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REPLY TO
ATTN OF: GP

October 15, 1970

TO: USI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General
Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned
U.S. Patents in STAR

In accordance with the procedures contained in the Code GP to Code USI memorandum on this subject, dated June 8, 1970, the attached NASA-owned U.S. patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No.	:	<u>3,276,865</u>
Corporate Source	:	<u>Lewis Research Center</u>
Supplementary Corporate Source	:	<u></u>
NASA Patent Case No.:	:	<u>XLE-02991</u>



Gayle Parker

Enclosure:
Copy of Patent

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3,276,865

HIGH TEMPERATURE COBALT-BASE ALLOY

John C. Freche, Fairview Park, Richard L. Ashbrook, Cleveland, and Gary D. Sandrock, Fairview Park, Ohio, assigns to the United States of America as represented by the Administrator of the National Aeronautics and Space Administration

No Drawing. Filed June 15, 1964, Ser. No. 375,401

4 Claims. (Cl. 75-170)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to an improved cobalt-base alloy having high strength at elevated temperatures up to 2200° F. The invention is further concerned with a cobalt-base alloy that is resistant both to corrosion by liquid metals and to sublimation in a vacuum environment.

Various components of turbo-electric space power systems, especially the ducting for the liquid metal heat transfer media, present difficult material problems because they are subjected to the dual environment of liquid metals on one surface and a high vacuum on the other. Also, materials for these components must be workable and weldable to permit forming into sheet or tubing for ducting applications. Commercially available materials considered for such applications are certain stainless steels as well as wrought nickel- and cobalt-base alloys. Refractory metal alloys of columbium have been considered for temperatures of 2000° F. and above.

Turbine engine parts and other engineering structures which operate in air at high temperatures must have adequate oxidation resistance or be capable of operating satisfactorily with protective coatings. Both cobalt- and nickel-base alloys have been proposed for such structures.

Each of the classes of commercially available material considered for turbo-electric space power systems has certain limitations. For example, stainless steels are restricted to applications where the temperature does not exceed approximately 1400° F. if long life in the neighborhood of 10,000 hours is to be obtained, even at the relatively low stress levels, such as 5,000 p.s.i., which are likely to be encountered in ducting applications. Wrought commercial cobalt- and nickel-base alloys are limited to applications where the temperatures do not exceed approximately 1600° and 1700° F., respectively, at similar stress levels.

The vapor pressures of various metals differ, and this imposes another limitation on the use of certain commercially available materials. As a result of these differences in vapor pressures some metals tend to evaporate more than others in a high vacuum. Chromium and aluminum are particularly susceptible to evaporation losses. Virtually all stainless steels as well as cobalt- and nickel-base alloys contain appreciable quantities of chromium, and most nickel-base superalloys contain aluminum, as well. Therefore, evaporation of chromium and aluminum may occur during long time exposure of these alloys to a high vacuum environment, and the structural integrity of these alloys may be affected. The manner in which the alloying element is tied up in the

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metal matrix can greatly affect this process. It would be expected that a reduction in the percent of high vapor pressure alloying elements in the alloys used would lessen this problem.

From a corrosion resistance standpoint, cobalt resists corrosion by mercury more than nickel but less than iron. It appears that cobalt is at least equivalent to nickel in corrosion resistance in alkali metals up to the limit of its useful temperature range. Certain stainless steels, although acceptable up to 1600° F. in contact with the alkali metals, show a low compatibility with mercury if they have a high nickel and/or a high chromium content. Nickel-base alloys are not compatible with mercury, but may be used with the alkali metals up to approximately 1700° F. Refractory columbium alloys, although having excellent elevated temperature strength characteristics and corrosion resistance to both mercury and the alkali metals, are very subject to oxidation. This makes pilot or ground tests of prototype units using this material extremely difficult and expensive.

It is, therefore, an object of the present invention to provide an improved cobalt-base alloy having high strength at temperatures up to 2200° F.

Another object of the invention is to provide an improved cobalt-base alloy which is resistant both to corrosion by liquid metals and to sublimation in a vacuum environment.

A further object of the invention is to provide an improved cobalt-base alloy which is workable and weldable to permit forming into sheet or tubing for ducting applications.

These and other advantages of the invention will be apparent from the specification which follows.

