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SULFIDATION RESISTANT COBALT-BASE ALLOY

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ABSTRACT OF THE DISCLOSURE

A sulfidation resistant cobalt-base alloy comprises a major amount of cobalt, between about 5 and about 30% chromium between about 0.05% and about 3.0% by weight of a metal selected from the group consisting of scandium, lanthanum and lanthanide series metal, between about 1.0% and about 6.0% by weight aluminum and preferably also containing tungsten and/or molybdenum, columbium and/or tantalum and carbon.

BACKGROUND OF THE INVENTION

There has been a search for some time for metal alloy compositions which are resistant to the high-temperature corrosive combustion products of gas turbines. Such deterioration referred to hereinafter as sulfidation takes place particularly in the heated sections of gas turbines which are exposed to gaseous combustion products of sulfur containing fuels such as fuel oils, diesel fuel, aviation gasoline and the like. The metallic parts on which deterioration by sulfidation is greatest consists of machined parts, such as gas turbine wheels and/or blades, and nozzle vanes, which are directly exposed at high-temperatures to the sulfur containing gaseous combustion products. Sulfidation corrodes these parts especially after long exposures to the combustion gases at high temperatures thereby not only weakening the metallic structures but literally decomposing substantial portions. Such corrosion not only results in continued deterioration of the turbine engine efficiency, but in time may result in actual failure of the engine to produce sufficient thrust to be useful. This problem is especially serious under desert or salt water atmosphere conditions where the presence of alkali or alkaline-earth metal salts such as sodium chloride, even in concentrations as low as 0.1 part per million, are found to catalyze the sulfidation reaction.

Although certain nickel-base alloys have been known to provide good oxidation resistance under high-temperature conditions, known cobalt-base alloys are rather poor by comparison. Addition of aluminum to a chromium containing cobalt-base alloy has been found to improve oxidation resistance. However, such compositions still do not possess satisfactory sulfidation resistance at high temperatures. On the other hand, while the presence of a small amount of scandium, lanthanum or other lanthanide series metals yields somewhat improved oxidation and sulfidation resistance to the cobalt-base alloys, the improvement is far from the extent desired for corrosive resistant metals to be used in turbine engines. In some cases, the sulfidation resistance provided by the presence of these metals in the absence of aluminum is practically negligible.

The present invention relates to the discovery that scandium, lanthanum and other metals of the lanthanide series metals (commonly referred to as rare earth metals) in combination with chromium and aluminum yield extremely sulfidation and oxidation resistant cobalt-base alloys. This fact is further surprising since nickel-base alloys, which have nominally the same composition as the sulfidation resistant cobalt-base alloys of the invention, with the replacement of cobalt with nickel, possess sulfidation resistance which is sometimes worse than a nickel-base alloy which contains no scandium or lanthanide series metal.

DESCRIPTION OF THE INVENTION

The superior sulfidation resistant alloys of the invention are cobalt-base alloys containing a small amount of scandium, lanthanum or lanthanide series metal, chromium and aluminum and preferably other additional metals which enhance the strength properties of the alloy. By the term "cobalt-base alloy" as used herein and understood in the art, is meant a metallic composition wherein the major metal present is cobalt and preferably wherein cobalt is present in a major amount. More specifically, it has found, according to the invention, that cobalt-base alloys containing from about 0.05 to about 3.0% by weight scandium, lanthanum or lanthanide series metal, at least about 5.0% chromium and from about 1.0 to 6.0% by weight aluminum possess outstanding sulfidation as well as oxidation resistance.

The metal used in small quantities as a synergistic sulfidation inhibitor with chromium and aluminum for cobalt-base alloys according to the invention consists of scandium, lanthanum or other lanthanide series metal. The metals within the scope of the lanthanide series, in addition to lanthanum, consist of cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. The naturally occurring lanthanide series metals are preferred and accordingly promethium, being only artificially prepared, is somewhat impractical. Although available, scandium, europium, terbium, thulium and lutetium are presently of relatively high cost. In addition, it is preferred to use those metals which have melting points approaching that of cobalt. Lanthanum, cerium, europium and ytterbium have relatively low melting points as compared to cobalt, thereby making them somewhat more difficult to use. The more preferred metals are dysprosium and holmium because of their practical availability and melting points. Dysprosium is especially preferred in view of its outstanding performance in combination with chromium and aluminum in reducing sulfidation corrosion of the alloys of the invention.

