Jan. 12, 1960 J. D. NISBET ET AL 2,920,956

METHOD OF PREPARING HIGH TEMPERATURE ALLOYS

Filed Oct. 8, 1956 3 Sheets-Sheet 1

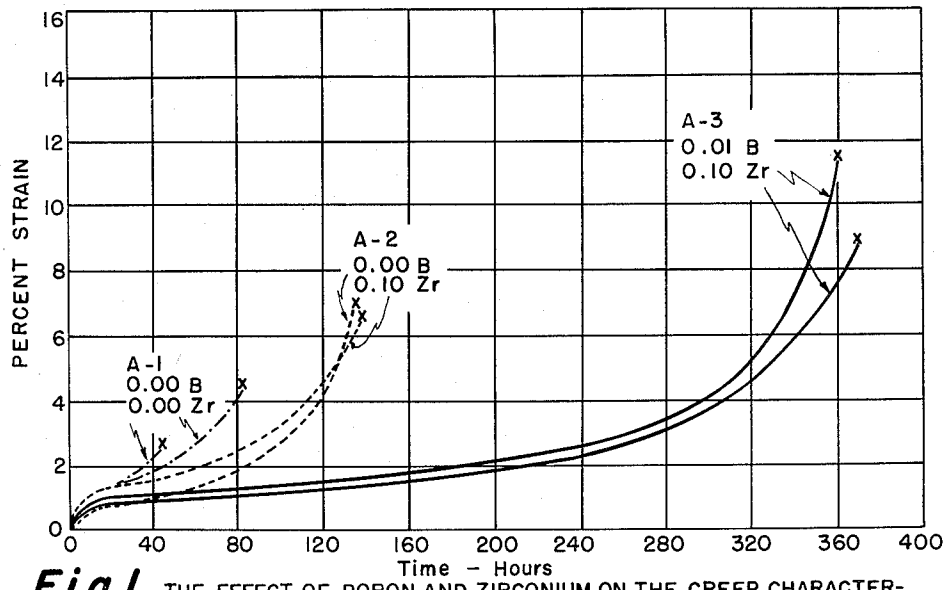


Fig. 1. THE EFFECT OF BORON AND ZIRCONIUM ON THE CREEP CHARACTERISTICS OF ALLOY "A". ALL TESTS WERE RUN AT 1600°F, AND 20,160 PSI.

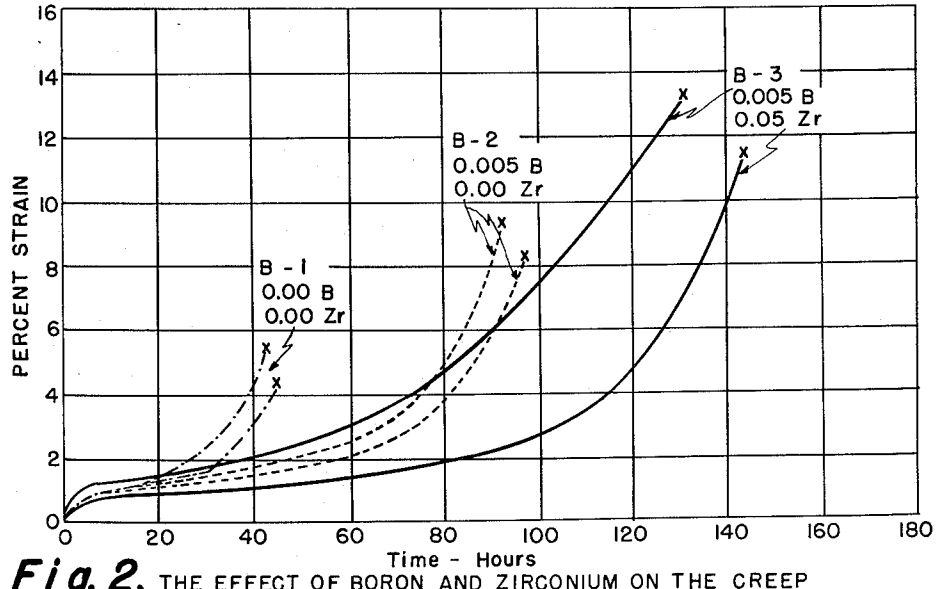


Fig. 2. THE EFFECT OF BORON AND ZIRCONIUM ON THE CREEP CHARACTERISTICS OF ALLOY "B". ALL TESTS WERE RUN AT 1600°F., AND 28,000 PSI ON FORGED DIP SAMPLES.

