50% to about 85% of the alloy. The term "balance" as used herein includes small amounts of other incidental elements and impurities commonly present in nickel alloys, for example, silicon, manganese, copper, magnesium, etc. As will be appreciated by those skilled in the art, small amounts of other elements, such as vanadium, cerium, tungsten, etc., may be added to the alloy for purposes well known in the art, including grain refinement, malleabilization, strengthening, etc. With regard to the silicon and manganese contents, it is preferred that each of these elements should not exceed 1% of the alloy content and each should more preferably be maintained below 1% although manganese can be as high as 2% or even 3% and silicon as high as 2%. The copper content of the alloy should be maintained below 2% and preferably below about 0.5% or 1%. Magnesium may advantageously be present in small amounts, e.g., 0.002%, up to about 0.1%. Impurities, such as lead, bismuth, tellurium, sulfur, selenium, arsenic, antimony, etc., should be kept as low as is commercially practicable. It is preferred that the impurities lead, bismuth and tellurium be held to 0.01% maximum of each while sulfur, selenium, arsenic and antimony are preferably maintained below 0.05%, and more preferably below 0.02%, of each. When the alloy contemplated by the present invention is characterized as being columbium-free and tungsten-free, it is to be understood that this characterization is intended to denote that the strategic elements columbium and tungsten might not be present or deliberately added to achieve the properties described herein. As will be appreciated by those skilled in the art, it is not intended to exclude the presence of either or both of these elements as an incidental element introduced with the raw materials employed to produce the alloy, to treat the molten bath of the alloy, etc. A feature of the alloy provided by the present invention is the fact that the presence of these elements is not required to achieve the properties indicated herein.

The aforescribed alloys contemplated in accordance with the invention may be hot worked, e.g., by forging, rolling, extruding, etc., into the physical form of thermal members. When desired, thermal members produced in these alloys can be cast directly to shape. In such cases, the boron content of the alloy may be increased to as much as about 0.02%, e.g., about 0.0002% to about 0.02%, and the carbon content may be increased to as much as about 0.5%, e.g., about 0.05% to about 0.5%, with the remainder of the alloy consisting of elements in the ranges set forth hereinbefore. The boron content of the castings should not exceed about 0.02% as otherwise difficulties in welding are encountered. When the carbon content exceeds about 0.5%, it is found that the strength of the castings is detrimentally affected.

Preferably, the aluminum plus titanium content of the alloys contemplated by the present invention will lie in the range of about 5% to about 7% when optimum rupture strength at the service temperature is required. For maximum ductility at the service temperature, the aluminum plus titanium content preferably will be about 4.5% to about 6%. In either of these preferred cases, the ratio of aluminum to titanium preferably will be about 0.8:1 to about 1.6:1.

When alloys produced in accordance with the invention are employed in the form of fabricated thermal members in heat engines and the like, it is preferred that the

wrought alloys be subjected to a heat treatment comprising a high temperature heating in the temperature range of about 2000° F. to about 2400° F. for about at least ¼ hour up to about 8 hours, e.g., about 2 hours, cooling rapidly, e.g., as by air cooling or quenching, and then reheating for at least 1 hour within the temperature range of about 1350° F. to 1800° F. for a period of time not substantially exceeding about 48 hours, e.g., about 4 hours to 24 hours. In general, the temperature employed for the high temperature heat treatment should be increased toward the upper part of the heating range when the aluminum plus titanium content of the alloy is about 5% or more in order to provide the best high temperature properties for the particular alloy. It is also to be noted that the optimum temperature to be employed in the high temperature heating is influenced by the composition and characteristics of the particular alloy being heated. For example, in the high temperature heating, undesirable coarsening of the grains may result. Those skilled in the art will appreciate that the heat treatment, when applied to wrought alloys, may be applied entirely after the alloy has been fabricated into thermal members or may be applied partly before fabrication or during fabrication or partly after fabrication. Thus, the high temperature heating may be applied in combination with the hot working operation. In this instance, the metal will be subjected initially to a high temperature, for example, 2100° F., 2200° F., 2300° F., etc., and then worked rapidly, as for example, by extrusion, in order to finish the hot working operation while the alloy is still at a temperature above about 2000° F., e.g., about 2100° F. In this manner, the heat remaining from the hot working operation is utilized to effect the high temperature heating of the heat treatment. Such a combination of high temperature and hot working may be desirable when fine grain size is important in the application where the wrought thermal member is to be used.

Alloys contemplated in accordance with the invention are highly resistant to oxidation and provide a highly desirable combination of properties in the temperature range of interest in the heat engine art. Stress rupture tests made on the nickel-chromium alloy provided by the invention have demonstrated that the alloy has a rupture life of at least about 50 or 150 hours or much longer when subjected to a stress of 30,000 p.s.i. at 1500° F. Thermal members made by hot and/or cold working operations of the heat treated alloy exhibit a high combination of properties, including strength, ductility and resistance to stress, to creep, to rupture, to heat, to corrosion, to erosion, to oxidation, to pitting and to other destructive influences of other various operating media at elevated temperatures.

High cobalt alloys

For applications involving exposure of thermal members to combinations of very high service temperatures and high stresses, e.g., in rotor blades for aircraft jet engines, special alloys within the scope of the invention comprise about 12% to 18% chromium, about 20% to 40% cobalt, about 1% to 10% molybdenum, with an aluminum plus titanium content of about 4.8% to 8.5% and with the ratio of aluminum to titanium being within the range of about 0.5:1 and about 3:1, preferably about 0.8:1 and 1.6:1, about 0.05% to about 0.35% carbon, up to about 5% iron, and the balance essentially nickel. More preferred high cobalt alloys comprise about 14% to about 17% chromium, about 23% to 35% cobalt, especially about 23% to about 30% cobalt, about 2% to 4% molybdenum, about 5% to 7% of aluminum plus

titanium with the ratio of aluminum to titanium being between about 0.8:1 and 1.6:1, about 0.10% to about 0.25% carbon and the balance essentially nickel.

The aforescribed high cobalt alloys preferably contain small amounts of boron and zirconium in order to provide optimum strength at elevated temperatures. When employed in the wrought condition, the alloys contain about 0.0002% to 0.009% boron and about 0.01% to about 0.25% zirconium. Preferably, the alloys will contain about 0.0004% to 0.007% boron and 0.01% to 0.15% zirconium or, more preferably, about 0.0005% to 0.005% boron and about 0.03% to about 0.08% zirconium. It is to be understood that the aforescribed preferred high cobalt alloys are malleable and can be produced in the form of wrought thermal members in the absence of boron or zirconium. When it is desired to produce the preferred high cobalt alloys in the form of castings, the boron content can be increased to a value as high as 0.02% and the carbon content may be within the range of about 0.05% to about 0.5%. Those skilled in the art are aware that, in general, cast articles made of high temperature alloys possess superior high temperature strength properties as compared to wrought articles of the same or substantially the same composition. However, a practical drawback existing with the production of the castings is the lack of uniformity which has been found to characterize finished parts made of cast alloys even when the castings are made from the same heat of metal.

