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3,677,746 HEAT TREATABLE ALLOY Carl H. Lund, Arlington Heights, John Hockin, Palatine, and Michael J. Woulds, Schaumburg, Ill., assignors to Martin Marietta Corporation, New York, N.Y. 5 No Drawing. Continuation-in-part of application Ser. No. 841,602, July 14, 1969. This application Jan. 19, 1970, Ser. No. 4,044 Int. Cl. C22c 19/00

U.S. Cl. 75-171 3 Claims 10

ABSTRACT OF THE DISCLOSURE

An alloy and castings made therefrom containing in 15percent by weight about 0.08% carbon, about 15% chromium, about 18.5% cobalt, about 5.2% molybdenum, about 3.5% titanium, about 4.3% aluminum, about 0.03% boron, up to about 0.3% zirconium, about 0.8% to about 2% hafnium with the balance being essentially 20 nickel.

The present application is a continuation-in-part of application Ser. No. 841,602, filed July 14, 1969 (now 25abandoned).

The present invention is concerned with an alloy and, more particularly, with castings made from said alloy, said castings being particularly adapted for use as blades in gas turbine engines.

30 In U.S. patent application Ser. No. 725,074, filed Apr. 29, 1968, now abandoned it was disclosed that additions of hafnium to high temperature nickel-base alloys suitable for use as castings were effective in several respects to overcome defects and deficiencies therein. The present invention is concerned with overcoming 35 deficiencies and defects in castings of a particular alloy which was initially developed as a heat treatable bar alloy that is an alloy which is designed to be wrought after being initially cast into a billet or other rudimentary form 40 and thereafter heat treated to provide good high temperature characteristics. The nominal composition in percent by weight of this alloy is as follows: **n** ,

Pe	rcent	
Carbon	0.08	4.00
Carbon Chromium	15.0	45
Cobalt	18.5	
Molybdenum	5.2	
Titanium	3.5	
AluminumBoron	4.3	~0
Boron	0.03	90
Nickel Ba	lance	

This particular alloy, identified hereinafter as "Alloy Z," is currently being used as castings for various high temperature uses. When cast Alloy Z is to be used as certain 55 second stage blades in the turbine section of a gas turbine engine, the engine manufacturer requires that specimens machined from blades (m.f.b. specimens) and heat treated by solution treatment at 2125° F. for two hours, furnace cooled at 100° in Fahrenheit units per hour to 1975° F., 60 cooled to room temperature and then held at 1400° F. for 16 hours exhibit a life-to-rupture of at least 23 hours with at least 4% prior creep (elongation at least two hours prior to failure) when tested at 1400° F. under a load of 85 thousands of pounds per square inch (k.s.i.) 65 and a life of at least 23 hours with at least 5.0% prior

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creep when tested at 1600° F. under a load of 48 k.s.i. Normally, there is no problem of qualifying metal using the 1600° F. test. Quite often, however, for no apparent reason, heats of Alloy Z will fail to qualify under the 1400° F. test. There appears to be no noticeable differences in composition or handling between heats of Alloy Z which qualify and those heats which do not. The failure of certain heats of Alloy Z to qualify for use as second stage turbine blades is a particularly irksome phenomenon because the alloy manufacturer heretofore had no means of overcoming the problem. Further, on the theory that non-qualifying heats contained some unknown contaminant, an alloy manufacturer was reluctant to use the metal of such heats in diluted form for fear of spreading the contamination.

It has now been discovered that by inclusion of about 0.8% to about 2% by weight of hafnium in the composition, non-qualifying heats of Alloy Z can be substantially eliminated provided due care, as is customary in the art of high temperature alloy manufacture, be used in the formulating and treating of the alloy.

It is an object of the present invention to provide a new, highly advantageous alloy.

Another object of the present invention is to provide novel castings made from said new alloy.

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

Generally speaking, the present invention contemplates alloys and castings made therefrom having a chemical compsition within the range (in percent by weight) as set forth in Table I:

TABLE I	

	Percent
Carbon	 0.05-0.13
Chromium	 13-17
Cobalt	 14.00-20
Molybdenum	 3.90-6
Titanium	
Aluminum	
Boron	 0.005-0.05
Zirconium	 Up to 0.3
Hafnium	 0.8-2
Nickel, Balance essentially.	

The alloy as set forth in Table I can also contain small amounts of impurities and incidental elements normally associated with the ingredients thereof and such impurities and incidental elements are intended to be included witho in the term "essentially" when such term modifies the phase "balance nickel." The alloy of Table I is made by melting the alloying ingredients including, if desired, graded and selected scrap and revert in a vacuum induction furnace and castings are made therefrom by pouring the molten alloy while under vacuum into suitably shaped precision investment molds. The metal is allowed to freeze in said molds and, when cool, is removed from the molds. After gates, risers and the like are cut from the cast objects, the objects are heat treated by solution treatment at 2100° F. to 2150° F. for about 2 hours, furnace cooled at a rate of about 100° F. per hour to about 1975° F. and then cooled freely to room temperature. Subsequently the objects are reheated to about 1400° F. and held, for example, for 16 hours to effect further precipitation of gamma prime phase in the alloy structure.