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METHOD OF PREPARING HIGH TEMPERATURE ALLOYS

Filed Oct. 8, 1956 3 Sheets-Sheet 2

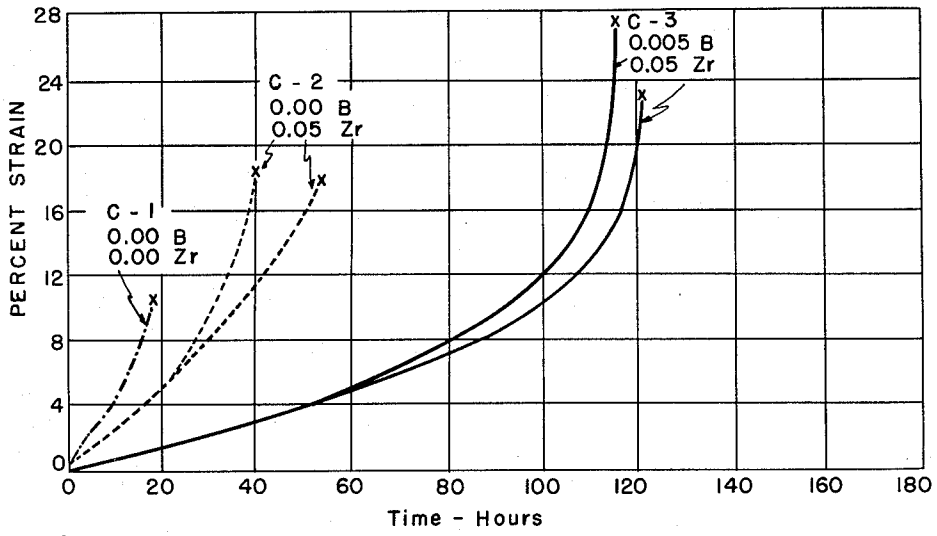


Fig. 3. THE EFFECT OF BORON AND ZIRCONIUM ON THE CREEP CHARACTERISTICS OF ALLOY "C." ALL TESTS WERE RUN AT 1650°F., AND 20,000 PSI ON FORGED DIP SAMPLES.

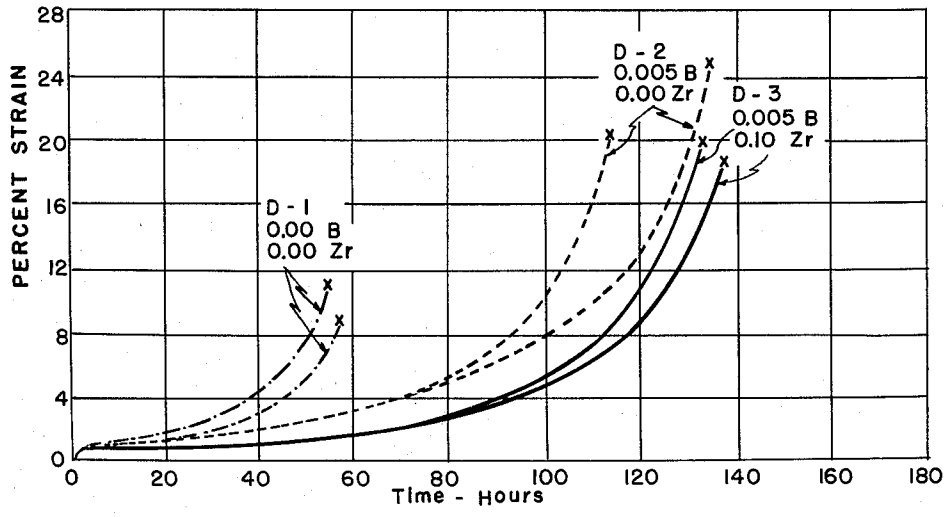


Fig. 4. THE EFFECT OF BORON AND ZIRCONIUM ON THE CREEP CHARACTERISTICS OF ALLOY "D." ALL TESTS WERE RUN AT 1500°F., AND 40,000 PSI ON FORGED DIP SAMPLES.