In order to provide improved strength in service at elevated temperatures, wrought thermal members made from the preferred high cobalt alloys described hereinbefore are subjected to a heat treatment before use at elevated temperature service. The heat treatment may comprise a double heating including a high heating at about 2000° F. to about 2400° F. for at least about ¼ hour up to about 4 hours, e.g., about 1 hour, followed by a reheating at a lower temperature of about 1500° F. to about 1800° F. for at least about ¼ hour to about 48 hours, e.g., about 4 hours to about 24 hours. It has been found that certain alloys develop optimum properties after a triple heating in which each successive heating is conducted at a lower temperature. Such a heat treatment comprises a high heating under the same conditions as for the double heating treatment and preferably about 2150° F. to about 2300° F. for about ¼ to about 4 hours, followed by a reheating at about 1700° F. to about 2100° F. for about ½ to 8 hours, e.g., about one hour, and a reheating at about 1500° F. to about 1800° F. such as that described for the double heating treatment. A furnace cooling of about 100° F. after the first heating operation may be employed if desired. A feature of the very high strength alloys containing the aforementioned special amounts of cobalt is that these alloys cannot be softened to any substantial extent by heating to a high temperature followed by a rapid cooling. The preferred high cobalt alloys provide a high combination of properties at all temperatures of interest in the heat engine art. These alloys when suitably heat treated have good notch strength and resist the undesired germination of grains which sometimes occurs in other alloys subjected to critical straining at elevated temperatures.

The heat treated preferred high cobalt alloys described hereinbefore provide outstanding properties and an outstanding service life when employed in the form of highly stressed thermal members at high temperatures, e.g., temperatures in the range of about 1500° F. to about 1700° F. For example, it can be said that heat treated alloys which have been subjected to an optimum heat treatment involving a high heat at about 2300° F. and containing the preferred cobalt contents within the

range of about 23% to 35% will have a rupture life of at least about 200 hours when tested at 1600° F. under a stress of about 25,000 p.s.i. Heat treated alloys will have a rupture life of at least about 600 hours, and often at least about 1000 hours or even 1500 hours or more, when subjected in the heat treated condition to a rupture test at a stress of about 30,000 p.s.i. at 1500° F. The preferred high cobalt alloy is found to develop high rupture strength when subjected, in the form of wrought thermal members, e.g., turbine blades, to a heat treatment comprising only the lower temperature reheating described hereinbefore.

The following table contains the analysis of satisfactory high cobalt alloys produced in accordance with the invention:

TABLE I

Alloy No.	Percent Cr	Percent Co	Percent Mo	Percent Al	Percent Ti	Percent Zr	Percent C	Percent Ni ¹
1	13.92	23.34	3.08	2.88	2.66	0.041	0.11	Bal.
2	14.81	28.66	3.04	2.87	2.17	0.051	0.12	Bal.
3	14.83	28.38	2.97	2.74	2.21	0.010	0.12	Bal.
4	14.72	29.35	3.04	2.97	1.96	0.041	0.07	Bal.
5	14.79	28.83	3.06	2.75	2.37	0.045	0.10	Bal.
6	14.64	28.24	3.01	2.77	2.56	0.048	0.10	Bal.
7	14.96	29.12	2.96	2.91	2.85	0.041	0.11	Bal.
8	14.87	28.90	3.04	3.10	2.62	0.046	0.06	Bal.
9	14.90	28.40	3.03	2.40	2.90	0.045	0.12	Bal.
10	13.15	29.03	3.10	2.74	2.72	0.052	0.11	Bal.
11	14.85	32.08	2.69	2.83	2.64	0.050	0.09	Bal.
12	14.98	27.7	3.01	2.06	3.01	0.043	0.13	Bal.
13	14.60	29.27	3.09	2.78	2.41	0.052	0.13	Bal.
14	15.01	29.40	2.93	2.74	2.29	0.040	0.11	Bal.
15	15.01	29.55	3.12	3.05	2.01	0.039	0.10	Bal.
16	15.07	29.27	3.12	1.99	3.10	0.041	0.05	Bal.
17	14.67	28.16	3.03	2.89	2.46	0.046	0.10	Bal.
18	16.02	29.35	2.93	2.91	2.22	0.046	0.12	Bal.
19	14.76	38.67	3.19	2.82	2.37	0.040	0.12	Bal.
20	15.22	39.43	3.14	2.07	3.05	0.040	0.06	Bal.
21	14.92	29.40	1.54	2.79	2.21	0.052	0.10	Bal.
22	14.94	28.96	4.83	2.81	2.14	0.040	0.11	Bal.
23	15.22	28.59	6.6	3.02	2.20	0.046	0.12	Bal.
24	15.16	28.62	9.46	2.99	2.14	0.038	0.11	Bal.
25	11.30	29.15	2.95	3.33	2.02	0.060	0.10	Bal.
26	12.89	29.25	3.89	2.84	2.22	0.041	0.11	Bal.
27	15.59	29.40	3.01	2.37	2.35	0.048	0.10	Bal.
28	18.55	28.16	3.05	3.17	2.25	N.D.	0.11	Bal.
29	15.22	39.43	3.14	2.07	3.05	0.040	0.06	Bal.
30	14.78	28.40	3.03	2.05	2.94	0.045	0.06	Bal.
31	16.27	28.53	3.02	3.25	2.16	0.050	0.12	Bal.
32	16.73	24.73	2.64	3.12	2.15	0.025	0.12	Bal.
33	15.87	30.08	3.09	3.05	2.58	0.050	0.12	Bal.
34	14.90	27.61	2.92	2.85	2.22	0.050	0.10	Bal.
35	15.41	30.05	2.79	2.99	2.12	0.050	0.11	Bal.

NOTE.—Alloy No. 2 had no boron addition. Alloy No. 3 contained boron resulting from a boron addition of about 0.001% while Alloy No. 6 contained boron resulting from a boron addition of about 0.005% and the remaining alloys in Table I contained boron resulting from a boron addition of about 0.003%.

¹ Balance includes small amounts of manganese, magnesium, silicon, copper, etc.

N.D.=Not determined.

In manufacturing the foregoing alloys, nickel and cobalt rondelles were melted and oxidized slightly to remove the variable excess of carbon contained in the cobalt rondelles which had been reduced from the oxide by carbon. The chromium was then added followed by the molybdenum. Carbon was next added in the form of a master alloy containing about 10% carbon and about 90% chromium. Thereafter, about one-half of the aluminum was added, followed by an addition of magnesium and zirconium. The balance of the aluminum was added next, followed by the introduction of the titanium and finally the boron. Usually the zirconium and boron, and sometimes the magnesium and titanium, are added as master alloys. With respect to titanium, it is preferred to add the titanium in the purest elemental form available. It would also be preferable to add the cobalt in the pure elemental form when available. The molten bath was then poured into a cast iron mold. After

solidification, the ingot was heated and then extruded and rolled to five-eighths inch diameter hot rolled rods. The ingot was heated to a temperature of about 2225° F. for the extrusion and hot rolling operations. Samples were cut from the hot rolled rods and then given a heat treatment before being subjected to the rupture test. Heat treatments which have been employed in accordance with the present invention are set forth in the following table:

TABLE II

Heat Treatment	Initial Heating	Reheating
15 A	2,325° F.—2 hrs., A.C.	1,600° F.—4 hrs., A.C.
B	2,325° F.—2 hrs., A.C.	1,600° F.—16 hrs., A.C.
C	2,325° F.—2 hrs., A.C.	2,000° F.—1 hr., A.C.; 1,500° F.—16 hrs., A.C.
D	2,350° F.—1½ hr., A.C.	1,500° F.—4 hrs., A.C.
E	2,350° F.—1 hr., A.C.	1,500° F.—4 hrs., A.C.
F	2,350° F.—1 hr., F.C.; 100° F., A.C.	1,500° F.—16 hrs., A.C.
20 G	2,325° F.—1 hr., A.C.	1,500° F.—16 hrs., A.C.
H	2,350° F.—½ hr., A.C.	1,900° F.—1 hr., A.C.; 1,500° F.—4 hrs., A.C.
I	2,300° F.—2 hrs., A.C.	1,500° F.—4 hrs., A.C.
J	2,300° F.—1½ hr., A.C.	1,500° F.—4 hrs., A.C.
K	2,225° F.—½ hr., A.C.	1,350° F.—4 hrs., A.C.
L	2,325° F.—2 hrs., F.C.; 100° F., A.C.	2,000° F.—1 hr., A.C.; 1,500° F.—16 hrs., A.C.
25 M	2,300° F.—1 hr., A.C.	1,500° F.—4 hrs., A.C.
N	2,300° F.—1 hr., A.C.	1,500° F.—20 hrs., A.C.
O	2,275° F.—2 hrs., A.C.	1,600° F.—16 hrs., A.C.
P	2,200° F.—2 hrs., A.C.	1,600° F.—16 hrs., A.C.
Q	2,325° F.—2 hrs., F.C.; 100° F., A.C.	2,000° F.—1 hr., A.C.; 1,600° F.—16 hrs., A.C.
30 R	2,275° F.—2 hrs., F.C.; 100° F., A.C.	2,000° F.—1 hr., A.C.; 1,500° F.—16 hrs., A.C.
S	2,325° F.—2 hrs., F.C.; 100° F., A.C.	2,000° F.—1 hr., A.C.; 1,600° F.—4 hrs., A.C.
T	2,275° F.—2 hrs., A.C.	1,500° F.—16 hrs., A.C.
U	2,350° F.—1 hr., A.C.	1,500° F.—20 hrs., A.C.
V	2,350° F.—1½ hr., A.C.	1,350° F.—4 hrs., A.C.
W	2,160° F.—2 hrs., A.C.	1,600° F.—4 hrs., A.C.
35 X	2,275° F.—2 hrs., A.C.; 2,000° F.—1 hr., A.C.	1,500° F.—16 hrs., A.C.

A.C.=Air cooled.

F.C.=Furnace cooled for interval noted.

40 Machined rupture test specimens cut from the hot rolled rods and heat treated in accordance with one of the aforementioned heat treatments were then subjected to various stress rupture tests. The results of the stress rupture tests are set forth in the following schedule:

TABLE III

[Test Conditions—1600° F. and 25,000 p.s.i.]

Alloy No.	Heat Treatment	Rupture Life, hours
1	G	626
2	A	203
3	B	200
4	C	196
5	D	187
6	E	419
7	F	389
8	G	483
9	H	473
10	I	446
11	J	371
12	K	462
13	L	184
14	M	330
15	N	340
16	O	237
17	P	313
18	Q	288
19	R	301
20	S	187
21	T	259
22	U	260
23	V	153
24	W	327
25	X	230
26	Y	259
27	Z	179
28	AA	230
29	AB	296
30	AC	375
31	AD	392
32	AE	309
33	AF	301
34	AG	301

9
TABLE IV

[Test Conditions—1600° F. and 30,000 p.s.i.]

Alloy No.	Heat Treatment	Rupture Life, Hours
21.....	A	135
22.....	A	137
23.....	A	125
24.....	A	96

In order to demonstrate the high order of stress rupture properties developed by the preferred cobalt-containing alloys contemplated in accordance with the invention at temperatures of 1500° F., 1600° F., 1700° F., and 1800° F., the following table sets forth the results of stress rupture tests conducted upon Alloy 18 at these temperatures. The test specimens were prepared from hot rolled bar stock and were subjected to a heat treatment comprising heating to about 2275° F., furnace cooling 100° F., air cooling, heating to about 2000° F. for about 1 hour, air cooling, heating to about 1600° F. for about 4 hours and air cooling.

TABLE V

Stress Rupture Test Conditions		Life, Hrs.	Elongation, Percent
Temp., ° F.	Stress, p.s.i.		
1,500.....	60,000	6	7.5
	40,000	168	10
	30,000	1,085	10
	25,000	1,587	5
1,600.....	40,000	8	13.5
	30,000	67	13.5
	25,000	280	15
	20,000	748	14
1,700.....	25,000	8	22
	20,000	38	30
	15,000	113	13.5
	12,000	184	7.5
1,800.....	8,000	1,048	2.5
	10,000	11	52.5
	8,000	36.5	11.5
	6,000	167	

A further series of stress rupture tests were conducted upon hot rolled bar stock from Alloy 18 which had been heat treated at 2150° F. for 2 hours, air cooled, and then heated 1600° F. for about 4 hours. This heat treatment is designed to provide a finer grain size with high properties. The data are presented in the following table:

TABLE VI

Stress Rupture Test Conditions		Life, Hrs.	Elongation, Percent
Temp., ° F.	Stress, p.s.i.		
1,500.....	40,000	145	9.0
	32,500	722	11.5
	35,000	15	16.5
	30,000	50	21.0
1,600.....	25,000	125	21.0
	20,000	456	15.0
	15,000	1,550	17.5
	15,000	91	23.5
1,700.....	8,900	33	32.5
	6,000	91	25.0

10

A series of stress rupture tests was conducted upon Alloy 35 to demonstrate the effects of heat treatment upon the rupture life of the alloy at 1600° F. and 28,000 p.s.i. The heat treatments and the accompanying rupture lives under the foregoing conditions are given in the following Table VII:

TABLE VII

	High Heating Temperature, ° F. (2-hour treatment), A.C.	Reheating Conditions, ° F./hrs.	Rupture Life, Hours	Elongation, Percent
15	2,160.....	1,600/4	114	13.0
	2,160.....	1,600/8	120	11.5
	2,160.....	1,600/24	101	14.0
	2,160.....	1,650/2	73	12.0
	2,160.....	1,650/4	91	9.5
20	2,160.....	1,650/8	91	10.5
	2,160.....	1,650/16	88	9.0
	2,160.....	1,650/24	88	13.0
	2,160.....	1,700/2	85	13.5
	2,160.....	1,700/4	89	11.5
	2,160.....	1,700/8	97	14.5
	2,160.....	1,700/16	68	14.5
25	2,160.....	1,700/24	105	11.0
	2,275.....	1,600/4	260	9.0
	2,275.....	1,600/8	231	5.5
	2,275.....	1,600/24	227	7.5
	2,275.....	1,650/4	209	7.5
	2,275.....	1,650/8	164	8.5
	2,275.....	1,650/24	180	10.0
30	2,275.....	1,700/2	207	10.0
	2,275.....	1,700/4	262	7.5
	2,275.....	1,700/8	230	10.0
	2,275.....	1,700/16	168	12.0
	2,275.....	1,700/24	197	15.5

It was observed that the alloys subjected to the foregoing tests were also highly resistant to creep, another factor which is very important in evaluating metals for use in thermal members which are subjected to high temperatures and high stresses in service. In addition, the heat treated wrought alloys are characterized by a high strength and adequate ductility at ordinary temperatures as evidenced by a yield strength of at least about 100,000 p.s.i., a tensile strength of at least about 160,000 p.s.i. and an elongation of at least about 20% in 2 inches when measured at atmospheric temperatures.

As previously noted, preferred cobalt-containing cast alloys within the present invention provide high properties at elevated temperatures. The compositions of satisfactory cast alloys are given in the following table:

TABLE VIII

Alloy No.	Per-cent Cr	Per-cent Co	Per-cent Mo	Per-cent Al	Per-cent Ti	Per-cent C	Per-cent Ni ¹
36.....	15.36	28.7	3.20	3.26	2.22	0.15	Bal.
37.....	14.81	28.0	3.28	3.78	2.53	0.18	Bal.
38.....	14.96	28	3.40	4.86	2.83	0.18	Bal.
39.....	14.65	28	1.20	3.22	2.02	0.13	Bal.

¹ Including small amounts of boron and zirconium resulting from the additions of about 0.003% and about 0.05% of these elements, respectively.