The advantages of the present invention are best exemplified by a case history of a particular heat of Alloy Z. This heat had the following composition in percent by weight:

Carbon	0.06	5
Chromium	14.4	
Cobalt	15.0	
Molybdenum	4.29	
Titanium	3.26	
Aluminum	4.50	10
Boron	.018	
Zirconium	<.03	
Copper	<.1	
Iron	0.13	
Manganese	<.1	15
Silicon	<.1	
Sulfur	0.004	
Nickel Ba	lance	
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Repeatedly metal of this heat was cast into turbine blade $_{20}$ clusters, samples were taken and heat treated and subjected to qualification tests at 1400° F. under a load of 85 k.s.i. The results are set forth in Table II:

TABLE II

Cluster	Average life (hours)	Average prior creep (percent)
1	15.7	2.30
2	6.7	1.46
3	15.9	1.92
4	37.6	3.08

The data in Table II shows that this heat of Alloy Z is clearly not acceptable to the gas turbine engine manufacturer. Statistical analysis of the data in Table II shows that if a very large number of m.f.b. samples were made 35 from this heat of Alloy Z, greater than 99.9% of these samples would fail to meet the criterion of 4% prior creep. Furthermore, only about 33% of the samples would be expected to exceed the requirement of at least 23 hours of life-to-rupture. 40

One and one-half percent of hafnium was added to the particular heat of Alloy Z which exhibited the results set forth in Table II. The modified heat had the following composition (in percent by weight):

Carbon	0.06	45
Chromium	14.2	ŦŨ
Cobalt	14.8	
Molybdenum	4.23	
Titanium	3.21	
Aluminum	4.43	50
Boron	.018	00
Zirconium	<.03	
Copper	<.1	
Hafnium	1.45	
Iron	0.13	55
Manganese	<.1	00
Silicon	<.1	
Sulfur	0.004	
Nickel Ba	lance	
TTL		

The modified alloy was poured into a turbine blade cluster 60 identical to the clusters formed with the unmodified alloy. Samples were taken and treated in exactly the same manner as had been done previously. Results of creep tests at 1400° F. and 85 k.s.i. with this cluster are set forth in Table III: 65

TAE	BLE III	
Blade number	Life-to- rupture (hours)	Prior creep (percent)
	53.3 76.0	4.30
	81.0	6.64
	94.4 88.8	8.64 6.35

Statistical analysis of the data in Table III indicates that if a very large number of m.f.b. samples were made from 75 the modified alloy, greater than 95% of such samples would exhibit greater than 4% prior creep and greater than 99% of such samples would exhibit a life-to-rupture in excess of 23 hours. The data in Table III clearly shows that by inclusion of about 1.5% hafnium in the unacceptable heat of Alloy Z, the unacceptable heat was transformed into a heat that is clearly acceptable under the criterion laid down by the gas turbine engine manufacturer.

10 The advantages of the present invention are obtained when the alloys of the invention contain from about 0.8% to 2% or even more of hafnium. The inclusion of hafnium in said alloys is not known to significantly degrade any useful characteristics of Alloy Z and is highly advanta-15 geous in that it eliminates, for all practical purposes, heats of Alloy Z which, for no apparent reason, fail to qualify for cast turbine blade usage. The novel modified Alloy Z of the present invention can be advantageously used in the wrought form as well as in the cast form and is 20 useful in the manufacture of various items subjected in use to stress at high temperature, e.g. gas turbine blades and other items of gas turbine hardware.

When hafnium is included in heats of Alloy Z which are not inherently defective, substantial advantages are 25 also obtained. The data set forth in Table IV are representative of creep rupture data obtained on heat-treated samples machined from blades when tested at 1400° F. under a load of 85,000 p.s.i.

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30		Percent		
	Life (hours)	Prior creep	Elongation	Reduction in area
	58.1	4.93	5.2	11.8
	55.9	4.81	9.4	11.3
35	25.8		4.0	11.2
	50.6		3.6	7.8
	58.0	3.62	3.7	12.7
	29.2		2.8	9.8
	31.2	0.10	2.3	10.8
	40.5	4, 21	6.0	6.6

Similar heat-treated samples of modified Alloy Z containing 1.5% hafnium in place of an equal weight percent of nickel exhibit, under the same test conditions, the creep rupture characteristics as set forth in Table V.