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Jan. 12, 1960 J. D. NISBET ET AL 2,920,956

METHOD OF PREPARING HIGH TEMPERATURE ALLOYS

Filed Oct. 8, 1956 3 Sheets-Sheet 3

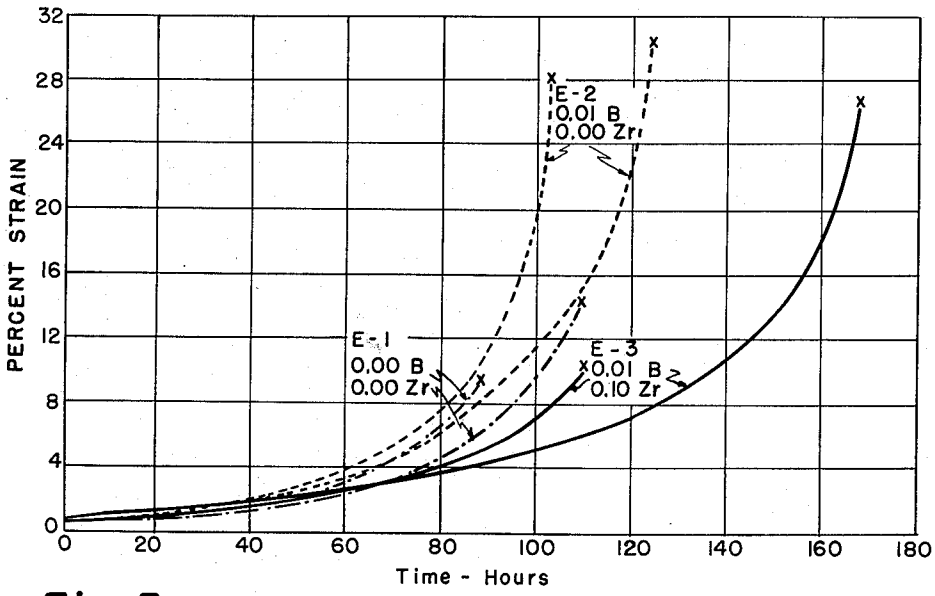


Fig. 5. THE EFFECT OF BORON AND ZIRCONIUM ON THE CREEP CHARACTERISTICS OF ALLOY "E." ALL TESTS WERE RUN AT 1500°F., AND 35,000 PSI ON FORGED DIP SAMPLES.

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METHOD OF PREPARING HIGH TEMPERATURE ALLOYS

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Application October 8, 1956, Serial No. 614,350

3 Claims. (Cl. 75—171)

This invention relates to high temperature alloys and the method of producing them. More particularly, it relates to the nickel-base and cobalt-base alloys.

Alloys of the type just mentioned are used for parts in jet engines, gas turbines and other high temperatures applications where it is necessary that the alloys have high strength properties, resistance to creep, resistance to oxidation, and good general mechanical properties, and that they are capable of being forged, rolled or fabricated into suitable articles or of being cast approximately to the shape of the finished article. While certain nickel-base and cobalt-base alloys in use up to the present time have been adequate for certain applications, they have restricted the design of high temperature parts because of the limited high temperature properties. The rapidly continuing advancement in the field of use of high temperature alloys requires an unceasing search for materials having improved properties at high temperatures. An alloy with improved properties is a major contribution to the advancement of the industry.

The primary object of this invention, therefore, is to provide nickel-base and cobalt-base alloys which possess consistently high minimum strength at elevated temperatures, enhanced rupture properties, creep resistance and ductility and which can be used in the as-cast condition or in the wrought condition after being subjected to proper heat treatment when such treatment is required.