The present invention is embodied in alloys having the following composition range wherein the percentages are by weight:

Cobalt	-----	From about 36% to about 89.4%.
Tungsten	-----	From about 10% to about 45%.
Titanium	-----	From about .5% to about 2%.
Carbon	-----	From about .1% to about 1%.
Zirconium	-----	From about 0% to about 3%.
Chromium	-----	From about 0% to about 10%.
Rhenium	-----	From about 0% to about 3%.

The above alloy composition represents an improvement over the alloy disclosed in copending United States patent application Serial No. 355,126, filed March 26, 1964. The present alloys include chromium and rhenium in addition to the alloying constituents disclosed in the copending application.

Chromium is included because it is one of the most effective elements for strengthening the binary alloy Co-25W. The presence of chromium in relatively small amounts in alloys is not as detrimental, insofar as evaporation loss is concerned, as the relatively large amounts in the range of 20% to 25% present in conventional cobalt-base alloys. If present in small quantities, the concentration of chromium at the surface is less, as would be any concentration gradient that occurred in service, and consequently the driving force for diffusion of chromium to the surface would be less. A preferred alloy having

chromium added to the alloy disclosed in the copending application has the following composition:

Cobalt	Percent	
Tungsten	About 69.6	5
Titanium	About 25	
Zirconium	About 1	
Chromium	About 3	
Carbon	About 4	

A comparison of as-cast stress-rupture properties of the present alloy with those of a preferred alloy disclosed in the copending application is shown in Table I wherein the samples are uncoated and nominal compositions are listed.

TABLE I

Alloy	Stress, p.s.i.	Temp., ° F.	Average Rupture Life in Air, hrs.
Co-25W-1Ti-1Zr-0.4C	15,000	1,850	92
Co-25W-1Ti-1Zr-3Cr-0.4C	15,000	1,850	131

Rhenium is added to the above alloy because it is a potential solid-solution strengthener and stable carbide former. The evaporative loss rate of rhenium is extremely low, and another preferred alloy having rhenium added to the above preferred alloy has the following nominal composition:

Cobalt	Percent	
Tungsten	About 67.6	
Titanium	About 25	
Zirconium	About 1	
Chromium	About 3	
Rhenium	About 2	
Carbon	About 4	

Uncoated samples having one of the preferred nominal compositions, Co-25W-1Ti-1Zr-3Cr-2Re-0.4C, were stress-rupture tested in air at various conditions. The resulting data are summarized in Table II below. The 15,000 p.s.i., 1850° F. data are directly comparable to the data of Table I and show further improvement in stress rupture life over the alloys listed therein. Also shown are data for several of the strongest known commercially available cobalt-base alloys.

TABLE II

Alloy	Stress, p.s.i.	Temp., ° F.	Average Rupture Life in Air, hrs.
3Cr-2Re	20,000	1,850	29
3Cr-2Re	15,000	1,850	185
3Cr-2Re	10,000	1,850	1,007
3Cr-2Re	20,000	2,000	1
3Cr-2Re	15,000	2,000	9
3Cr-2Re	10,000	2,000	81
3Cr-2Re	10,000	2,100	9
3Cr-2Re	7,500	2,100	24
3Cr-2Re	5,000	2,100	80
3Cr-2Re	5,000	2,200	23
3Cr-2Re	2,500	2,200	58
SM-302	10,000	2,000	9
SM-322	15,000	2,000	2

The short-time high temperature strength of the aforementioned preferred alloys is shown in Table III wherein ultimate tensile strengths of both preferred alloys as-cast and in sheet form are given for various temperatures. The ultimate tensile strength of a preferred alloy of the copending application at room temperature is presented for comparison purposes.

TABLE III

Alloy	Temp., ° F.	Average Ultimate Tensile Strength, p.s.i.
Co-25W-1Ti-1Zr-0.4C (As Cast)	Room	98,580
Co-25W-1Ti-1Zr-3Cr-0.4C (As Cast)	Room	96,425
Co-25W-1Ti-1Zr-3Cr-0.4C (As Cast)	1,645	63,000
Co-25W-1Ti-1Zr-3Cr-0.4C (As Cast)	1,800	37,400
Co-25W-1Ti-1Zr-3Cr-0.4C (As Cast)	2,000	24,000
Co-25W-1Ti-1Zr-3Cr-0.4C (As Cast)	2,045	21,800
Co-25W-1Ti-1Zr-3Cr-0.4C (As Cast)	2,100	20,800
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (As Cast)	Room	98,050
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (As Cast)	1,600	73,500
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (As Cast)	1,645	57,600
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (As Cast)	1,800	35,700
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (As Cast)	2,000	25,300
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (As Cast)	2,045	24,100
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (As Cast)	2,100	19,650

SHEET ALLOYS

20 Co-25W-1Ti-1Zr-0.4C (As rolled)	Room	179,330
Co-25W-1Ti-1Zr-3Cr-0.4C (As rolled)	Room	221,330
Co-25W-1Ti-1Zr-3Cr-0.4C (Annealed)	Room	173,750
Co-25W-1Ti-1Zr-3Cr-0.4C (Annealed)	1,600	71,150
Co-25W-1Ti-1Zr-3Cr-0.4C (Annealed)	1,800	37,100
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (As rolled)	Room	211,150
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (Annealed)	Room	181,750
25 Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (Annealed)	1,600	77,650
Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (Annealed)	1,800	37,200

The cobalt-base alloys of the present invention can be prepared either by vacuum induction melting or by induction melting under an inert gas blanket. In inert gas melting the bottom of a cold zirconia crucible is covered with a small quantity of electrolytic cobalt. Carbon in the form of lamp black compacts is placed in the crucible and covered with briquetted titanium, and the whole is covered with electrolytic cobalt nearly filling the crucible. A cylindrical shield is placed around the top of the crucible, and a flow of argon is directed at the top of the charge.

Once the charge begins to settle, the remaining cobalt is added. When this portion of the charge is completely melted, tungsten is added in the form of short length rods. The melt is then superheated to 3050° F. and held for three minutes to insure dissolving of the tungsten. The melt is then allowed to cool to 2900° F. and poured. During pouring the inert gas coverage is removed. Melts are poured into investment molds heated to 1600° F. and permitted to cool to room temperature naturally without speeding up the process artificially.

Alloys of this series have also been prepared by the more complex technique of vacuum melting in order that the effectiveness as alloying constituents of such elements as titanium and zirconium should not be reduced by their reaction with atmospheric gases. This melting technique can result in further improvement in the properties. Improved cleanliness of the resulting vacuum melt can also result in better strength as well as improved ductility. Thus, by introducing a higher degree of complexity in the casting process, improved alloys can be obtained. Examples of rupture data from vacuum melts for two alloys are shown in Table IV.

TABLE IV

Alloy	Stress, p.s.i.	Temp., ° F.	Rupture Life in Air, hrs.
Co-25W-1Ti-5Zr-6C	15,000	1,850	115
Co-25W-1Ti-5Zr-7.75Cr-6C	15,000	1,850	100

The alloys of this invention derive their high elevated temperature strength from several mechanisms which can include solid solution strengthening of the cobalt matrix by tungsten, chromium and rhenium, by the precipitation of the intermetallic WCo₃ phase and by the formation of various carbides of Ti, Zr, Cr, W and Re.

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In an alternate embodiment of the invention this alloy series can readily be produced in either a cast or wrought form. These alloys have excellent characteristics for investment casting; yet, chill cast slabs can be hot rolled without prior working to thin strip with almost no edge cracking. Thin sheet sections of these alloys are readily weldable using electron beam welding procedures, an important requirement for ducting components.

What is claimed is:

1. A cobalt-base alloy capable of high load carrying capacity at elevated temperatures consisting essentially of from 39% to 89.4% cobalt, from 10% to 45% tungsten, from 0.5% to 2% titanium, from 0.1% to 1% carbon, from 0% to 3% zirconium, and from 0% to 10% chromium.

2. The cobalt-base alloy of claim 1 additionally containing up to 3% rhenium, the cobalt content of said alloy being adjusted to accommodate the addition.

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3. A cobalt-base alloy capable of high load carrying capacity at elevated temperatures consisting essentially of 69.6% cobalt, 25% tungsten, 1% titanium, 1% zirconium, 3% chromium, and .4% carbon.

4. A cobalt-base alloy capable of high load carrying capacity at elevated temperatures consisting essentially of 67.6% cobalt, 25% tungsten, 1% titanium, 1% zirconium, 3% chromium, 2% rhenium, and 0.4% carbon.

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