United States Patent [19]

Griffiths et al.

[11] **3,753,800**

[45] **Aug. 21, 1973**

[54] **METHOD OF MAKING NICKEL-CHROMIUM-BERYLLIUM ALLOY**

[75] Inventors: **Leonard B. Griffiths; Yuan-Shou Shen,** both of North Reading, Mass.

[73] Assignee: **P. R. Mallory & Co., Inc.,** Indianapolis, Ind.

[22] Filed: **Apr. 21, 1971**

[21] Appl. No.: **136,229**

Related U.S. Application Data

[60] Division of Ser. No. 832,335, June 11, 1969, Pat. No. 3,704,182, which is a continuation-in-part of Ser. No. 793,814, Jan. 24, 1969, abandoned.

[52] **U.S. Cl.** **148/162**

[51] **Int. Cl.** **C22f 1/10**

[58] **Field of Search** 148/162, 3, 32, 32.5; 75/171

[56] **References Cited**

UNITED STATES PATENTS

2,469,718	5/1949	Edlund et al.	75/171
3,464,817	9/1969	Griffiths	75/171
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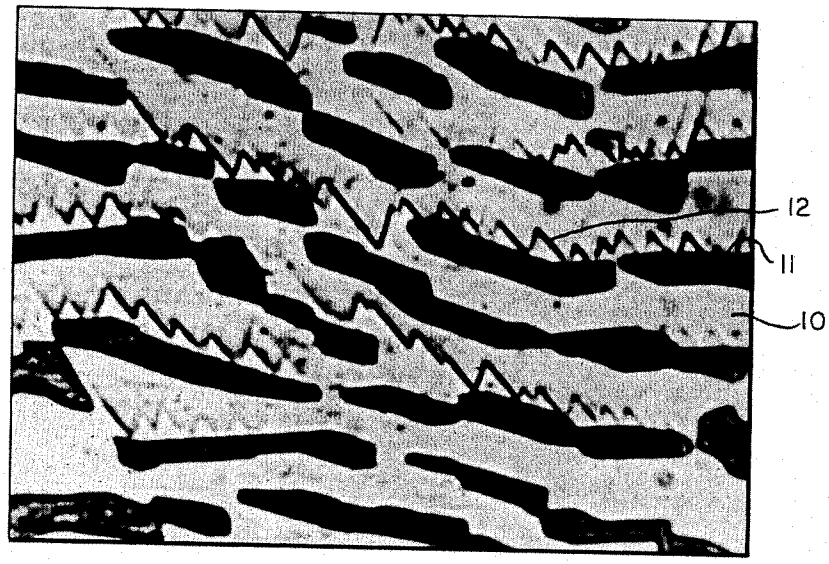
Primary Examiner—Richard O. Dean

Attorney—Charles W. Hoffmann

[57] **ABSTRACT**

This invention relates to a method of making nickel-chromium-beryllium alloy having a microstructure which provides obstacles to plastic flow in the nickel rich matrix phase so that high strength properties are obtained at both room and elevated temperatures. The alloy may also contain other additives including aluminum and/or titanium together with hardeners including molybdenum and/or tungsten, with or without carbon. A method of processing the alloy comprises melting the alloying ingredients in a crucible while avoiding the presence of oxygen; raising the temperature to 1,450° to 1,550°C; casting the alloy in a mold. The alloy may be remelted and cast in an apparatus to effect abstraction of heat from the casting from one direction only to obtain a directionally orientated microstructure.