The properties of the foregoing cast alloys tested in the as-cast condition and at 1600° F. and 30,000 p.s.i. are as follows:

11
TABLE IX

Alloy No.	Rupture Properties		Room Temperature Tensile Properties	
	Life, Hrs.	Elongation, Percent	T.S., p.s.i. ¹	El., Percent ²
36.....	124	12	120,000	7.0
37.....	233	12	141,000	10
38.....	350	9	138,000	12
39.....	127	14	120,000	8

¹ T.S., p.s.i.=Tensile Strength in pounds per square inch.

² El., Percent=Elongation in percent.

Low cobalt alloys

It has also been discovered that certain alloys free of columbium and tungsten and containing relatively low amounts of cobalt comprehended in the scope of the present invention will provide very satisfactory heat and stress resisting thermal members and possess commercial malleability. These alloys possess advantages in that the highly strategic elements columbium and tungsten are unnecessary for their production and no cobalt or only small amounts of cobalt, which is itself a strategic element, are required. Such alloys comprise about 0.05% to about 0.35% carbon, about 5% to 17% chromium, up to about 10% cobalt, about 1% to 10% molybdenum, about 3.5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being about 0.5:1 up to about 3:1. These alloys desirably contain boron and zirconium in very small amounts in order to provide optimum strength at elevated temperatures. It is to be understood that these alloys likewise are malleable in the absence of either or both of boron and zirconium. When boron is present, it is employed in quantities of a few ten-thousandths of one per cent, e.g., about 0.0002% or 0.0003% up to about 0.009%, preferably 0.0005% to 0.009%, e.g., 0.0007% to 0.007%. Zirconium, when used, may be present in amounts of about 0.01% to about 0.25%, e.g., about 0.03% to about 0.08%.

Special wrought alloys having relatively low cobalt contents include those set forth in the following schedule:

TABLE X

Element	A	B	C	D
C.....	0.05-0.25	0.05-0.25	0.05-0.25	0.05-0.25
Cr.....	8-13	7-13	7-13	10-15
Co.....	0-3	0-3	3-8	3-8
Mo.....	2-4	2-4	2-4	2-4
Al+Ti.....	4.5-6	5-7	5-7	4.5-6
Al:Ti.....	3:2 to 1:1	3:2 to 1:1	3:2 to 1:1	3:2 to 1:1
Ni.....	Bal.	Bal.	Bal.	Bal.

Improved high temperature properties are developed in the foregoing low cobalt alloys, including cobalt-free alloys, when boron and zirconium are present in very small amounts within the ranges set forth hereinbefore.

It is to be understood that the alloys of column A in the foregoing schedule are preferred in applications where ductility at service temperatures in the range of about 1200° F. to about 1600° F. is of prime importance, e.g., rotor wheels. When high strength at the service temperature range of about 1500° F. to about 1800° F. is required, as in turbine blades, then the alloys defined in column B of the foregoing schedule are desirable. For optimum strength, including high rupture life at the service temperature range of about 1500° F. to about 1800° F., the alloys of column C in the foregoing schedule are preferred. When high notch strength at service temperatures in the range of about 1200° F. to about 1500° F. is of prime importance, the alloys of column D in the foregoing schedule are preferred.

The copresence of molybdenum, boron, carbon and zirconium in combination with chromium, aluminum and titanium in the special proportions indicated hereinbefore for the special low-cobalt alloys contemplated in accordance with the present invention enables the production of wrought nickel alloys having high rupture life of the same or higher order than other wrought alloys containing the strategic elements columbium and tungsten and/or containing larger amounts of cobalt. The presence of chromium in the aforementioned ranges is important and the presence of chromium in combination with the other elements imparts oxidation resistance to the alloy and is also important as a matrix stiffening or hardening element. Aluminum and titanium are important hardening and stiffening elements. Aluminum is also advantageous in imparting oxidation resistance to the alloy. Carbon is important in combination with the other ingredients of the low cobalt compositions as set forth hereinbefore. Carbon preferably is present in amounts of about 0.08% to about 0.18% in order to assist in maintaining fine grain size and to impart improved rupture strength at elevated temperatures. The presence of molybdenum in the alloy is particularly effective in combination with the amounts of the other elements of the low cobalt compositions set forth hereinbefore, especially in enabling the production of alloys having good high temperature properties and the molybdenum preferably is present in amounts of about 2% to about 4%. Iron is an optional element and may be present in amounts up to about 5%.

Molybdenum, like chromium, has a matrix stiffening or hardening effect on all the alloys described herein and is about twice as effective as chromium as a matrix hardener. In the special low-cobalt alloys defined in columns B and C of Table X, it is more preferred when the aluminum plus titanium content is at least about 5.5% or 6% and up to about 7% that the chromium content should not exceed about 11%, e.g., that the chromium content should be about 7% to about 11%. When this more preferred relationship of chromium with aluminum plus titanium is observed in the low cobalt alloys, the alloys are readily wrought and have a high combination of properties at elevated temperatures.

It is also to be understood that the low cobalt alloys defined hereinbefore are malleable and may be worked into thermal members such as blades for aircraft turbo-jet engines and the like. The alloys may also be fabricated as castings for use as thermal members. In cases where it is desired to employ the alloy in the form of cast thermal members, the boron content may be increased to as high as about 0.02% and the carbon content may be increased to as high as about 0.5%. As noted hereinbefore, it is generally thought that cast thermal members are not as consistent in properties from piece to piece as is the case when the thermal members are worked to shape as by forging, hot rolling, extrusion, etc.

It is to be understood that the aforementioned wrought low cobalt alloys develop their best properties at high temperatures when subjected to a heat treatment such as the double heating treatment or the triple heating treatment described hereinbefore for the wrought high cobalt alloys. Like the cobalt-containing alloys described hereinbefore, the preferred low cobalt alloys comprehended in accordance with the present invention are characterized by the fact that they cannot be substantially softened by heating to a high temperature, followed by a rapid cooling.

In order to provide those skilled in the art with a better appreciation of the advantages of the invention as applied to the aforementioned low cobalt alloys, the following table containing analyses of satisfactory alloys is presented:

TABLE XI

Alloy No.	Per- cent Cr	Per- cent Co	Per- cent Fe	Per- cent Al	Per- cent Ti	Per- cent Mo	Per- cent C	Per- cent Zr	Per- cent Ni ¹
40.....	10.59	—	0.23	2.93	1.84	3.11	0.06	0.072	Bal.
41.....	11.53	—	0.32	2.51	2.62	2.36	0.08	0.053	Bal.
42.....	10.77	—	0.13	2.73	1.80	3.05	0.06	0.057	Bal.
43.....	10.85	—	3.64	2.84	1.83	2.94	0.05	0.050	Bal.
44.....	10.62	—	3.95	2.73	1.85	2.95	0.06	0.061	Bal.
45.....	10.25	—	0.15	2.91	2.51	2.95	0.07	0.057	Bal.
46.....	10.92	—	1.53	3.0	3.0	3.03	0.08	0.041	Bal.
47.....	8.16	1.09	1.83	3.8	2.7	3.12	0.08	0.041	Bal.
48.....	10.33	—	0.18	3.43	2.40	3.03	0.08	0.018	Bal.
49.....	8.31	—	0.18	3.63	2.67	3.00	0.09	0.055	Bal.
50.....	7.91	—	0.40	3.64	2.70	3.32	0.09	0.092	Bal.
51.....	7.80	—	0.14	3.32	2.46	4.86	0.10	0.050	Bal.
52.....	10.16	4.76	0.18	3.13	2.22	3.03	0.08	0.053	Bal.
53.....	9.54	4.73	0.20	3.60	2.66	3.02	0.09	0.062	Bal.
54.....	8.56	5.04	0.16	3.56	2.37	3.04	0.10	0.052	Bal.
55.....	14.73	4.78	0.17	2.83	1.77	3.02	0.08	0.052	Bal.
56.....	10.16	—	0.16	2.30	3.20	2.86	0.06	0.051	Bal.
57.....	11.09	8.10	0.16	3.0	2.5	3.07	0.08	0.048	Bal.
58.....	8.44	4.83	0.20	3.59	2.67	2.93	0.08	0.057	Bal.
59.....	11.56	8.16	0.16	3.3	2.0	3.05	0.07	0.041	Bal.
60.....	11.13	7.73	0.19	3.0	2.4	2.96	0.09	0.046	Bal.
61.....	8.30	4.84	0.30	3.71	2.74	3.01	0.09	0.055	Bal.
62.....	11.87	—	0.15	2.86	2.53	2.95	0.10	0.041	Bal.
63.....	8.11	5.43	1.03	3.8	2.7	2.89	0.09	0.041	Bal.
64.....	10.39	—	0.19	3.16	2.26	2.95	0.07	0.052	Bal.
65.....	9.75	1.01	0.41	3.46	2.57	2.85	0.09	0.053	Bal.
66.....	11.86	4.94	0.16	3.02	2.35	3.03	0.08	0.046	Bal.
67.....	14.27	4.96	0.30	3.16	2.25	3.03	0.08	0.041	Bal.