We have discovered that, by adding boron or zirconium, or both boron and zirconium, in controlled amounts to nickel-base and cobalt-base alloys of the character described herein, we can obtain an appreciable improvement in the rupture life and ductility of such alloys, together with increased creep resistance. The alloys of our invention possess these properties at the high temperatures and heavy loads to which they are normally subjected in use. These alloys are precipitation hardenable by heat treatment although such treatment is not always necessary for the untreated alloy may be put into use and the temperature at which the part operates is at times sufficient to result in the required properties.

We have discovered that these properties can be obtained in nickel-base alloys containing from about 4.0 to 30.0% chromium, from about 35.0 to 90.0% nickel, and one or more of the elements titanium, aluminum, molybdenum, and tungsten, in addition to from 0.0005 to 0.05% boron or from about 0.005 to 0.50% zirconium, or both boron and zirconium. In addition, in such nickel-base alloys some iron, cobalt, columbium, or vanadium may be present. In such alloys, the carbon content preferably should be kept below 0.50% and manganese and silicon each should be kept below a maximum of approximately 3.0%.

We have also discovered that these improved properties can be obtained in cobalt-base alloys containing from about 4.0 to 30.0% chromium, from 0 to 30.0% nickel, from about 35.0 to about 90.0% cobalt, and one or more of the elements titanium, aluminum, molybdenum, tungsten, columbium, and vanadium, in addition to from about 0.0005 to 0.05% boron or 0.005 to 0.50% zirconium, or both boron and zirconium. In such cobalt-base alloys, the carbon content should be below about 0.50% and manganese and silicon should each be kept below about 3.0% maximum.

While we have mentioned above the nickel content of the nickel-base alloys and the cobalt content of the cobalt-base alloys of our invention, it will be understood that, in each case, the nickel or the cobalt, as the case may be, will constitute the balance of the alloy, except for other incidental elements not inconsistent with the desired properties.

As to the nickel-base alloys, in addition to the chromium and nickel the other elements mentioned above may be present in approximately the following amounts:

C	0–0.50%.
Co	0–30.0%.
Fe	0–30.0%.
Ti	0–8.0%.
Al	0–8.0%.
Mo	0–30.0%.
W	0–15.0%.
Cb and/or Ta	0–6.0%.
V	0–3.0%.
B	0.0005–0.05%, preferably 0.002–0.02%.
Zr	0.005–0.50%, preferably 0.05–0.20%.

As to the cobalt-base alloys, in addition to chromium and cobalt the other elements mentioned above may be present in the following amounts:

C	0–0.50%.
Ni	0–30.0%.
Fe	0–30.0%.
Ti	0–8.0%.
Al	0–8.0%.
Mo	0–30.0%.
W	0–15.0%.
Cb and/or Ta	0–6.0%.
V	0–3.0%.
B	0.0005–0.05%, preferably 0.002–0.02%.
Zr	0.005–0.50%, preferably 0.05–0.20%.

Although the individual elements may vary within wide limits, as stated above, the most practical ranges of composition are those in which the value of 7 aluminum+4 titanium+2 columbium+2 tantalum+1 molybednum+½ tungsten will be greater than 10 and less than 60.

The following alloys are illustrative of the nickel-base and cobalt-base alloys coming within the present invention:

	C	Cr	Co	Ti	Al	Mo	Fe	Cb+Ta	W	B	Zr	Ni	Mn	Si
Alloy No. 1	0.10-0.20	18.0-20.0	9.0-11.0	2.25-2.75	0.75-1.25	9.0-11.0	5.0 max.			0.005-0.02	0.05-0.20	Bal.		
Alloy No. 2	0.08-0.12	14.5-16.5	27.0-30.0	2.0-2.5	2.75-3.25	2.5-3.5	1.0 max.			0.005-0.02	0.05-0.20	Bal.		
Alloy No. 3	0.10 max.	18.0-24.0	12.0-15.0	2.75-3.25	1.0-1.5	3.5-5.0	2.0 max.			0.005-0.02	0.05-0.20	Bal.		
Alloy No. 4	0.05-0.10	18.0-21.0	18.0-21.0	2.2-3.0	1.2-2.0		5.0 max.			0.005-0.02	0.05-0.20	Bal.		
Alloy No. 5	0.15 max.	15.0-20.0	13.0-20.0	2.5-3.25	2.5-3.25	3.0-5.0	4.0 max.			0.005-0.02	0.05-0.20	Bal.		
Alloy No. 6	0.10 max.	19.0-22.0	1.0 max.	2.0-2.75	0.90-1.5		2.0 max.			0.005-0.02	0.05-0.20	Bal.	1.0 max.	1.0 max.
Alloy No. 7	0.08 max.	14.0-17.0	1.0 max.	2.25-2.75	0.40-1.0		5.0-9.0	.70-1.20		0.005-0.02	0.05-0.20	Bal.	1.0 max.	0.5 max.
Alloy No. 8	0.05-0.15	20.5-23.0	0.50-2.50			8.0-10.0	17.0-20.0		0.20-1.0	0.005-0.02	0.05-0.20	Bal.		
Alloy No. 9	0.15-0.25	19.0-21.0	36.5-38.5	3.7-4.7			2.5 max.		6.0-8.0	0.005-0.02	0.05-0.20	28.0-30.0		