8 Claims, 7 Drawing Figures



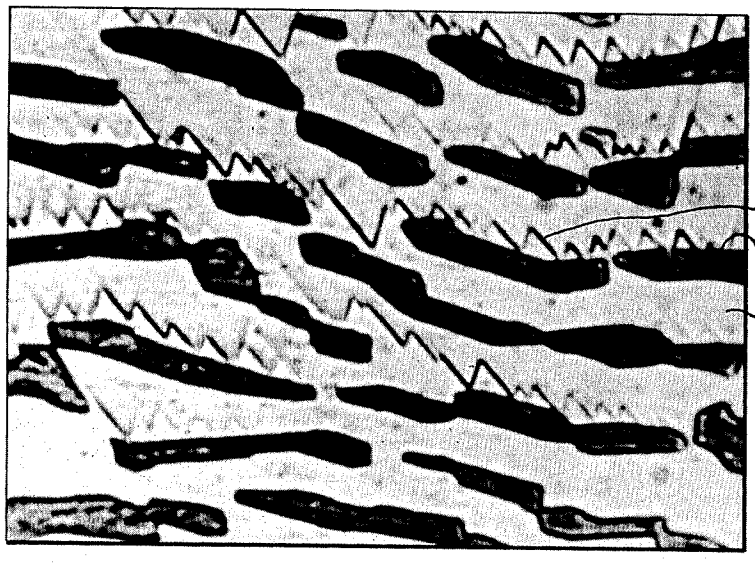


FIG. 1

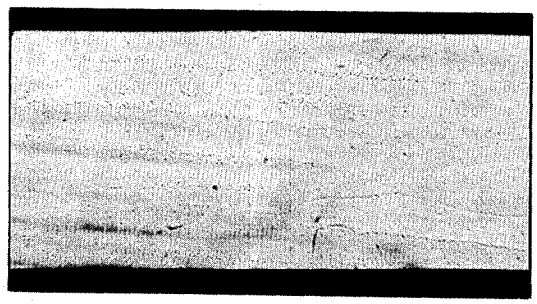


FIG. 5

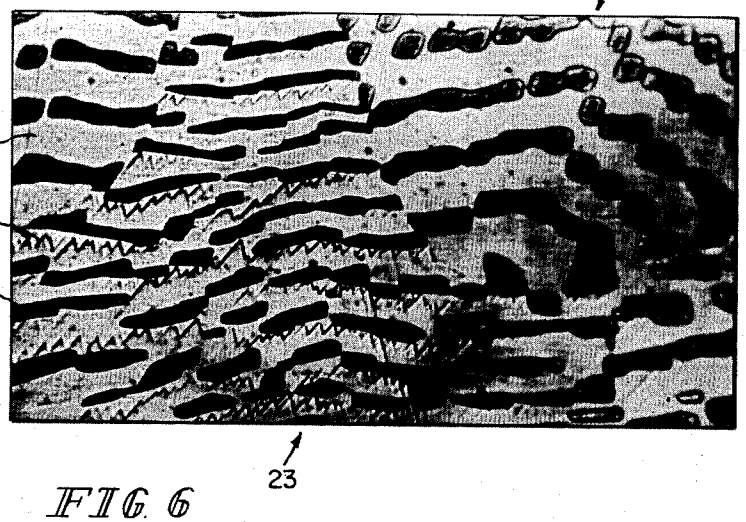


FIG. 6

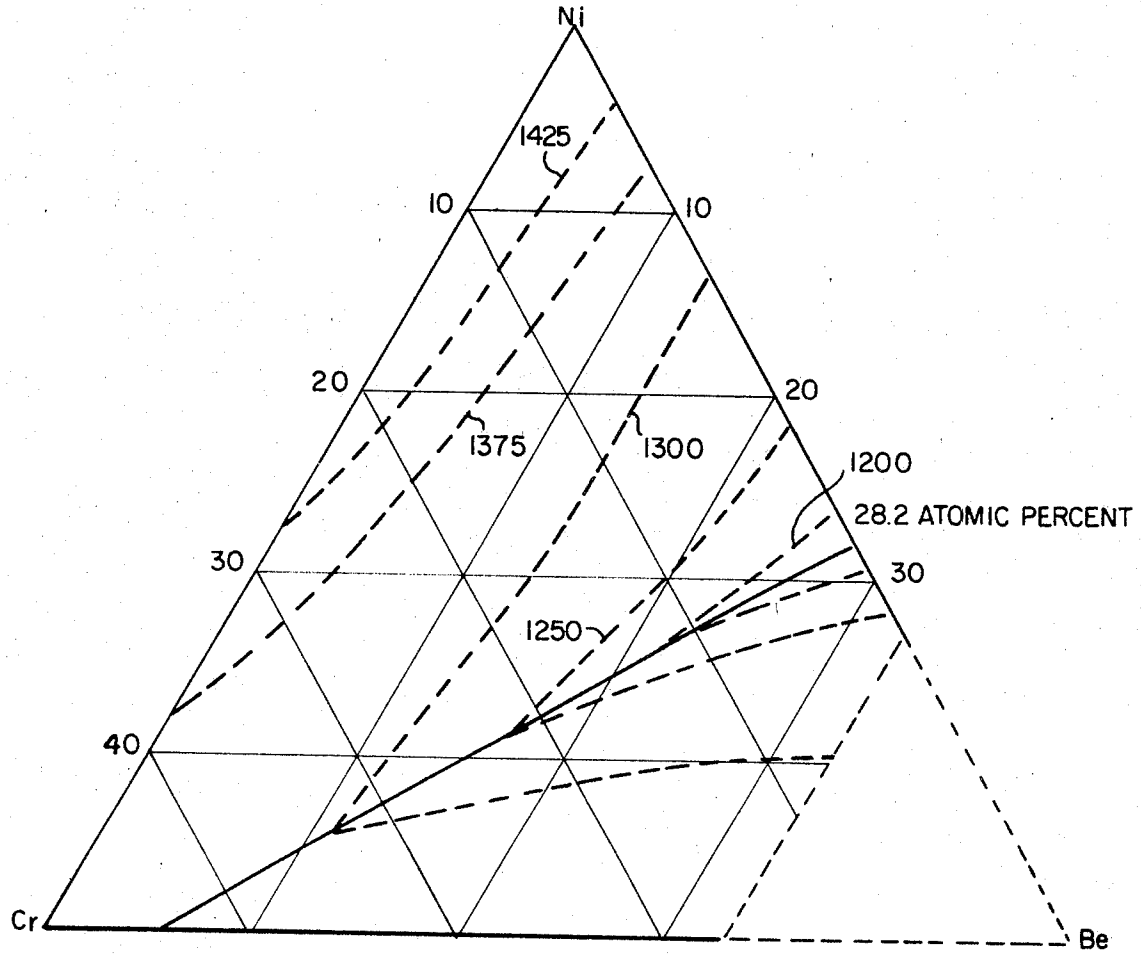

Ni
1425
10
10
20
20
1375
1300
1200
28.2 ATOMIC PERCENT
30
30
1250
40
Cr
Be

FIG 2

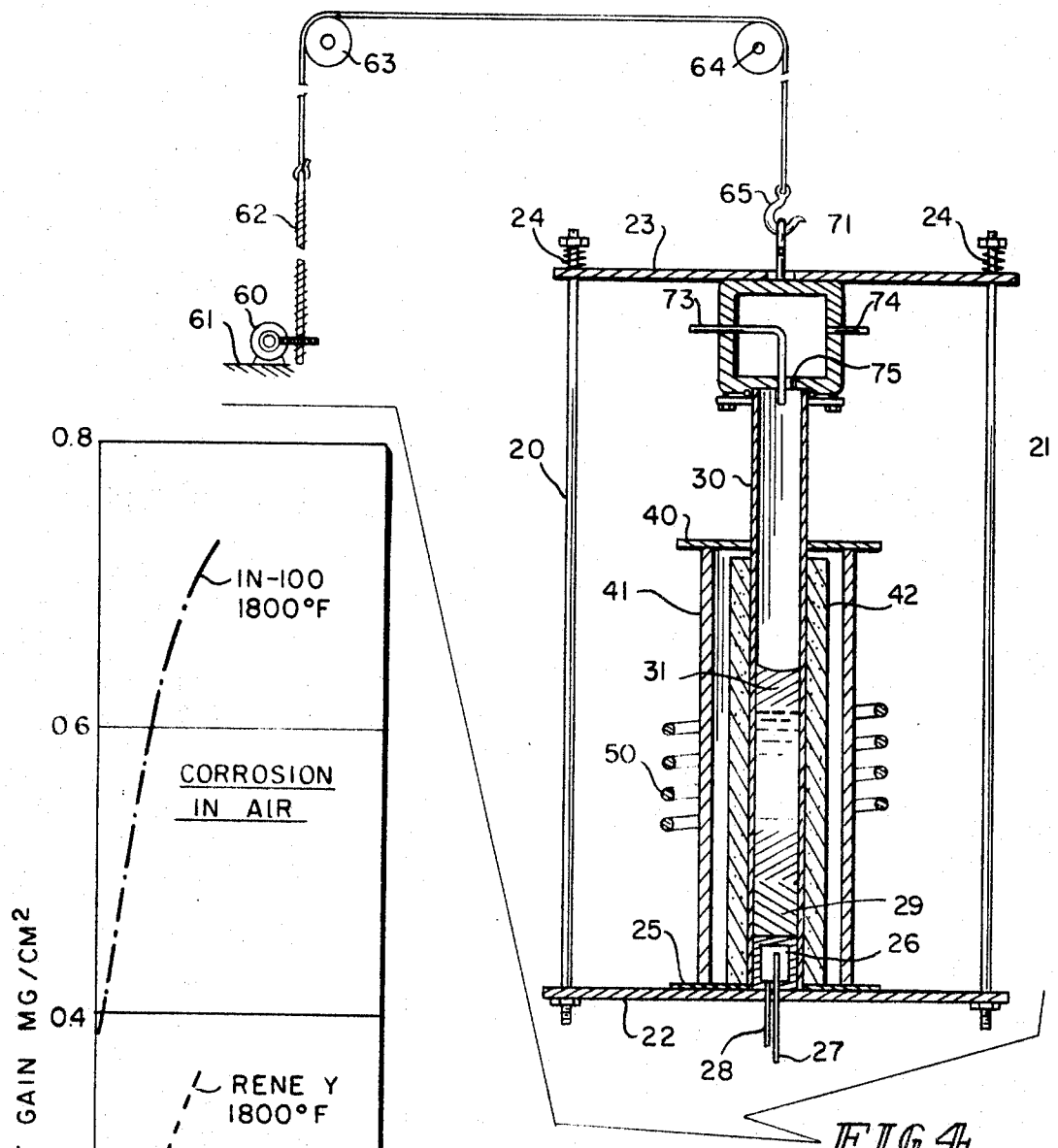