NOTE.—Alloys 40 to 44 contained about 0.002%, 0.007%, 0.007%, 0.007%, and 0.003% boron, respectively. Alloys 45 to 52, 55 to 59, 61 to 64, 66 and 67 contained boron resulting from an addition of about 0.003% boron to the respective melts and Alloys 53, 54, 60 and 65 contained boron resulting from an addition of about 0.005% boron to the respective melts.

¹ Balance includes small amounts of manganese, magnesium, silicon, copper, etc.

The rupture life of heat treated alloys 40 through 44 at 1500° F. and a load of 30,000 p.s.i. is given in the following table:

TABLE XII

Alloy No.	Rupture Life, ¹ Hours	Rupture Life, ² Hours
40.....	132	144
41.....	124	—
42.....	159	101
43.....	171	—
44.....	119	134

¹ Heated for about 4 hours at about 2100° F., air cooled, and heated about 20 hours at about 1300° F., air cooled.

² Heated for about 8 hours at about 1975° F., air cooled, and heated about 20 hours at about 1300° F.

The rupture lives of other alloys after the indicated heat treatments and under the indicated conditions are shown in the following tables:

TABLE XIII

[Test Conditions—1600° F. and 25,000 p.s.i.]

Alloy No.	Heat Treat- ment	Rupture Life, hours
45.....	L.....	151
46.....	X.....	163
47.....	R.....	356
48.....	Q.....	135
49.....	L.....	240
50.....	Q.....	239
51.....	B.....	169
52.....	C.....	158
53.....	S.....	337
54.....	A.....	379
56.....	L.....	140
57.....	V.....	120
58.....	T.....	319
59.....	X.....	161
60.....	C.....	279
61.....	B.....	517
63.....	S.....	361
64.....	L.....	138
65.....	S.....	239
66.....	C.....	172

TABLE XIV

[Test Conditions—1350° F. and 70,000 p.s.i.]

Alloy No.	Heat Treat- ment, ¹ ° F.	Rupture Life, hours	Elongation, percent
45.....	2,000	57	7.5
52.....	2,200	115	5.5
53.....	2,200	87.3	2
55.....	2,200	129	8.5
62.....	2,275	84	2
64.....	2,000	54	7.5
66.....	2,200	192	4

¹ Alloys heated 2 hours at temperature noted, air cooled, and then heated at 1,600° F. for about 4 hours.

TABLE XV

[Test Conditions—1800° F. and 8,000 p.s.i.]

Alloy No.	Heat Treat- ment	Rupture Life, Hours
46.....	B.....	103
47.....	Z.....	248
50.....	B.....	160
53.....	2,200° F.	112
55.....	V.....	44
58.....	2,325° F.	108
67.....	V.....	142

¹ Alloys heat treated 2 hours at the indicated temperature, air cooled and then heated for about 4 hours at 1600° F.

In manufacturing the foregoing alloys, nickel and chromium were melted in an induction furnace and the molybdenum was then incorporated in the melt. Carbon was then added in the form of a master alloy containing about 10% carbon and 90% chromium. Thereafter, about one-half of the aluminum was added, followed by an addition of magnesium and zirconium. The balance of the aluminum was added next, followed by the introduction of the titanium and finally the boron. Usually, the zirconium and boron, and sometimes the magnesium and titanium, are added as master alloys. With respect to titanium, it is preferred to add the titanium in the purest elemental form available. The molten bath was

then poured into a cast iron mold. After solidification, the ingot was heated and then forged and rolled to five-eighths inch diameter hot rolled rods. The ingot was heated to a temperature of about 2225° F. for the forging and hot rolling operations.

Low chromium, high cobalt alloys

It has been found in applications involving exposure of wrought thermal members to very high service temperatures on the order of about 1700° F. or higher, and involving the requirement for a high order of commercial forgeability, that special alloys within the inven-

scribed low chromium, high cobalt alloys preferably are subjected to a heat treatment before being employed in service. Either the double heating treatment or the triple heating treatment described hereinbefore in conjunction with other high cobalt alloys within the scope of the invention may be employed in treating the low chromium, high cobalt alloys. These alloys in the heat treated condition will have a rupture life of at least about 100 hours, and usually about 200 hours or more, when tested at about 1600° F. and 25,000 p.s.i. The following table contains the analyses of satisfactory low chromium, high cobalt alloys produced in accordance with the invention:

TABLE A

Alloy No.	Per-cent Cr	Per-cent Co	Per-cent Mo	Per-cent Al	Per-cent Ti	Per-cent Zr	Per-cent B ¹	Per-cent C	Per-cent Ni ²
68.....	8.12	9.90	2.93	3.55	2.73	0.055	0.002	0.10	Bal.
69.....	8.32	13.39	3.01	3.64	2.77	0.048	0.004	0.12	Bal.
70.....	8.66	28.34	3.0	3.43	2.54	0.045	0.003	0.11	Bal.

¹ Amounts added to melt.

² Balance includes small amounts of manganese, magnesium, iron, silicon, copper, etc.

tion are particularly suitable. These alloys contain about 7% to 9% or 11% chromium, at least about 8%, e.g., about 10% up to about 30%, cobalt, about 5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being within the range of about 0.5 to 1 and about 3 to 1, about 1% to 10% molybdenum, up to about 5% iron, and the balance essentially nickel. Preferably, such alloys contain about 2% to 6% molybdenum and having a ratio of aluminum to titanium which is between about 0.8 to 1 and about 1.6 to 1.

In order to provide optimum strength at service temperatures of about 1700° F. or higher, it is preferable that these alloys contain small amounts of boron and zirconium within the range of about 0.0002% to 0.009% boron and about 0.01% to about 0.25% zirconium. Preferably, the alloys will contain about 0.0004% to 0.007% boron and .01% to 0.15% zirconium or, more preferably, about 0.0005% to 0.005% boron and about 0.03% to about 0.08% zirconium.

Wrought thermal members made from the aforede-

scribed low chromium, high cobalt alloys preferably are subjected to a heat treatment before being employed in service. Either the double heating treatment or the triple heating treatment described hereinbefore in conjunction with other high cobalt alloys within the scope of the invention may be employed in treating the low chromium, high cobalt alloys. These alloys in the heat treated condition will have a rupture life of at least about 100 hours, and usually about 200 hours or more, when tested at about 1600° F. and 25,000 p.s.i. The following table contains the analyses of satisfactory low chromium, high cobalt alloys produced in accordance with the invention:

TABLE B

Alloy No.	Heat Treatment	Rupture Life, hours
68.....	Q	205
69.....	A	251
70.....	B	201

Alloy No. 70, when given Heat Treatment B and subjected to a stress rupture test at 1800° F. and 8,000 p.s.i., exhibited a rupture life of 141 hours.