In the above-mentioned illustrative alloys, we have specified both boron and zirconium, but it will be understood that either boron or zirconium or both may be used.

The alloys of this invention have especially improved properties when vacuum melted although it is believed that with the use of proper melting practices the improvements, at least to some degree, would be obtained by other means of melting.

The procedure followed in the vacuum melting of alloys of this invention consists of charging the crucible of the furnace in the vacuum chamber with the essential ingredients having the carbon distributed so that approximately one-half of the carbon charged is on the bottom of the crucible and the other one-half is midway between the bottom and top of the crucible. After charging is completed pumping down and out gassing the furnace is started. Power is put on the furnace. As pumping down proceeds, argon gas is added to the chamber sufficient to control the rate of gas evolution so as not to boil the molten metal out of the crucible. The pressure of argon at this point is held at about 20 millimeters of mercury, although the actual pressure maintained is not critical. When the charge has become molten and the boiling has become reasonably quiet, pumping down of the chamber to remove argon is begun. During this period, the temperature is maintained sufficiently high to prevent the formation of a skull over the molten bath. Complete carbon deoxidation is achieved by pumping down to a uniform minimum pressure of about 15 microns. That is, at this point, the deoxidation obtained is that limited to the deoxidizing ability of the carbon and does not represent complete deoxidation of the molten metal. A more complete deoxidation is obtained by treatment with boron and/or zirconium as described later in this procedure. After the carbon boil has been completed, any highly active elements such as silicon, vanadium, aluminum, titanium, etc., are added, if required. However, boron and/or zirconium are preferably not added at this point. When the additions have melted down and the bath mixed, samples are taken for preliminary analysis, if necessary. Any alloy additions necessary to bring the composition within the specification ranges are made and the temperature adjusted to proper level for tapping the heat. At this point, the boron and/or zirconium addition is made. The heat is held for 15 minutes after the boron and/or zirconium addition and is then tapped.

The boron and/or zirconium treatment referred to not only serves to more completely deoxidize the molten bath but sufficient of either or both of the elements is retained in the metal to have a beneficial effect on the high temperature properties of the resulting alloy.

These alloys may be used in the cast condition or processed to intermediate products such as bars, wire, sheet, strip, etc., as well as for fabricating into shapes by machining, forging or other methods.

Improved creep and stress rupture properties are obtained with the alloys of this invention. These alloys are usually subjected to heat treatment in order to obtain the desired properties. Generally, the alloy is heated to a temperature sufficiently high to dissolve to some degree any of the intermetallic compounds that may be present and is then either air cooled or quenched in some suitable manner. It is generally given an aging treatment at a suitable temperature and for a suitable time and is thereafter cooled. The temperatures and times employed will vary somewhat depending upon the particular composition, the prior fabricating history and the application of the alloy being heat treated. A preferred hardening treatment for certain uses for a composition such as alloy No. 1 is to heat the material at a temperature of approximately 1950° F. for 4 hours, then air cool, and then age for a period of 15 hours at 1400° F. and air cool. A suitable treatment for alloy No. 9 mentioned above is to heat for 2 hours at a temperature of 2150° F., then air cool the alloy, then age it for 24 hours at 1650° F. and then air cool.