63
64
65
62
60
61
24
23
71
24
73
74
75
20
21
30
40
41
42
31
50
29
25
26
22
28
27

FIG 4

0.8
0.6
0.4
0.2
0
IN-100
1800°F
CORROSION
IN AIR
RENE Y
1800°F
1800°F
1750°F
WEIGHT GAIN MG/CM²
0
100
200
HOURS

FIG. 3

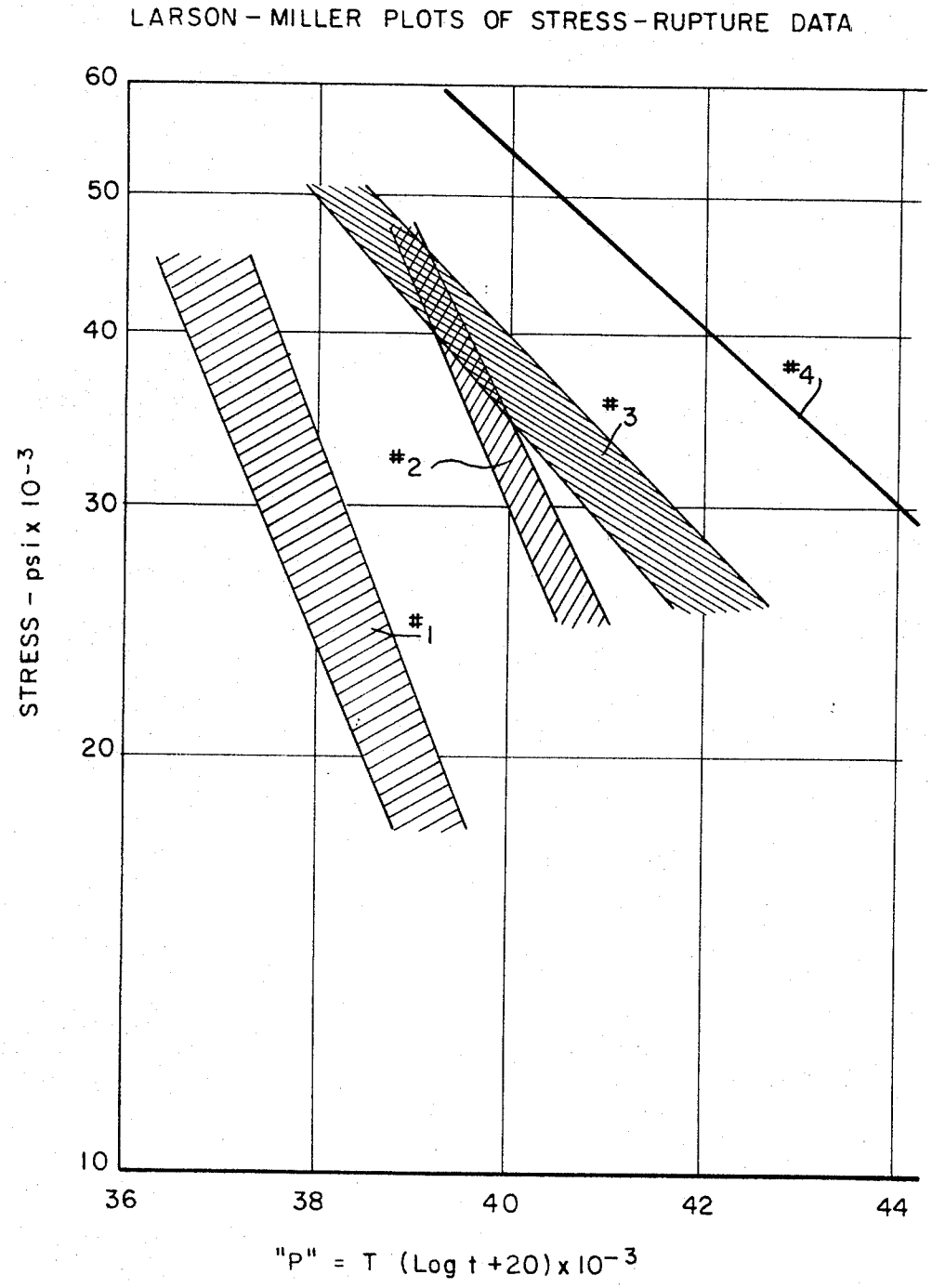

LARSON - MILLER PLOTS OF STRESS - RUPTURE DATA
60
50
40
30
20
10
STRESS - psi x 10-3
#1
#2
#3
#4
36
38
40
42
44
"P" = T (Log t +20) x 10-3

FIG 1

METHOD OF MAKING NICKEL-CHROMIUM-BERYLLIUM ALLOY

This is a division of application Ser. No. 832,335, filed June 11, 1969, now U.S. Pat. No. 3,704,182 which in turn is a continuation-in-part of application Ser. No. 793,814, filed Jan. 24, 1969, now abandoned.