Concentration of these metals between about 0.05 and about 3.0% is critical. The presence of less than about sulfidation resistance of the alloys at elevated temperatures. However, concentrations above of about 3.0% weight of the metallic alloy are believed to result in grain boundary segregation which causes embrittlement of the metal during hot working, hot shortness in casting and general deterioration of mechanical properties. The metals may be used in their essentially pure form, or on the other hand, may be present in mixtures available in the form of misch metals consisting of a major amount of a lanthanide series metal plus traces of carbon, aluminum, silicon, iron, copper, calcium, and the like. Specific mixtures often include cerium, neodymium, praseodyminum, samarium, lanthanum, gadolinium, dysprosium, erbium, ytterbium, etc.

The concentrations of aluminum and chromium are also somewhat critical. Amounts of aluminum below about 1% do not offer sufficient corrosion resistance, while concentrations above about 6% are found to result in brittle alloys of questionable use. The presence of chromium in amounts of at least about 5% by weight is necessary to achieve desired sulfidation resistance. Concentrations between about 5 and about 30% are preferred with amounts between about 10 and about 25% offering both superior sulfidation resistant and high strength alloys.

Preferably, the cobalt-base alloys of the invention contain between about 50 and 80% cobalt. In order to provide high strength cobalt-base alloys it is also necessary for the compositions to contain tungsten and/or tantalum wherein the total amount of this group of metals is between about 3 and about 20% by weight of the alloy. The pre-

ferred amounts of these metals individually are between 0 and 15% and more preferably between about 4 and about 10% individually for tungsten and tantalum with the total amount of this group of metals being no more than about 20% by weight of the alloy composition. Alternatively, molybdenum may be present to replace all or part of the tungsten and columbium may be present to replace a part or all of the tantalum. Molybdenum, preferably, may be present up to about 10% and columbium up to about 2% by weight of the alloy. The presence of a small amount of carbon also increases the strength of the alloy. However, where the carbon content is above about 0.5% by weight, oxidation resistance is sacrificed somewhat. Suitable carbon concentrations are between about 0.05 and about 0.5% by weight.

A convenient manner of expressing the concentrations of the preferred cobalt-base alloys of the invention is by mole ratios based on cobalt. Thus, the preferred alloy compositions corresponding to the concentrations set forth above are as follows:

Metal:	Metal: Co
Al+"x"	1:50–1:7
Cr	1:7–1:2.5
W, Ta, Mo, Cb	1:6–1:3

where "x" is scandium, lanthanum or a lanthanide series metal.

The following examples are provided to illustrate the manner in which the invention is carried out. Unless otherwise specified, parts and percents set forth are given by weight.

Example I

In order to show the sulfidation resistance of the cobalt-base alloys of the invention a number of alloys were prepared and subjected to high-temperature environments in a furnace containing an atmosphere simulating JP–5 fuel combustion products with about 100 times the normal sulfur content and also containing NaCl. The test procedure was as follows:

A furnace was purged for 30 minutes with 2.0 c.f.h. N_2, 0.072 c.f.h. CO_2, and 0.013 c.f.h. H_2S. The alloy specimens were placed in a silica retort which was in turn placed in the furnace, containing the aforementioned gases for two hours. For the following 20 hours the furnace was supplied with a mixture of 2.0 c.f.h. air, 0.072 c.f.h. CO_2 and 0.013 c.f.h. SO_2 which gases were bubbled through a 10% aqueous sodium chloride solution. Accordingly, the gaseous atmosphere within the furnace contained about 1 p.p.m. sodium chloride. During the 22 hours of the test, the temperature of the furnace was maintained at 1950° F. Following the exposure to the high temperature conditions, the alloys were cooled and cleaned and weighed to determine the weight loss caused by sulfidation corrosion. The use of two different atmospheres during the test duplicates a gas turbine engine combustion exhaust, whereupon at start up excess H_2S is present and thereafter during continuous operation SO_2 is present in the gaseous exhaust mixture.

The alloy compositions subjected to the severe sulfidation test set forth above consisted of a cobalt-base alloy corresponding to a well known commercially available cobalt-base alloy identified as WI–52, having the following analysis:

	Percent
Co	66.2
Cr	21.0
W	10.5
C	0.5
Cb+Ta	1.8

The above alloy composition was modified by the addition of 4.5 weight percent aluminum, 0.1% scandium, lanthanum or other naturally occurring lanthanide series metals, and combinations of each of these metals with aluminum respectively. The compositions of the alloys and

the sulfidation corrosion exhibited by each of the alloys is set forth in the table below.

TABLE I

Sulfidation test results

[22 hours at 1950° F.]