The improved properties obtained by our invention are illustrated in the comparative data contained in the tables below.

In Table I, we have shown a comparison of our alloys and like alloys without boron or zirconium. Alloys A–1, B–1, C–1, D–1 and E–1 are not alloys embodying our invention; whereas, alloys A–2, A–3, B–2, B–3, C–2, C–3, D–2, D–3, E–2, E–3 are alloys embodying our invention. The heat treatments to which the alloys were subjected are recited in the table.

In Table II, which is set forth below, we have shown the improvement factors due to boron and zirconium additions with respect to creep and rupture properties. As in the case of Table I, alloys A–1, B–1, etc., are not alloys of our invention; whereas alloys A–2, A–3, B–2, etc., are alloys embodying our invention. The manner in which the values were obtained is indicated at the end of Table II. An improvement factor of two for rupture life indicates that the rupture life has been doubled, and an improvement factor of two for the minimum creep rate indicates that the creep rate has been halved.

TABLE I

Comparison of creep and rupture properties of our alloys and like alloys without boron or zirconium

Item No.	Alloy	Percent B Added	Percent Zr Added	Rupture Test Data			
				Minimum Creep Rate (Percent/hr.)	Rupture Life (Hours)	Elongation, Percent	Reduction of Area, Percent
[Specimens tested at 1,600° F. and 20,160 p.s.i. Heat treatment: 8 hours at 1,975° F., air cool plus 16 hours at 1,290° F., air cool.]							
1	A-1	0.00	0.00	0.055	44.2	2.6	7.4
2				0.055	80.1	4.4	5.9
3	A-2	0.00	0.10	0.023	133.8	7.0	7.4
4				0.023	136.9	6.7	9.5
5	A-3	0.01	0.10	0.019	361.0	11.6	22.3
6				0.019	370.2	8.8	13.5
[Specimens tested at 1,600° F. and 28,000 p.s.i. Heat treatment: 2 hours at 2,160° F., air cool plus 4 hours at 1,600° F., air cool.]							
7	B-1	0.00	0.00	0.029	45.6	4.3	5.6
8				0.046	43.9	5.4	2.5
9				0.033	26.5	2.6	6.5
10				0.040	55.0	4.4	7.7
11	B-2	0.005	0.00	0.020	97.7	8.3	12.5
12				0.029	93.2	9.4	16.1
13				0.027	71.3	4.7	11.8
14	B-3	0.005	0.05	0.040	132.5	13.2	18.8
15				0.023	143.9	11.4	19.4
16				0.030	101.7	12.8	23.1
[Specimens tested at 1,650° F. and 20,000 p.s.i. Heat treatment: 2 hours at 2,150° F., air cool plus 24 hours at 1,650° F., air cool.]							
17	C-1	0.00	0.00	0.48	18.2	10.5	7.7
18	C-2	0.00	0.05	0.20	54.4	18.0	36.4
19				0.092	39.9	18.6	33.2
20	C-3	0.005	0.05	0.053	115.4	27.6	40.2
21				0.053	122.2	23.0	35.6
[Specimens tested at 1,500° F. and 40,000 p.s.i. Heat treatment: 4 hours at 1,975° F., air cool plus 24 hours at 1,550° F, air cool plus 16 hours at 1,400° F., air cool.]							
22	D-1	0.00	0.00	0.058	54.0	10.8	13.0
23				0.025	57.4	8.9	10.2
24	D-2	0.005	0.00	0.042	135.0	25.0	26.1
25				0.031	112.8	20.1	34.0
26				0.021	113.1	24.5	33.0
27	D-3	0.005	0.10	0.010	137.3	18.5	30.4
28				0.015	134.2	20.3	33.9
29				0.028	110.1	23.6	29.1
30				0.037	127.2	24.1	30.7
[Specimens tested at 1,500° F. and 35,000 p.s.i. Heat treatment: 4 hours at 1,950° F., air cool plus 15 hours at 1,400° F., air cool.]							
31	E-1	0.00	0.00	0.035	87.6	9.3	21.3
32				0.020	109.4	14.5	23.3
33	E-2	0.01	0.00	0.050	103.2	28.6	44.3
34				0.038	124.3	31.6	40.6
35	E-3	0.01	0.10	0.030	166.6	24.7	43.6
36				0.026	108.8	10.3	37.2
[Specimens tested at 1,500° F. and 40,000 p.s.i. Heat treatment: Mill annealed 1 hour at 2,050° F. plus 4 hours at 1,950° F., air cool plus 15 hours at 1400° F., air cool.]							
37	E-1	0.00	0.00	0.065	48.6	5.4	7.2
38	E-2	0.01	0.00	0.035	77.5	18.7	20.6
39	E-3	0.01	0.10	0.036	88.0	17.6	27.9