The following table sets forth the compositions of other alloys contemplated in accordance with the present invention:

TABLE XVI

Alloy No.	Per-cent Cr	Per-cent Co	Per-cent Fe	Per-cent Al	Per-cent Ti	Per-cent Mo	Per-cent C	Per-cent Zr	Per-cent B	Per-cent Ni ¹
71.....	15.60		0.34	2.38	1.55	3.15	0.08	0.046	0.003	Bal.
72.....	14.82		0.92	2.33	1.58	2.84	0.07	0.056	0.015	Bal.
73.....	14.98		0.24	2.28	1.62	3.17	0.07	0.065	0.006	Bal.
74.....	10.98		2.70	2.84	1.60	3.01	0.06	0.053	0.015	Bal.
75.....	10.82		3.79	2.36	1.85	2.88	0.06	0.053	0.001	Bal.
76.....	15.27		0.16	2.35	1.54	1.10	0.07	0.090	0.003	Bal.
77.....	15.27		0.15	2.35	1.53	1.60	0.06	0.057	0.003	Bal.
78.....	15.24		0.13	2.40	1.47	3.09	0.08	0.053	0.003	Bal.
79.....	14.96		0.19	2.34	1.52	3.04	0.10	0.062	0.003	Bal.
80.....	15.78		0.46	2.84	1.15	2.90	0.09	0.034	0.003	Bal.
81.....	14.88		0.15	2.47	1.44	4.04	0.09	0.058	0.005	Bal.
82.....	15.57		0.25	1.30	2.70	3.17	0.05	0.048	0.003	Bal.
83.....	11.84		4.75	2.36	1.72	3.04	0.08	0.053	0.003	Bal.
84.....	12.04		0.22	2.56	1.59	3.12	0.07	0.079	0.003	Bal.
85.....	12.84		0.30	2.39	1.59	3.12	0.07	0.055	0.003	Bal.
86.....	12.02		0.21	2.69	1.60	2.82	0.07	0.072	0.003	Bal.
87.....	10.22		4.30	2.42	1.51	3.03	0.06	0.053	0.007	Bal.
88.....	10.78		3.62	2.26	1.56	2.93	0.06	0.040	0.005	Bal.
89.....	10.69		3.76	2.43	1.56	3.31	0.07	0.046	0.003	Bal.
90.....	10.82		3.71	2.40	1.55	4.71	0.08	0.045	0.007	Bal.
91.....	5.83		0.12	2.09	1.52	2.94	0.06	0.058	0.003	Bal.
92.....	5.38		0.18	3.41	2.09	3.03	0.06	0.085	0.005	Bal.
93.....	6.57		0.28	2.72	1.81	7.37	0.05	0.065	0.007	Bal.
94.....	15.87	19.40	0.25	2.39	1.51	2.85	0.11	0.056	0.003	Bal.
95.....	15.81	19.42	0.17	2.37	1.55	3.05	0.08	0.055	0.003	Bal.
96.....	15.27	19.09	0.30	2.84	1.54	3.07	0.11	0.092	0.003	Bal.
97.....	15.36	19.82	0.30	2.33	1.39	2.88	0.10	0.057	0.003	Bal.
98.....	16.00	12.96	0.22	1.32	2.58	3.34	0.13	0.057	0.005	Bal.
99.....	12.77	7.73	0.31	2.53	1.09	3.08	0.07	0.062	0.002	Bal.
100.....	10.81	7.26	0.77	2.73	1.64	2.89	0.06	0.058	0.002	Bal.
101.....	10.75	8.06	3.99	2.33	1.60	3.16	0.07	0.053	0.003	Bal.
102.....	10.21	19.09	0.26	2.58	1.70	3.04	0.07	0.050	0.005	Bal.
103.....	15.13	19.21	0.11	2.85	0.99	3.99	0.07	0.072	0.004	Bal.
104.....	10.90	9.74	0.21	2.57	2.05	3.15	0.07	0.052	0.003	Bal.
105.....	20.38		0.14	2.33	1.45	1.15	0.07	0.062	0.003	Bal.
106.....	20.12		0.39	2.20	1.56	2.92	0.10	0.053	0.003	Bal.
107.....	19.98		0.44	2.35	1.76	2.95	0.11	0.053	0.003	Bal.
108.....	19.94		1.14	1.17	2.57	3.01	0.04	0.052	0.003	Bal.

¹Balance includes small amounts of manganese, magnesium, silicon, copper, etc.

17

The rupture lives of the foregoing alloys, as determined at 1500° F. and 30,000 p.s.i. after a heat treatment as noted, are given in the following table:

TABLE XVII

Alloy No.	Rupture Life, Hours	
	Heat Treatment No. 1	Heat Treatment No. 2
71.....	105	112
72.....	115	182
73.....	139	152
74.....	105	95
75.....	109	96
76.....	57	124
77.....	93	134
78.....	80	79
79.....	149	159
80.....	66	54
81.....	63	64
82.....	99	64
83.....	79	102
84.....	77	78
85.....	66	48
86.....	115	152
87.....	72	48
88.....	76	69
89.....	84	65
90.....	115	59
91.....	53	47
92.....	121	-----
93.....	155	98
94.....	274	348
95.....	293	229
96.....	456	469
97.....	419	-----
98.....	221	266
99.....	173	149
100.....	377	175
101.....	149	-----
102.....	361	178
103.....	309	310
104.....	693	116
105.....	55	68
106.....	67	66
107.....	73	49
108.....	77	154

1. Heated for about 4 hours at about 2100° F., air cooled, and heated for about 2 hours at about 1300° F., air cooled.

2. Heated for about 8 hours at about 1975° F., air cooled, and heated about 20 hours at about 1300° F.

18

TABLE XVIII

Alloy No.	Per- cent Co	Per- cent Mo	Per- cent Cr	Per- cent Al	Per- cent Ti	Per- cent C	Per- cent B	Per- cent Zr
109.....	39.03	3.13	15.07	4.71	1.65	0.13	-----	-----
110.....	29.86	3.04	14.91	4.77	1.54	0.14	-----	-----
111.....	29.21	2.81	15.13	3.73	2.69	0.16	0.003	-----
112.....	29.79	2.93	15.02	3.90	2.61	0.15	-----	0.048
113.....	30.23	3.11	14.54	3.70	2.42	0.16	0.003	0.045
114.....	29.43	3.03	15.10	3.92	2.56	0.16	0.003	0.065

Specimens made from the foregoing alloys were heat treated and subjected to stress rupture tests at 1700° F. and 20,000 p.s.i. with the following results:

TABLE XIX

Heat Treating Temperature, ° F. ¹	Rupture Life, Hours					
	Alloy 109	Alloy 110	Alloy 111	Alloy 112	Alloy 113	Alloy 114
2000.....	7.1	3.5	-----	-----	-----	-----
2169.....	8.4	10.5	16.9	15.9	22.8	31.6
2200.....	7.2	4.9	11.8	7.4	24.3	42.8
2225.....	9.7	8.7	14.3	3.5	34.6	44.0
2300.....	28.3	16.0	42.3	15.3	86.7	77.6

¹ Specimens held for about 2 hours at temperature noted, air cooled, and reheated at about 1600° F. for about 24 hours.