Alloys containing nickel-chromium and beryllium have been known for some time. For example, such alloys are disclosed in British Pat. No. 404,012 (for use in surgical sewing needles and dental instruments) and U.S. Pat. Nos. 2,089,587, (for dentures) and 2,150,205 (for engine valves).

However, the advantage of using these alloys in specific proportions resulting in a specific microstructure for both room temperature and high temperature applications requiring high mechanical properties has not previously been recognized.

It is, therefore, an object of the present invention to provide a Ni-Cr-Be alloy having high strength at elevated temperatures.

It is another object of the present invention to provide an alloy which is resistant to oxidation at elevated temperatures.

It is another object of the present invention to provide an alloy having high stress-to-rupture values at elevated temperature.

It is another object of the present invention to provide an alloy having good mechanical properties at room temperature.

It is another object of the present invention to provide an alloy having a microstructure which is resistant to plastic flow at both room and elevated temperatures.

It is another object of the present invention to provide a high temperature alloy which avoids the use of carbides for strengthening.

It is still another object of the present invention to provide a method for processing a high temperature alloy containing nickel-chromium-beryllium in order to obtain a microstructure which has resistance to plastic flow at room and elevated temperatures.

It is another object of the present invention to provide a process for treating an alloy in order to obtain uniaxial as-cast structure.

Other objects will be apparent from the following description and drawings in which:

FIG. 1 is a view of an exemplary microstructure of the alloy of the present invention at 2,700 magnifications.

FIG. 2 is a ternary Ni-Cr-Be diagram showing the composition of the eutectic alloy utilized in obtaining the desired microstructure according to the present invention.

FIG. 3 is a plot of weight gain (oxidation) as a function of time, at various temperatures, for the alloy of the present invention and other representative alloys of the prior art.

FIG. 4 is a schematic diagram of apparatus which may be used in casting the alloy of the present invention.

FIG. 5 is a view of the as-cast ingot showing the microscopic directionality of the casting at 20 magnifications.

FIG. 6 is a view of the microstructure of the alloy of the present invention in the directionally cast condition at 1,300 magnifications.

FIG. 7 is a Larsen-Miller plot of the stress-rupture data obtained in Example II.

As can be seen from FIG. 1, the microstructure of the nickel-chromium-beryllium alloy of the present invention is composed of a nickel rich solid solution matrix **10** having chromium dissolved therein in solid solution and nickel-beryllide rods (NiBe) **11**, in which chromium is also dissolved, interspersed within said matrix.

While the structure is actually the result of a three phase equilibrium transformation, it is useful to consider it as a binary eutectic in which:

$$\text{(1)} \qquad \text{Liquid} \rightleftarrows Ni_{(ss)} + NiBe$$

The reaction occurs at the base of a liquidus valley bounded by the two-phase fields, liquid + Ni(Cr) and liquid + Ni(Cr)Be, within the Ni-Cr-Be constitutional system. As can be seen from FIG. 2, the composition at which this reaction takes place is within the temperature range of 1,175° to 1,275°C. The nickel content of the alloy of the present invention should be about 54 to 72.5 atomic percent. The chromium content should be about 32.5 to 2.5 atomic percent and the beryllium content about 14.5 to 25.5 atomic percent. Furthermore, the composition should be such that upon freezing no two-phase field is intersected, but rather the reaction proceeds at all times in accordance with the three phase reaction given in equation (1). This occurs at compositions substantially as shown by the solid line in FIG. 2. A variance of about ±2 atomic percent of the Ni-Be ratio on either side of the solid line in FIG. 2 may also be used and the desired microstructure will be obtained. Since freezing occurs essentially within the liquidus valley, the temperature dependence of which is only slight, a substantially uniform microstructure is obtained throughout the ingot, in contrast to alloys having a long freezing range.

The presence of the Ni(Cr)Be rods **11** is to be contrasted with the nickel-beryllium binary system wherein the NiBe phase is plate-like. It has been found according to the present invention that the addition of chromium results in the desired rod-shaped beryllide phase.

Generally, in two phase structures of this type, one of the phases predominates at the grain boundaries which results in either brittleness or low strength; however, the beryllide rods extend completely to the colony boundaries in the alloy of the present invention, as shown in FIG. 6. This phenomenon is very important. The beryllide rods provide obstacles to plastic flow in the nickel rich phase. This feature can be seen in FIGS. 1, and 6; showing slip lines **12** are prevented from propogation by the hard beryllide phase **11**. This phenomenon yields a relatively high rate of work hardening. Spacing between rods within a colony is usually within the range of about 2 to 20 u, and preferably about 4 to 8 u. This is computed on the basis of the mean free path distance.