TABLE II

Improvement factors due to boron and zirconium additions with respect to creep and rupture properties of several alloys of our invention

Item No.	Alloy	B Added, Percent	Zr Added, Percent	Improvement Factors [1]—Rupture Test Properties: Minimum Creep Rate (Percent/hour)	Rupture Life, Hours	Elongation, Percent
[Tested at 1,600° F. and 20,160 p.s.i.]						
1	A–1	0.00	0.00	1.00	1.00	1.00
2	A–2	0.00	0.10	2.39	2.18	1.94
3	A–3	0.01	0.10	2.89	5.88	2.92
[Tested at 1,600° F. and 28,000 p.s.i.]						
4	B–1	0.00	0.00	1.00	1.00	1.00
5	B–2	0.005	0.00	1.51	2.13	1.83
6	B–3	0.005	0.05	1.16	3.10	2.56
[Tested at 1,650° F. and 20,000 p.s.i.]						
7	C–1	0.00	0.00	1.00	1.00	1.00
8	C–2	0.00	0.05	3.29	2.60	1.74
9	C–3	0.005	0.05	9.05	6.52	2.41
[Tested at 1,500° F. and 40,000 p.s.i.]						
10	D–1	0.00	0.00	1.00	1.00	1.00
11	D–2	0.005	0.00	1.14	2.22	2.30
12	D–3	0.005	0.10	3.32	2.44	1.98
[Tested at 1,500° F. and 35,000 p.s.i.]						
13	E–1	0.00	0.00	1.00	1.00	1.00
14	E–2	0.01	0.00	0.62	1.15	2.53
15	E–3	0.01	0.10	1.00	1.40	1.47

[1] Improvement factor for percent creep in 1 hour

$$= \frac{\text{values for alloys without B and Zr.}}{\text{values for alloys with B and/or Zr.}}$$

Improvement factor for rupture life and rupture elongation

$$= \frac{\text{values for alloys with B and/or Zr.}}{\text{values for alloys without B and Zr.}}$$

In Table III, which is set forth below, we have shown the overall improvement factors created by the addition of boron and/or zirconium with respect to the elevated temperature properties of our alloys.

TABLE III

The overall improvement factors created by boron and/or zirconium additions with respect to the elevated temperature properties of our alloys [a]

	Improvement Factors—Creep and Rupture Properties [e]: Minimum Creep Rate	Rupture Life	Elongation, Percent
Boron [b]	1.09	1.83	2.22
Zirconium [c]	2.84	2.39	1.84
Boron and Zirconium [d]	3.48	3.87	2.27

[a] Our alloys of the A, B, C, D and E Series.
[b] Additions actually used for data: 0.005% or 0.010% boron.
[c] Additions actually used for data: 0.05% or 0.10% zirconium.
[d] Additions actually used for data: 0.005% or 0.01% boron+0.05% or 0.10% zirconium.
[e] Rupture tests were conducted under the following conditions:

Alloy	Temperature, ° F.	Load, p.s.i.
A	1,600	20,160
B	1,600	28,000
C	1,650	20,000
D	1,500	40,000
E	1,500	35,000

In the foregoing tables, the alloys of our invention identified by the letter "A" were approximately of the composition of alloy No. 4. Those identified by the letter "B" were approximately of the composition of alloy No. 2. Those identified by the letter "C" were approximately the composition of alloy No. 9. Those identified by the letter "D" were approximately of the composition of alloy No. 3. And those identified by the letter "E" were approximately of the composition of alloy No. 1.