Two other series of tests were conducted to illustrate the effects of the zirconium-boron treatment upon the rupture life of forged and rolled alloys with the following results:

TABLE XX

Alloy No.	Per- cent Co	Per- cent Mo	Per- cent Cr	Per- cent Al	Per- cent Ti	Per- cent C	Per- cent B	Per- cent Zr	Rup- ture Life, Hrs. ²
115.....	30	3	15	3.0	2.3	0.10	n.a.	n.a.	100.5
116.....	30	3	15	3.0	2.3	0.10	n.a.	(¹)	205
117.....	30	3	15	3.0	2.3	0.10	(¹)	(¹)	367
118.....	30	3	15	3.0	2.8	0.10	(¹)	n.a.	301
119.....	30	3	15	3.0	2.8	0.10	(¹)	(¹)	626

¹ Contains boron resulting from addition of 0.003% and/or contains zirconium resulting from addition of 0.05%.

² Test conditions: 1600° F. and 25,000 p.s.i. stress.

n.a.=none added.

As has previously been noted herein, the inclusion of minute amounts of boron and zirconium in alloys contemplated in accordance with the invention provides a marked improvement in rupture life to the alloys. The desired commercial practice in producing the aforedescribed alloys contemplates additions to the melt of about 0.003% boron and about 0.05% zirconium shortly before casting the alloy melt.

In order to demonstrate the effects of minute amounts of boron and zirconium upon the properties of alloys contemplated in accordance with the present invention, the following alloys were produced:

The foregoing alloys were subjected to heat treatments as follows:

TABLE XXI

Alloy No.	Initial Heating	Reheating
115.....	2,250° F.—½ hr., A.C.	1,500° F.—4 hrs., A.C.
116.....	2,325° F.—½ hr., A.C.	1,600° F.—16 hrs., A.C.
117.....	2,250° F.—½ hr., A.C.	1,500° F.—4 hrs., A.C.
118.....	2,325° F.—2 hrs., A.C.	1,500° F.—16 hrs., A.C.
119.....	2,325° F.—1 hr., A.C.	1,500° F.—16 hrs., A.C.

A.C.=Air cooled.

It is to be noted from the foregoing tabulation that the incorporation of special amounts of either, and particularly both, of the elements boron and zirconium in alloys contemplated by the present invention contributes to the high temperature strength properties achieved therein.

Alloys produced in accordance with the invention are resistant to germination or abnormal grain growth when subjected to elevated temperatures after straining. The alloys are also highly resistant to oxidation, a desirable characteristic in gas turbine blade applications. The alloys are also adaptable to production in wrought form such as bars, rods, billets and the like, starting with a big ingot casting. Many prior alloys have not been susceptible to mill processing starting with a big ingot and this lack has been undesirable from a number of standpoints, including higher cost of other processing methods, lack of uniformity in properties and structures from piece to piece, etc.

A preferred method for the mill processing of alloys contemplated in accordance with the invention comprises preparing a melt of the particular alloy in an induction furnace which may or may not be provided with a vacuum or other special atmosphere, casting the alloy into ingots approximately 9 inches in diameter and about 28 inches long, heating the ingots to a temperature in the range of about 2000° F. to about 2100° F., extruding the ingots with a glass lubricant to provide billets having a cross section of about 4 square inches to about 9 square inches, and thereafter hot rolling the billets thus prepared. It is preferred that the subsequent hot working, e.g., hot rolling, be accomplished within the temperature range of about 1900° F. to about 2225° F.

It has been found that the present nickel-chromium alloys possess both hot workability and cold workability and can be produced on an industrial scale into products acceptable to the trade. For instance, when nickel-chromium alloys, such as are illustrated hereinbefore, are made it has been found that they can be fabricated in modern machinery, such as by modern high-powered forging, rolling, drawing, upsetting, extrusion, machining, grinding, etc. The alloys of the present invention can also be employed in the cast form, e.g., as precision castings.

The present invention provides a special nickel-chromium alloy which is particularly applicable to the manufacture of and use as thermal members. The term "thermal members" as employed herein is intended to include structural members which in use are subjected to heat and stress at elevated temperatures, particularly such structural members of heat engines, such as jet engines, gas turbines, turbo-superchargers, exhaust-gas power recovery turbines, etc., by which heat is transformed into mechanical work. Illustrative examples of some of the thermal members contemplated by the invention include turbine blades such as rotor blades or buckets and stator blades or nozzle guide vanes, rotor wheels, structural rings for gas turbine assembly, etc.; valves, valve seats and accessories, exhaust manifolds and supports therefor, etc.; combustion liners or flame tubes, tail cones, after-burner parts, vaporizer tubes and other high temperature tubular members, high temperature gas seals, etc.; high temperature springs and other resilient members; high temperature bolts, studs, fasteners, nuts, etc.; high temperature stiffening and supporting members; etc.

The present application is a continuation-in-part of my co-pending applications Serial No. 250,161 and Serial No. 250,162, both filed October 6, 1951 and both now abandoned.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are con-

sidered to be within the purview and scope of the invention and appended claims.

I claim:

1. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 14% to 17% chromium, about 2% to 4% molybdenum, about 23% to 35% cobalt, about 0.1 to 0.25% carbon, about 5% to 7% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.8 to 1 up to about 1.6 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.15% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 200 hours at 1600° F. and 25,000 pounds per square inch.

2. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 12% to 18% chromium, about 1% to 10% molybdenum, about 20% to 40% cobalt, about 0.05 to 0.35% carbon, about 4.8% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.5 to 1 up to about 3 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 200 hours at 1600° F. and 25,000 pounds per square inch.

3. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 5% to 20% chromium, about 1% to 10% molybdenum, about 10% to 40% cobalt, about 0.05% to 0.35% carbon, about 4.5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.5 to 1 up to about 3 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

4. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 5% to 9% chromium, about 1% to 10% molybdenum, not more than about 10% cobalt, about 0.05% to 0.35% carbon, about 5.5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.5 to 1 up to about 3 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized by a high level of rupture strength in the temperature range of 1700° to 1800° F.

5. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 7% to 11% chromium, about 2% to 4% molybdenum, up to about 8% cobalt, about 0.05% to 0.25% carbon, about 5.5% to 7% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 3 to 2 up to about 1 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being readily wrought and

being characterized by a high combination of properties at elevated temperature.

6. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 10% to 15% chromium, about 2% to 4% molybdenum, about 3% to 8% cobalt, about 0.05% to 0.25% carbon, about 4.5% to 6% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 3 to 2 up to about 1 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy having a high notch strength at service temperatures of about 1200° to 1500° F.

7. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 7% to 13% chromium, about 2% to 4% molybdenum, about 3% to 8% cobalt, about 0.05% to 0.25% carbon, about 5% to 7% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 3 to 2 up to about 1 to 1, not more than about 5% iron from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.15% zirconium, and with the balance essentially nickel, said alloy having a high rupture life in the service temperature range of about 1500° to 1800° F.

8. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 7% to 13% chromium, about 2% to 4% molybdenum, up to about 3% cobalt, about 0.05% to 0.25% carbon, about 5% to 7% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 3 to 2 up to about 1 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.15% zirconium, and with the balance essentially nickel, said alloy having a high strength at service temperatures of about 1500° to 1800° F.

9. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 8% to 13% chromium, about 2% to 4% molybdenum, up to about 3% cobalt, about 0.05% to 0.25% carbon, about 4.5% to 6% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 3 to 2 up to about 1 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.15% zirconium, and with the balance essentially nickel, said alloy having high ductility at service temperatures of about 1200° to 1600° F.

10. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 5% to 17% chromium, about 1% to 10% molybdenum, up to about 10% cobalt, about 0.05% to 0.35% carbon, about 4.5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.51 to 1 up to about 3 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

11. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 7% to 11% chromium, about 2% to 6% molybdenum, about 10% to 30% cobalt, about 0.05% to 0.35% carbon, 75

about 5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.8 to 1 up to about 1.6 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

12. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 7% to 11% chromium, about 1% to 10% molybdenum, at least about 8% and up to about 30% cobalt, about 0.05% to 0.35% carbon, about 5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.5 to 1 up to about 3 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

13. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 5% to 20% chromium, about 1% to 10% molybdenum, up to about 40% cobalt, about 0.05% to 0.35% carbon, about 4.5% to 6% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.8 to 1 up to about 1.6 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

14. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 5% to 20% chromium, about 1% to 10% molybdenum, up to about 40% cobalt, about 0.05% to 0.35% carbon, about 5% to 7% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.8 to 1 up to about 1.6 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

15. A hot-workable, cold-workable, heat-resistant alloy particularly adapted to service as a thermal member for extended periods of time under conditions of high stress and elevated temperature which comprises about 5% to 20% chromium, about 1% to 10% molybdenum, up to about 40% cobalt, about 0.05% to 0.35% carbon, about 4.5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.5 to 1 up to about 3 to 1, not more than about 5% iron, from about 0.0002% to about 0.009% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

16. A thermal member particularly adapted to service for extended periods of time under conditions of high stress and elevated temperature which comprises about 5% to 20% chromium, about 1% to 10% molybdenum, up to about 40% cobalt, about 0.05% to 0.5% carbon, about 4.5% to 8.5% of aluminum plus titanium with

the ratio of aluminum to titanium being in the range of about 0.5 to 1 up to about 3 to 1, not more than about 5% iron, from about 0.0002% to about 0.02% boron, from about 0.01% to about 0.25% zirconium, and with the balance essentially nickel, said thermal member being characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

17. The method for improving the stress rupture properties of thermal members for service at high stress levels for extended periods of time which comprises establishing a molten bath of an alloy containing about 5% to 20% chromium, about 1% to 10% molybdenum, up to about 40% cobalt, up to about 5% iron, about 4.5% to about 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being in the range of about 0.5 to 1 up to about 3 to 1 and with the balance essentially nickel and introducing into said bath shortly before casting boron and zirconium in amounts sufficient to provide respective contents thereof of about 0.0002% to 0.009% and 0.01% to 0.25% in metal cast from the thus-treated bath, casting metal from the thus-treated bath to ingot form and hot working said ingot to provide wrought thermal members characterized in the heat treated condition by a rupture life of at least about 100 hours when tested at 1600° F. and 25,000 pounds per square inch.

18. A hot-workable, cold-workable, heat-resistant alloy particularly adapted for service for extended periods of time under conditions of high stress and elevated temperature which comprises about 11% chromium, about 3% molybdenum, about 10% cobalt, about 0.7% carbon, about 2.6% aluminum, about 2.7% titanium, about 0.2% iron, about 0.003% boron, from about 0.01% to about 0.15% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by high rupture strength at temperatures of about 1500° F. and higher.

19. A hot-workable, cold-workable, heat-resistant alloy particularly adapted for service for extended periods of time under conditions of high stress and elevated temperature which comprises about 14% chromium, about 3% molybdenum, about 28% cobalt, about 0.11% carbon, about 2.9% aluminum, about 2.7% titanium, about 0.003% boron, about 0.04% zirconium, and with the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about 200 hours when tested at 1600° F. and 25,000 pounds per square inch.

20. A hot-workable, cold-workable, heat-resistant alloy particularly adapted for service at extended periods of time under conditions of high stress and elevated temperature which comprises about 8% chromium, about 5% cobalt, about 0.3% iron, about 3.7% aluminum, about 2.7% titanium, about 3% molybdenum, about 0.05% zirconium, about 0.10% carbon, about 0.003% boron and the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of about 517 hours when tested at 1600 F. and 25,000 pounds per square inch.

21. A hot-workable, cold-workable, heat-resistant alloy particularly adapted for service at extended periods of time under conditions of high stress and elevated temperature which comprises about 8% chromium, about 13% cobalt, about 3% molybdenum, about 0.12% carbon, about 3.6% aluminum, about 2.8% titanium, about 0.05% zirconium, about 0.004% boron and the balance essentially nickel, said alloy being characterized in the heat treated condition by a rupture life of at least about

200 hours when tested at 1600° F. and 25,000 pounds per inch.

22. A nickel base alloy containing about 15 percent to 20 percent chromium, about 15 percent to 30 percent cobalt, about 1.5 percent to 10 percent molybdenum, about 2.5 percent to 5.66 percent titanium, about 2.75 percent to 5 percent aluminum, the alloy being capable of withstanding an applied stress of thirty-five thousand pounds per square inch at 1500° F. for a time in excess of two hundred hours continuously, without rupture.

23. A nickel-base alloy containing from about 5% to 20% chromium, from about 1% to 10% molybdenum, from about 10% to 40% cobalt, from about 4.8% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being from about 0.5 to 1 to 3 to 1, the alloy being capable of withstanding an applied stress of thirty-five thousand pounds per square inch at 1500° F. for a time in excess of 200 hours continuously, without rupture.

24. A nickel-base alloy containing from about 5% to 20% chromium, from about 1% to 10% molybdenum, up to about 40% cobalt, from about 4.5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being from about 0.5 to 1 to 3 to 1, the alloy being capable of withstanding an applied stress of thirty-five thousand pounds per square inch at 1500° F. for a time in excess of 200 hours continuously, without rupture.

25. An alloy containing about 5% to 20% chromium, about 1% to 10% molybdenum, about 10% to about 40% cobalt, about 4.8% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being from about 0.5 to 1 to 3 to 1, about 0.05% to 0.5% carbon, not more than about 5% iron, up to about 0.02% boron, up to about 0.25% zirconium and the balance being essentially nickel, the alloy being capable of withstanding an applied stress of thirty-five thousand pounds per square inch at 1500° F. for a time in excess of 200 hours continuously, without rupture.

26. A nickel-base alloy containing from about 5% to 20% chromium, from about 1% to 10% molybdenum, up to about 40% cobalt, from about 4.5% to 8.5% of aluminum plus titanium with the ratio of aluminum to titanium being from about 0.5 to 1 to 3 to 1, about 0.0002% to 0.009% boron, up to about 0.25% zirconium, the alloy being capable of withstanding an applied stress of thirty-five thousand pounds per square inch at 1500° F. for a time in excess of 200 hours continuously, without rupture.

27. A nickel-base alloy containing about 15% to 20% chromium, about 15% to 30% cobalt, about 1.5% to 10% molybdenum, about 2.5% to 5.66% titanium, about 2.75% to 5% aluminum, about 0.0002% to 0.009% boron, about 0.01% to 0.25% zirconium, the alloy being capable of withstanding an applied stress of thirty-five thousand pounds per square inch at 1500° F. for a time in excess of 200 hours continuously, without rupture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,150,095	Kayes	Mar. 7, 1939
2,570,193	Bieber et al.	Oct. 9, 1951
2,575,915	Guy	Nov. 20, 1951
2,688,536	Callaway et al.	Sept. 7, 1954
2,712,498	Gresham et al.	July 5, 1955

FOREIGN PATENTS

632,712	Great Britain	Dec. 5, 1949
---------	---------------	--------------

UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,977,222

March 28, 1961

Clarence George Bieber

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 42, for "tunsten" read -- tungsten --;
column 15, line 32, for "having" read -- have --; line 40,
for ".01%" read -- 0.1% --; column 20, line 9, for "0.1"
read -- 0.1% --; line 24, for "0.05" read -- 0.05% --; same
column 20, line 68, for "molybednum" read -- molybdenum --;
column 21, line 63, for "0.51" read -- 0.5 --; column 23, line
17, for "aobut" read -- about --; line 32, for "0.7%" read
-- 0.07% --.

Signed and sealed this 29th day of August 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents