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COBALT-BASE ALLOY

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This invention relates to a cobalt-base alloy for high temperature service and, more particularly, to a cobalt-base alloy suitable for high temperature service in either cast or wrought form.

Research directed to increasing the power and efficiency of jet propulsion and gas turbine engines has provided designs for engines that will operate at higher temperatures than currently known metals and alloys can withstand. Metals and alloys capable of withstanding these high temperature stresses are avidly sought therefore. Of especial interest are alloys having high creep resistance strength which are thereby suitable for extended service. Furthermore, alloys are sought which, in addition to possessing outstanding high temperature strength, must also be capable of being fabricated into useful parts by known methods.

In some cases the alloys may be employed in the form of castings, while for other operations these alloys must be capable of being hot-worked into sheet and strip, or subjected to cold-working or machining. Furthermore, materials fabricated from these alloys must have good oxidation, impact and thermal shock resistance.

While several alloys have been proposed for high temperature service under the conditions set forth above, none have possessed the required combination of high strength, high heat resistance and high workability.

The primary object of this invention, therefore, is to provide an alloy which has higher tensile, stress-rupture, and creep-rupture strength than alloys heretofore known, as well as increased ductility and impact resistance, to enable its use in a wide variety of applications at temperatures higher than the limiting temperatures of currently known alloys of this type and up to a temperature of about 1800° F.

Another object of this invention is to provide an alloy with high oxidation resistance and fatigue strength at elevated temperatures.

A further object of the invention is to provide an alloy suitable for use at elevated temperatures which may be fabricated by casting or forging, and which can be cold-worked to increase its hardness.

Other aims and advantages of the invention will be apparent from the following description and appended claims.

In accordance with the present invention, a cobalt-base alloy is provided having compositions defined by the ranges given in Table A.

TABLE A

Constituents:	Percentage by weight
Chromium	15 to 25.
Tungsten	10 to 15.
Molybdenum	Up to 5.
Iron	Up to 3.
Carbon	Up to 0.70.
Cobalt	At least 55.
Nickel	Up to 10.
Boron	Up to 0.20.
Nitrogen	Up to 0.06.

To this composition should be added at least one modifying element selected from the group consisting of titanium, magnesium and zirconium such that the minimum amount of said modifying elements present is defined by the following equation:

(1) $Ti+50\times Mg+Zr=0.05$

percent by weight of the alloy wherein Ti equals the percent by weight titanium, Mg equals the percent by weight magnesium, Zr equals the percent by weight zirconium, the maximum allowable amount of said titanium present being 2 percent by weight, the maximum allowable amount of said magnesium present being 0.50 percent by weight, and the maximum allowable amount of said zirconium present being 1 percent by weight.

According to Equation 1 if titanium is the only modifying metal selected, there must be a minimum of 0.05 percent titanium present. Or if magnesium is the only modifying metal selected, there must a minimum of 0.001 percent magnesium. Similarly there must a minimum amount of 0.05 percent zirconium present, if that metal is the only one selected. Of course more than one modifying metal may be selected and used in the alloy provided there is a minimum amount of said modifying metals present as defined by Equation 1 and up to the maximum amounts of each modifying metal listed above.

Silicon and manganese may be present in amounts up to 2 percent by weight of each.

A preferred composition is defined by the ranges listed in Table B.

Table B

Constituents:	Percentage by weight
Chromium	19 to 21.
Tungsten	11.5 to 13.5.
Molybdenum	3 maximum.
Iron	1 maximum.
Carbon	0.43 to 0.53.
Cobalt	Balance.
Nickel	1 maximum.
Boron	0.03 to 0.07.
Nitrogen	0.04 maximum.