The chromium, in addition to rendering the beryllide phase rodlike, confers some solid solution strengthening both on the nickel and on the beryllide phase. The chromium also provides oxidation resistance. This can be seen from FIG. 3. It is apparent from FIG. 3 that at 1800°F there is less weight gain (a measure of oxidation) with the alloy of the present invention than with the Inconel 100 (10 Cr, 15 Co, 5 Ti, 5.5 A1, 3 Mo, 0.18 C, Bal. Ni) and Rene-Y (Cr 22, Mo 9, Fe 18, W 1 max.,

Co 2 max., Mn 1.0, Si 1.0 max., 0.15 C, 0.15 La, Bal. Ni) prior art alloys.

Oxygen and nitrogen should each be below 0.5 percent by weight respectively. Carbon should be below 0.02 percent by weight unless carbides are to be formed as described hereinafter.

The alloy of the present invention may be prepared by melting together the constituents preferably in elemental form in a refractory crucible made, for example, of MgO, Al_2O_3 or BeO in the absence of oxygen. If desired, the melting may be carried out in an inert atmosphere such as argon or helium. It is also often desirable to utilize a reduced pressure or partial vacuum atmosphere. The melting temperature should be between about 1,450° to 1,550°C. in order to insure that ample fluidity for subsequent casting is obtained.

The mold to be used in casting the alloy of the present invention may be either of the permanent mold type, for example, made of copper or steel or graphite molds may be utilized. If graphite is utilized, it is preferred to use a beryllium oxide wash in the mold. The casting cooling rate for the casting operation is not critical.

After casting, the ingots are preferably remelted and subsequently frozen uniaxially in order to obtain the best properties. For example, one apparatus which may be used for the remelting operation is shown in FIG. **4.** The holding screws **20** and **21** hold plates **22** and **23** in place by means of spring fasteners **24.** A shielding plate **25** is placed upon the top of holding plate **22** and a chillplate **26** is placed thereon. The chillplate has a water inlet **27** and a water outlet **28** associated therewith which pass through plates **23** and **25** for circulating a cooling fluid therethrough. A starting stub **29** is mounted on the chill plate.

The ingot to be melted **31** is placed in a refractory crucible **30** which may be made of MgO, Al_2O_3 or BeO or other refractory oxide materials. In order to effect melting an RF coil **50** is energized to provide sufficient heat to reach the melting point temperature range given above.

The lowering mechanism comprises a motor **60** mounted on the base **61.** The motor is connected to a wire rope or chain **62,** which by means of idle wheels **63** and **64,** controls the decent of argon adaptor **70** by means of hook **65** in engagement with the flange **71** of the argon adaptor. The adaptor has an inlet **73** and an outlet **74** for circulation of argon gas. The inlet conduit **73** is in communication with the crucible **73** to provide an argon atmosphere during the melting operation which takes place in the vicinity of coil **50.** The argon then passes out of the crucible and through conduit **75** and **74.**

The argon adaptor is affixed to the crucible **30** by conventional fasteners (not shown) so that the adaptor, the crucible and the entire structure excepting coil **50** are lowered upon operation of motor **60,** causing the ingot to be melted to move through coil **50.** The amount of movement is limited, however, by the space between the coil and shielding sheet **40.**

Initially the motor **60** is utilized to place the meeting point of the starting stub and the ingot to be melted within RF coil **50.** RF coil is then energized sufficiently to melt a cross section of the ingot. The ingot is then gradually lowered as freezing occurs from the chill plate **26** upward under the action of the naturally occurring axial temperature gradient from the chill plate upward. For example, the ingot may be lowered at the rate of 1 inch to 2 inches per hour. The casting operation is stopped when the coil reaches a point near shielding sheet **40** or when all of the ingot has been melted.

It will be apparent that this arrangement results in a directionally frozen ingot as shown in FIG. **5.** However, it will be apparent to those skilled in the art that other casting apparatus which provides for directional freezing can also be utilized. For commercial scale operation, continuous casting equipment in which the ingot is continuously cooled by application of a cooling medium to the already cast portion of the ingot, could be utilized.

The microstructure of the alloy of the present invention in the directionally frozen condition is shown in FIG. **6** and the nickel-matrix **10** again surrounds the Ni(Cr)Be rods **11.** The microstructure is also composed of two phase colonies which are greatly elongated in the direction of casting growth; in other words, parallel to the growth axis as shown in FIG. **5.** The beryllide phase **21** is uninfluenced by growth conditions, and the axis of the rods varies from colony to colony. Note the rods in colonies **23** and **24.** There is a preferred direction however within each colony. The elongated colonies result in markedly reduced transverse colony boundary area.