TABLE	v
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45	1	ABLE V				
10				Percent		
	Life (hours)	Prior creep	Elongation	Reduction in area		
50	42.1	8.87 8.90 8.48 9.32 7.58 11.20 7.89 11.30	$10.7 \\ 10.1 \\ 9.6 \\ 10.9 \\ 9.5 \\ 15.3 \\ 10.1 \\ 15.2 \\ 15.2 \\ 15.2 \\ 10.1 \\ 15.2 \\ 10.1 \\ 15.2 \\ 10.1 \\ 15.2 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10.1 \\ 10$	31. 2 31. 9 26. 4 26. 0 20. 8 30. 2 21. 4 22. 2		

In each characteristic measured at 1400° F., modified Alloy Z is superior to unmodified Alloy Z. The life-torupture is longer; the percent prior creep is higher; the percent elongation is higher; and the percent reductionin-area is extraordinarily high. While most of these advantages of modified alloy as opposed to unmodified alloy apparent at 1400° F. appear to vanish at higher and lower temperatures, it has been noted that even at 1600° F. the modified alloy exhibits under creep rupture conditions an enhanced percent reduction-in-area. The data in Table VI is representative of creep rupture data obtained on heat-treated samples machined from blades and tested at 1600° F. under a load of 48,000 p.s.i.

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70			Percent	
		Life (hours)	Elongation	Reduction in area
75	Alloy Z Modified Alloy Z	66. 7 75	10 12	19.5 23.6

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It is believed that a high percent reduction-in-area is advantageous as to resistance to low cycle fatigue since it would appear to permit relatively high localized deformation overall stretching or formation of incipient cracks in a member subjected to low cycle fatiguing conditions.

Part of the improvement of 1600° F. reduction-in-area observed to be obtained in Alloy Z by virture of the inclusion of hafnium therein could be due to a grain nucleation effect. It is possible that, during solidification, hafnium combines with carbon to form ultra-microscopic 10 hafnium carbide aggregates which permeate the solidifying metal. These carbide aggregates could serve to form crystallization sites as do the nucleation catalysts normally employed on investment mold surfaces. The difference between the nucleation actions of the conventionally used 15 catalysts and the carbide aggregates is essentially a matter of location. Conventional catalysts are strictly surface acting whereas the carbide aggregates are distributed throughout the mass of metal. At the lower levels of permissible carbon, for example, 0.05% to 0.09%, the car- 20 bide aggregates are sub-microscopic and the solidified alloy micro-structure appears to be substantially devoid of carbides. This apparent absence of carbides is accompanied by a substantial increase in the grain size of the cast alloy. Chemical analysis, of course, as well as the 25 level of mechanical characteristics demonstrates that, even though it cannot be seen as carbides, carbon is certainly present in the alloys of the invention and serves its ordinary functions therein.

While the present invention has been described in conjunction with advantageous embodiments, those skilled in the art will recognize that modifications and variations may be resorted to without departing from the spirit and

scope of the invention. Such modifications and variations are considered to be within the purview and scope of the invention.

What is claimed is:

1. A novel heat treatable alloy consisting in percent by weight essentially of about 0.05% to about 0.13% carbon, about 13% to about 17% chromium, about 14% to about 20% cobalt, about 3.9% to about 6% molybdenum, about 3% to about 4% titanium, about 3.5% to about 5.0% aluminum, about 0.005% to about 0.05% boron, up to about 0.3% zirconium, about 0.8% to about 2% hafnium with the balance being essentially nickel.

2. A casting of the alloy of claim 1 having been heat treated for about 2 hours at 2100° F, to 2150° F, then furnace cooled at about 100° F. per hour to about 1975° F., then cooled to room temperature and subsequently subjected to a precipitation treatment at about 1400° F.

3. An alloy as in claim 1 consisting of about 0.08% carbon, about 15% chromium, about 18.5% cobalt, about 5.2% molybdenum, about 3.5% titanium, about 4.3% aluminum, about 0.03% boron, up to about 0.3% zirconium, about 0.8% to about 2% hafnium, with the balance being essentially nickel.

References Cited

UNITED STATES PATENTS

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RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

148-32.5, 162

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,677,746

Dated July 18, 1972

Inventor(s) Carl H. Lund, et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 51 - "phase" should be --phrase --.

Column 4, line 14 - "characteristics" should be --characteristic --.

Column 4, Table VI - column marked "Reduction in area" should be --Reduction-in-Area --.

Column 5, line 4 - before "overall" the word -- without -- was omitted.

Signed and sealed this 26th day of December 1972.

(SEAL) Attest:

EDWARD M.FLETCHER, JR. Attesting Officer

ROBERT GOTTSCHALK Commissioner of Patents

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