In the accompanying drawings, we have illustrated the effects of boron and zirconium on the creep characteristics of alloys A to E, inclusive. Figure 1 relates to alloys A, Figure 2 to alloys B, Figure 3 to alloys C, Figure 4 to alloys D and Figure 5 to alloys E. As in the case of the tables, alloys carrying the numeral "1" such as A–1, B–1, C–1, etc., were not the alloys of our invention; whereas, the alloys carrying the numerals "2" and "3" such as A–2 and A–3 were alloys made in accordance with our invention. These figures illustrate graphically the substantially improved creep characteristics of our alloys as set forth in Table I.

While we have indicated in the foregoing specification the nature of our invention and the highly improved results obtained by the use thereof, our invention is not limited to the specific ranges or methods set forth above, but may be otherwise enjoyed within the scope of the appended claims.

We claim:

1. The method of preparing an alloy characterized by high strength at elevated temperatures and improved rupture properties, creep resistance and ductility which comprises melting chromium and at least one element of the group consisting of nickel and cobalt in the presence of carbon allowing the carbon deoxidation of the melt to proceed to substantial completion, thereafter adding to the melt at least one highly reactive element selected from the group consisting of silicon, vanadium, aluminum and titanium, completing the melting of such highly reactive elements, adjusting the temperature of the melt to approximately the desired tapping temperature and adding to the melt at least one element of the group consisting of boron and zirconium in an amount sufficient to complete deoxidation of the melt and provide in the resulting alloy at least one element of said group within the ranges of 0.0005 to 0.05% boron and 0.005 to 0.5% zirconium, and thereafter tapping the heat, the amounts of chromium, carbon, the highly reactive elements and the element of the nickel-cobalt group employed being sufficient to provide in the resulting alloy 4 to 30% chromium, up to 0.50% carbon, up to 3.0% silicon, up to 3.0% vanadium, up to 8.0% aluminum, up to 8.0% titanium, and 35 to 90% of the element of the nickel-cobalt group.

2. The method of preparing an alloy characterized by high strength at elevated temperatures and improved rupture properties, creep resistance and ductility which comprises melting chromium and at least one element of the group consisting of nickel and cobalt in the presence of carbon allowing the carbon deoxidation of the melt to proceed to substantial completion, thereafter adding to the melt at least one highly reactive element selected from the group consisting of silicon, vanadium, aluminum and titanium, completing the melting of such highly reactive elements, adjusting the temperature of the melt to approximately the desired tapping temperature and adding to the melt boron in an amount sufficient to com-

plete deoxidation of the melt and provide in the resulting alloy boron within the range of 0.0005 to 0.05%, and thereafter tapping the heat, the amounts of chromium, carbon, the highly reactive elements and the element of the nickel-cobalt group employed being sufficient to provide in the resulting alloy 4 to 30% chromium, up to 0.50% carbon, up to 3.0% silicon, up to 3.0% vanadium, up to 8.0% aluminum, up to 8.0% titanium, and 35 to 90% of the element of the nickel-cobalt group.

3. The method of preparing an alloy characterized by high strength at elevated temperatures and improved rupture properties, creep resistance and ductility which comprises melting chromium and at least one element of the group consisting of nickel and cobalt in the presence of carbon while subjecting the melt to a vacuum, allowing the carbon deoxidation of the melt to proceed to substantial completion, thereafter adding to the melt at least one highly reactive element selected from the group consisting of silicon, vanadium, aluminum and titanium, completing the melting of such highly reactive elements, adjusting the temperature of the melt to approximately the desired tapping temperature and adding to the melt zirconium in an amount sufficient to complete deoxidation of the melt and provide in the resulting alloy zirconium

within the range of 0.005 to 0.5%, and thereafter tapping the heat, the amounts of chromium, carbon, the highly reactive elements and the element of the nickel-cobalt group employed being sufficient to provide in the resulting alloy 4 to 30% chromium, up to 0.50% carbon, up to 3.0% silicon, up to 3.0% vanadium, up to 8.0% aluminum, up to 8.0% titanium, and 35 to 90% of the element of the nickel-cobalt group.

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