In addition to the amounts of Ni, Cr and Be previously stated, a metal selected from the group consisting of aluminum, titanium and mixtures thereof is preferably added in the range of from about each 1 to 5 atomic percent, preferably 2 to 4 atomic percent, each. Preferably aluminum alone, or mixtures of aluminum and titanium are used. The aluminum and/or titanium present reacts with nickel to form the compounds such as Ni_3Al and Ni_3Ti. These compounds may be distributed throughout the nickel-rich phase by first providing a solution treatment at a temperature of about 1,950° to 2,150°F preferably about 2,000° to 2,150°F for a period of 2 to 75 hours, preferably 4 to 50 hours. This heating step is followed by ageing at a temperature of from about 1,200° to 1,500°F, preferably 1,200° to 1,400°F for about 2 to 30 hours, preferably 4 to 16 hours. This results in the Ni_3Al and/or (Ti, Al)Ni_3 precipitating from solid solution in the form of the α' phase well known in the art.

It is also preferred to add one or more hardening elements selected from the group consisting of Mo, W, Ta, Nb, Va, Zr, B, Mn, Fe, Co and mixtures thereof, in an amount of from about 2 to 10 atomic percent total. Preferably Mo and W are used in the range of about 2 to 2.5 atomic percent Mo and from about 1 to 1.5 atomic percent W. The hardening addition will affect an increase in strength by solid solution hardening of the nickel-rich phase.

The hardening elements will also form carbides if free carbon is present. While considerable strengthening can be obtained by carbide formation by including carbon in the range 0.06 to 0.12 percent by weight, according to the preferred embodiment of the invention the carbon content is restricted to not more than 0.02 percent by weight so that carbide formation is substantially avoided. During service at elevated temperature the carbides have a tendency to coarsen, causing embrittlement.

As to the properties of the alloy of the present invention, Table I shows that the alloy of the present invention is superior to representative alloys of the prior art from a standpoint of modulus of elasticity and specific modulus (modulus of elasticity divided by density).

TABLE I

Alloy	Modulus of Elasticity (PSI × 10^{-6})	Specific Modulus (inch × 10^{-6})
PW664	30	86.5
9Cr, 10 Co, 12 W, 5 Al, 2 Ti, 1 Ta + Cb, .13 C, Ni Bal.		
Hastelay X	30	100
22 Cr, 20Fe, 9 Mo, .15 C, Ni Bal.		
Inco 713C	30	104
13 Cr, 6.0 Al, 4.5 Mo, Ta + Cb 2, Ti .6, Co 1.0max., Mn 0.5, Si 1.5max., Fe 2.5max., 0.12 C, Ni Bal.		
Udinet 700	30	104
19 Co, 15 Cr, 5 Mo, 4.5 Al, 3.5 Ti, 4.0 max. Fe, .03 B, Ni Bal.		
Ni-Cr-Be Alloy of Present Invention	35	129

tal constituents in the crucible. The crucible was placed in a furnace and heated to above the melting point of the resulting alloy in an argon atomsphere. The alloys were poured at 1,450°C into steel molds.

The resulting castings were 7 inches long by 1¼ inches in diameter.

Those specimens which were directionally cast were remelted and directionally cast in the manner described above in regard to FIG. 4. Casting rates were 1 to 2 inches per hour.

The specimens which were heat treated were solution treated at 1,120°C for 4 hours and then air quenched to 760°C and held for 16 hours.

Tensile specimens were than prepared and standard tensile tests were carried out at the temperatures given in Table III. Room temperature was 68° to 75°F.

The tensile properites are reported in Table III. In the table C. C. indicates the specimens were conventionally cast; D. C. indicates the specimens were directionally cast and HT indicates that the specimens were heat treated prior to testing.

TABLE III

Mechanical Properties of Ni-Cr-Be Alloys

Alloy No.	Condition	Test temp., ° F.	Mechanical properties ×1000 p.s.i. Prop. limit	0.2% Y.S.	U.T.S.	Elong., percent	Specific mechanical properties ×1000 in. 0.2% Y.S.	U.T.S.
1	C.C.	Room	55.5	78.2	132.4	8	290	490
			−57.0	−78.6	−132.5		−294	−491
		1,400	76.2	80.6	90.1		299	334
			−91.0	−140.5	−110.5		−387	−409
	D.C.	Room	50	68	118.6	10	252	439
			−52	−72	−121.0		−266	−448
		1,200	56.7	64.8	93.6		240	347
		1,400	53.0	62.0	95.0		230	352
		1,500	48.3	57.2	75.6		212	280
2	D.C.	Room	94.2	113.0	162.8	14.3	418	601
	H.T.		−95.2	−114.0	−164.5		−422	−609
	D.C.	1,400	83.6	92.9	97.6		344	362
	H.T.							
	D.C.	1,600	47.2	48.6	51.8		180	192
3	D.C.	Room	84.0	111.2	151.4	4	412	561
	H.T.							
	D.C.	1,300	87.0	95.0	123.5	6	352	457
	H.T.							
	D.C.	1,400	82.5	92.6	115.0	7	343	426
	H.T.							
	D.C.	1,500	80.5	87.4	104.5	8	323	387
	H.T.							
4	D.C.	Room	103.5	146.0	170.0	4	541	629
	H.T.							
	D.C.	1,400	100.0	111.0	149.0	11	411	551
	H.T.							
	D.C.	1,500	87.0	101.0	117.0	13	322	434
	H.T.							