To this composition there should be added at least one modifying metal selected from the group consisting of titanium, magnesium and zirconium such that the minimum amount of said modifying metals present is defined by the following equation:

(2) $Ti+100\times Mg+Zr=0.10$

percent by weight of the alloy wherein Ti equals the percent by weight of titanium, Mg equals the percent by weight of magnesium, Zr equals the percent by weight of zirconium, the maximum allowable amount of said titanium present being 1 percent by weight, the maximum allowable amount of said magnesium present being 0.50 percent by weight, and the maximum allowable amount of said zirconium present being 1 percent by weight. According to Equation 2 the minimum amounts of titanium, magnesium and zirconium present in the preferred form of the alloy when only one of these modifying metals is selected is as follows: 0.10 percent titanium or 0.001 percent magnesium or 0.10 percent zirconium. When more than one of these metals is used, there should be enough of those selected to represent at least the minimum defined by Equation 2. The maximum of each metal to be used in any case is also listed above.

Silicon and manganese may be present in amounts up to 1 percent by weight of each.

By maintaining the composition within the specified critical limits, alloys are produced which exhibit the superior strength, creep-resistance and workability described herein.

Chromium and tungsten both improve the high temperature strength of the alloy, and give the alloy increased ability to resist deformation while under severe loading. Tungsten may be complemented by molybdenum in amounts up to 5 percent by weight molybdenum. The addition of molybdenum will increase high temperature tensile and stress-rupture strength at the expense of a loss of room temperature ductility. Therefore, the molybdenum content is limited in the preferred embodiment to 3 percent.

While the presence of nickel increases toughness at lower temperatures it causes a reduction in high temperature strength. Therefore the nickel content should be adjusted to achieve specific desired results. For high temperature service the nickel content should not be greater than one percent.

Carbon and boron are necessary additions for ductility and strength in products composed of this alloy. Although the addition of boron greatly increases the strength of this alloy, boron is detrimental to oxidation resistance, and therefore the desired level of boron content is dependent upon the anticipated service temperature of the alloy. However, while higher carbon contents are suitable for casting operations, when the alloy is to be rolled both the carbon and boron contents should be lowered.

The high temperature strength of the cobalt matrix is further increased by the existence of a precipitated phase, composed of carbides of the $Cr_{23}C_6$ type. Of especial importance are the rates of diffusion of chromium and carbon in the cobalt-rich matrix. If these elements are able to diffuse rapidly through the matrix, the carbides are readily formed and grow rapidly yielding a hardening through precipitation. However, beyond a limiting size and concentration, these carbides are no longer useful in increasing the strength of the alloy. Therefore by limiting the diffusion of carbon and chromium, the rate of growth of these carbides is diminished and their size kept within limits with the desired result that the alloy achieves maximum strength from this precipitated phase. Tungsten, chromium, and the nickel are effective in controlling the diffusion of carbon and the formation of carbides.

Furthermore in ordinary chromium-cobalt alloys, a condition occurs wherein alternate layers of the $Cr_{23}C_6$ type carbides and the cobalt-rich matrix form. Since the presence of this lamellar constituent lowers the fatigue resistance of the alloy, efforts were made to prevent its occurrence. This lamellar constituent is formed during cooling from the molten state and is not easily altered or removed by heat-treatment. In the alloy of this invention, however, the lamellar constituent is suppressed by the interactive effects of chromium, carbon, nitrogen, and titanium, magnesium or zirconium, singly or in combination. The fatigue resistance of products composed of the alloy is thus raised, especially at elevated temperatures. The elimination of this lamellar constituent and the control of the rate of diffusion of the carbides are the basis for the chosen composition of the alloy and the ranges given in the preceding paragraphs.

Manganese and silicon may be present in amounts up to 2 percent by weight of each. These elements are found as impurities in the constituents of the alloy and are useful as deoxidizers. However for a preferred composition of the alloy their presence should be limited to one percent maximum amounts of each.

Iron may be present in amounts up to 3 percent; but since iron does not contribute to high temperature strength, it should be limited to amounts not exceeding one percent in the preferred alloy composition.

The amount of nitrogen in the alloy is of critical importance. Heretofore it was thought that nitrogen was essential in alloys of this type, but it has been found to have a deleterious effect on these cobalt-base alloys. Table C clearly indicates the effect of varying nitrogen contents on a cobalt-base alloy having the following nominal composition: 20% chromium, 12.5% tungsten, 0.45% carbon, 0.05% boron, 0.10% titanium and the balance cobalt.

TABLE C

Stress-rupture data at 1700° F. and 20,000 p.s.i.

Nitrogen content, percent by weight	Life, Hours	Elongation, Percent
0.03	94.7	16
0.06	30.5	13
0.07	21.7	14
0.08	22.0	5
0.09	18.4	17

Therefore the nitrogen content should be kept below 0.06 percent by weight, and preferably below 0.04 percent for maximum strength in the alloy.

On the other hand, the presence of titanium, magnesium, and zirconium, alone or in combination, increases the stress-rupture life of the alloy at elevated temperatures. Furthermore, the addition of these metals also increases ductility. The beneficial effects of titanium, magnesium and zirconium additions are shown in Tables D, E and F. These tests were performed on cast specimens having the following composition by weight: 20 percent chromium, 12.5 percent tungsten, 0.48 percent carbon, 0.05 percent boron, 0.03 percent nitrogen, and the balance substantially all cobalt with varying additions of titanium and magnesium.

In Table D, the samples from the *"a"* subgroups represent three original heats of the alloy. The subgroups designated *"b"* and *"c"* demonstrate the effects of additions of magnesium, and magnesium and titanium, respectively, to the original heat.

Since the titanium and magnesium additions were partially vaporized out of the melt, the analysis of the titanium and magnesium contents of the cast products is also given.

The increase in stress-rupture life as a result of the additions is definite in each case. In each case the amount of magnesium in the cast material was below the level of exact quantitative determination, but it was ascertained spectrographically that the metal was present in amounts equal to about 0.001 percent by weight. The small amounts of magnesium remaining in the alloy prove to be effective, however. The presence of titanium nitrides has been noted in the structures of materials to which titanium has been added, indicating removal of nitrogen from the matrix.

TABLE D

Effect of titanium and magnesium additions on stress-rupture life at 1700° F. and 20,000 p.s.i.

No.	Addition to the molten alloy, percent by weight	Analysis of titanium and magnesium content of cast alloy, percent by weight	Life, Hours	Elongation, percent
1a	None		9.8	5
1b	0.10 Magnesium	trace of magnesium	42.1	38
1c	0.10 Magnesium+0.10 Titanium.	trace of magnesium, 0.06 titanium.	65.5	18
2a	None		23.2	3
2b	0.10 Magnesium	trace of magnesium	81.9	26
2c	0.10 Magnesium+0.25 Titanium.	trace of magnesium, 0.15 titanium.	155.9	33
3a	None		16.2	21
3b	0.10 Magnesium	trace of magnesium	51.3	25
3c	0.10 Magnesium+1.0 titanium.	trace of magnesium, 0.73 titanium.	136.6	15

Table E demonstrates the effects of additions of titanium to the alloy. The results of tests conducted on specimens containing varying amounts of titanium all indicate an increase in stress-rupture life with additions of titanium.

Table F shows the effects of additions of titanium and zirconium to the alloy. Again there is a marked increase in stress-rupture life accompanying the addition of these elements.

TABLE E

Effect of titanium additions on stress-rupture life at 1700° F. and 21,000 p.s.i.

Titanium addition, Percent by weight	Life, Hours	Elongation, Percent
None	[1] 10	
0.15	33.1	16
1.0	95.7	24
1.5	78.5	16

[1] An extrapolated value.

TABLE F

Effect of titanium and zirconium additions on stress-rupture life at 1700° F. and 22,000 p.s.i.

No.	Titanium, Percent by weight		Zirconium, Percent by weight		Life, Hours	Elongation, Percent
	Addition	Analysis [1]	Addition	Analysis [1]		
5a	none		none		[2] 5	
5b	2.5	1.45	none		19.5	45
5c	2.0	1.87	none		64.1	35
5d	none		0.50	0.07	11.1	31
5e	1.0	0.77	0.50	0.23	86.1	16

[1] Since the titanium and zirconium additions were partially vaporized out of the melt, the analysis of the titanium and zirconium content of the cast alloy is also given.
[2] An extrapolated value.

From the results of Tables D, E and F, the beneficial effects of additions of titanium, magnesium, and zirconium, either alone or in combination, are evident. Stress-rupture life and ductility at elevated temperatures show marked increases as a result of these additions. It is to be noted that titanium, magnesium and zirconium may be replaced by other elements of similar chemical characteristics, such as calcium, barium or vanadium. Magnesium may be replaced in equally effective amounts by calcium or barium; titanium and zirconium may be replaced by an equally effective amount of vanadium.

The alloy may be melted by standard furnacing procedures, such as by induction heating, but the melting should be conducted in the protective atmosphere of an inert gas, such as argon. This shielding of the molten metal by an inert gas will prevent contamination by the nitrogen in the air. The alloy may be used in the as-cast condition. A heat treatment is beneficial in enhancing the properties of the alloy, but it is not required.

Table G shows the short time tensile properties of this alloy in the as-cast condition.

TABLE G

Tensile test data for cast material

Temperature, ° F.	Ultimate Strength, p.s.i.	Yield Strength, p.s.i.	Elongation, Percent
Room	108,500	78,700	7
1,200	84,500	53,700	15

This alloy may also be fabricated by hot or cold working into useful parts. Alloys may be produced that can be mechanically fabricated by known methods to produce such items as wire, strip, rod, plate, bar, sheet, tubings, forgings, and extruded shapes. The preparation of ingots for use in these forging operations should preferably include melting under vacuum conditions to remove dissolved gases.

These products all have excellent mechanical properties at elevated temperatures. The alloy may also be rolled into sheets.

Alloys having especially significant mechanical properties in the wrought form may be prepared without the addition of the modifying metals titanium, magnesium or zirconium. These alloys are disclosed and claimed

in my copending application entitled Cobalt-Base Alloys, Serial No. 778,053, filed concurrently herewith, wherein compositions are defined containing from 19 to 22 percent by weight chromium, from 11.5 to 13.5 percent by weight tungsten, carbon below about 0.25 percent by weight, and boron below about 0.15 percent by weight, and the balance substantially all cobalt and incidental impurities. These alloys possess higher mechanical properties in the wrought form than heretofore known alloys.

Table H gives typical stress-rupture data for sheet products having the following composition by weight: 20 percent chromium, 12.35 percent tungsten, 0.16 percent carbon, 0.005 percent boron, 0.48 percent silicon, 0.72 percent manganese, and the balance substantially all cobalt.

TABLE H

Stress-rupture data for 0.040 inch thick sheet

Temperature, ° F.	Stress, p.s.i.	Life, Hours	Elongation, Percent
1,500	30,000	59.6	43
1,600	24,000	47.3	73
1,700	15,000	93.8	77
1,800	10,000	49.3	38

In the wrought form, the alloy has sufficient ductility to undergo cold-working to increase hardness. Table J shows the results of cold-working on sheet products.

TABLE J

Condition:	Hardness, Rockwell C test
As rolled	31
Cold-reduced 20 percent	49
Cold-reduced 25 percent	51

In addition the cold-worked alloy may be further hardened by heat treatment. Heat treatments at temperatures up to about 1200° F. will cause an increase in hardness without subjecting the alloy to temperatures so high as to cause distortion in the finished parts.

What is claimed is:

1. A cobalt-base alloy characterized by improved stress-rupture strength at temperatures of about 1700° F., said alloy consisting essentially of between 15 and 25 percent by weight chromium, between 10 and 15 percent by weight tungsten, up to 5 percent by weight molybdenum, up to 3 percent by weight iron, up to about 1 percent by weight nickel, up to 0.70 percent by weight carbon, up to 0.20 percent by weight boron, up to 0.04 percent by weight nitrogen, manganese and silicon in amounts up to 2 percent by weight of each, at least one modifying the metal selected from the group consisting of titanium, magnesium and zirconium, the minimum amount of modifying metal being defined by the following equation

$$Ti+50\times Mg+Zr=0.05 \text{ percent by weight of the alloy}$$

wherein Ti equals the percent by weight titanium, Mg equals the percent by weight magnesium, Zr equals the percent by weight zirconium, the maximum allowable amount of said titanium being 2 percent by weight, the maximum allowable amount of said magnesium being 0.50 percent by weight, the maximum allowable amount of said zirconium being 1 percent by weight, and the balance cobalt and incidental impurities, the minimum amount of cobalt being 55 percent by weight.

2. A cobalt-base alloy characterized by improved stress-rupture strength at temperatures of about 1700° F., said alloy consisting essentially of between 19 and 21 percent by weight chromium, between 11.5 and 13.5 percent by weight tungsten, up to 3 percent by weight molybdenum, up to 1 percent by weight iron, up to 1 percent by weight nickel, between 0.43 and 0.53 percent by weight carbon, between 0.03 and 0.07 by weight boron, up to 0.04 percent by weight nitrogen, manganese and silicon in amounts up to 1 percent by weight of each, at least one

modifying metal selected from the group consisting of titanium, magnesium and zirconium, the minimum amount of said modifying metal being defined by the following equation

$$Ti+100\times Mg+Zr=0.10 \text{ percent by weight of the alloy}$$

wherein Ti equals the percent by weight of titanium, Mg equals the percent by weight of magnesium, Zr equals the percent by weight of zirconium, the maximum allowable amount of said titanium being 1 percent by weight, the maximum allowable amount of said magnesium being 0.50 percent by weight, the maximum allowable amount of said zirconium being 1 percent by weight, and the balance cobalt and incidental impurities.

3. A cobalt-base alloy characterized by improved stress-rupture strength at temperatures of about 1700° F., said alloy consisting essentially of between 19 and 21 percent by weight chromium, between 11.5 and 13.5 percent by weight tungsten, less than 1 percent by weight iron, up to 1 percent by weight nickel, between 0.43 and 0.53 percent by weight carbon, between 0.03 and 0.07 percent by weight boron, up to 0.04 percent by weight nitrogen, between about 0.10 and 1 percent by weight titanium, between 0.001 and 0.50 percent by weight magnesium, up to 1 percent by weight zirconium, and the balance cobalt and incident impurities.

4. A cobalt-base alloy characterized by improved stress-rupture strength at temperatures of about 1700° F., said alloy consisting essentially of about 20 percent by weight chromium, about 12.5 percent by weight tungsten, about 0.48 percent by weight carbon, about 0.05 percent by weight boron, about 0.03 percent by weight nitrogen, about 0.15 percent by weight titanium, between 0.001 and 0.10 percent by weight magnesium, and the balance cobalt and incidental impurities.

5. A cobalt-base alloy characterized by improved stress-rupture strength at temperatures of about 1700° F., said alloy consisting essentially of about 20 percent by weight chromium, about 12.5 percent by weight tungsten, about 0.48 percent by weight carbon, about 0.05 percent by weight boron, about 0.03 percent by weight nitrogen, about 1 percent by weight titanium, and the balance cobalt and incidental impurities.

6. A cobalt-base alloy characterized by improved stress-rupture strength at temperatures of about 1700° F., said alloy consisting essentially of about 20 percent by weight chromium, about 12.5 percent by weight tungsten, about 0.48 percent by weight carbon, about 0.05 percent by weight boron, about 0.03 percent by weight nitrogen, about 0.77 percent by weight titanium, about 0.23 percent by weight zirconium, and the balance cobalt and incidental impurities.

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