EXAMPLE I

Tensile Tests

The alloy compositions chosen for testing are given in Table II.

TABLE II

ALLOY COMPOSITION ATOMIC %

Alloy No.	Ni	Cr	Be	Al	Mo	W	C
1	65.0	15.0	20.0				
2	59.5	20.0	16.0	2.0	2.5		
3	59.05	20.0	16.0	2.0	2.5		0.45
4	57.0	19.0	16.0	4.0	2.5	1.5	

Alloys having the composition given in Table II were melted in a refractory crucible, by placing the elemen-

EXAMPLE II

Stress-Rupture Tests

Test specimens of the alloys listed in Table IV were prepared 2¼ inches long with a gage length of three-quarters inch and a diameter of 0.187 to 0.189 inches in accordance with ASTM E–8.

The specimens were then placed in a standard elevated temperature tensile testing machine.

The specimens were stabilized for 15 to 30 minutes at temperature and then the stresses shown in Table IV were applied to the alloys indicated in Table IV at the temperatures indicated in Table IV in an air atmosphere.

The specimens failed after the time indicated in Table IV.

TABLE IV

STRESS RUPTURE PROPERTIES OF Ni-Cr-Be ALLOYS

Alloy No.	Condition	Stress psi	Rupture Time (hr.) 1200°F	1300°F	1400°F	1500°F
1	C. C.	45,000	98.1	20.35	1.45	0.2
	C. C.	35,000	174.4		2.30	0.25
2	D. C. H. T.	45,000			6.70	
	D. C. H. T.	35,000			18.40	3.0
3	D. C. H. T.	45,000		90.3	13.0	0.8
	D. C. H. T.	35,000	-	1280.75	33.95	3.4
4	D. C. H. T.	55,000		1146.9		
	D. C. H. T.	45,000			114.0	
	D. C. H. T.	35,000			563.9	

The data listed in Table IV is shown in a Larsen-Miller plot (described in Metals Handbook, 1961 Ed. pp. 472–473).

What is claimed is:

1. A method of preparing a Ni-Cr-Be type material including the steps of preparing in a non-oxidizing atmosphere a melt consisting essentially of about 54 to about 72.5 atomic percent Ni, about 32.5 to 2.5 atomic percent Cr and about 14.5 to about 25.5 atomic percent Be in amounts that solidification proceeds by the three phase reaction Liquid $\rightleftarrows Ni_{(ss)} + NiBe$, and solidifying the melt obtaining a microstructure comprising a rod-like phase containing Ni(Cr)Be dispersed in a Ni rich matrix.

2. The method of claim **1** including the further step of treating the microstructure to elongate colonies of the rod-like Ni(Cr)Be phase uniaxially.

3. The method of claim **2,** wherein the step of treating the microstructure includes the step of abstracting heat from the melt from one direction obtaining elongation of colonies of the rod-like Ni(Cr)Be phase uniaxially.

4. The method of claim **3,** including the further steps of, prior to the step of abstracting heat from the melt, cooling the melt of Ni-Cr-Be type material and remelting the Ni-Cr-Be type material.

5. The method of claim **1,** including the further step of adding to the melt up to about 5 atomic percent of a metal selected from the group consisting of Al, Ti or mixtures thereof.

6. The method of claim **1,** including a further step of adding to the melt up to about 10 atomic percent of a metal selected from the group consisting of Mo, W, Nb, Zr, B, Va, Ta, Mn, Fe, Co or mixtures thereof.

7. The method of claim **1,** including the further step of adding to the melt up to about 5 atomic percent of a metal selected from the group consisting of Al, Ti or mixures thereof, and adding to the melt up to about 10 atomic percent of a metal selected from the group consisting of Mo, W, Ta, Nb, Va, Zr, B, Mn, Fe, Co or mixtures thereof.

8. The method of claim **5,** including the further steps of heating the Ni-Cr-Be type material containing the additive metal or mixtures of additive metals for a sufficient time to dissolve additive metal or mixtures of additive metals in solid solution, and strengthening the Ni-Cr-Be type material by holding the material below the solution temperature for a sufficient time to effect strengthening.

* * * * *