Alloy:	Weight loss, mg./sq. cm.
(A) WI–52	714
(B) WI–52+0.1% Gd	405
(C) WI–52+0.1% Gd+4.5% Al	40
(D) WI–52+0.1% Sm	443
(E) WI–52+0.1% Sm+4.5% Al	61
(F) WI–52+0.1% Yb	356
(G) WI–52+0.1% Yb+4.5% Al	31
(H) WI–52+0.1% Sc	596
(I) WI–52+0.1% Sc+4.5% Al	67
(J) WI–52+0.1% Ho	508
(K) WI–52+0.1% Ho+4.5% Al	67
(L) WI–52+0.1% Ce	534
(M) WI–52+0.1% Ce+4.5% Al	76
(N) WI–52+0.1% La	282
(O) WI–52+0.1% La+4.5% Al	24
(P) WI–52+0.1% Nd	290
(Q) WI–52+0.1% Nd+4.5% Al	8
(R) WI–52+0.1% Pr	314
(S) WI–52+0.1% Pr+4.5% Al	13
(T) WI–52+0.1% Dy	326
(U) WI–52+0.1% Dy+4.5% Al	14

Example II

Additional cobalt-base alloys were prepared and tested for sulfidation resistance according to Example I.

	Alloy composition							
Alloy	Co	W	C	Cb and Ta	Cr	Al	Ce	Weight loss, mg./sq. cm.
1	87.2	10.5	0.5	1.8				878
2	87.2	10.5	0.5	1.8			0.1	518
3	83.2	10.0	0.5	1.8		4.5		431
4	83.1	10.0	0.5	1.8		4.5	0.1	338
5	78.7	9.5	0.5	1.6	5.0	4.5	0.1	220
6	74.4	9.0	0.4	1.5	10.0	4.5	1.0	80

The results show the criticality and marked superiority of the alloys of the invention.

Example III

The sulfidation test of Example I was repeated utilizing typical high-oxidation resisting, nickel-base alloy, identified as Inconel 713C having the following analysis:

	Percent
Ni	74.2
Cr	12.5
Mo	4.2
Cb	2.0
Ti	0.8
Al	6.1
B	0.012
Zr	0.010
C	0.12

Additional alloys were made by adding lanthanum, cerium and dysprosium, respectively, and tested at 1950° F. by the above procedure for sulfidation resistance. The results were as follows:

	Weight loss, mg./sq. cm.
Inconel 713C	295
Inconel 713C+0.1% La	313
Inconel 713C+0.1% Ce	330
Inconel 713C+0.1% Dy	209

Example IV

Samples of the alloys prepared and tested according to Example I were subjected to high-temperature oxidation at 2000° F. for 115 hours. The oxidation atmosphere consisted of slowly moving air. The samples were then cooled, cleaned with caustic, wire brushed and weighed

to determine the weight change caused by the oxidation. The oxidation test results are shown in Table II.

TABLE II

Oxidation in static air

[115 hours at temp.]

Composition:	Weight change, mg./sq. cm., 2000° F.
(A) WI—52	−41
(B) WI—52+0.1% Gd	−34
(C) WI—52+0.1% Gd+4.5% Al	+1
(D) WI—52+0.1% Sm	−81
(E) WI—52+0.1% Sm+4.5% Al	+1
(F) WI—52+0.1% Yb	−47
(G) WI—52+0.1% Yb+4.5% Al	+2
(H) WI—52+0.1% Sc	−106
(I) WI—52+0.1% Sc+4.5% Al	+2
(J) WI—52+0.1% Ho	−73
(K) WI—52+0.1% Ho+4.5% Al	+1
(L) WI—52+0.1% Ge	−92
(M) WI—52+0.1% Ce+4.5% Al	+1
(N) WI—52+0.1% La	−85
(O) WI—52+0.1% La+4.5% Al	+1
(P) WI—52+0.1% Nd	−24
(Q) WI—52+0.1% Nd+4.5% Al	+1
(R) WI—52+0.1% Pr	−91
(S) WI—52+0.1% Pr+4.5% Al	+1
(T) WI—52+0.1% Dy	−85
(U) WI—52+0.1% Dy+4.5% Al	+1

It is evident from the results of the above-described sulfidation and oxidation tests that the cobalt-base alloys of the invention containing chromium, aluminum and a small amount of scandium, lanthanum or naturally occurring lanthanide series metals possess vastly superior sulfidation resistance over other alloys including nickel-base alloys. The alloys of the invention may also contain small amounts of phosphorus and sulfur and preferably in amounts not over about 0.04%, silicon in an amount not over about 0.5% in weight. Nickel may be present in small amounts up to about 10% as well as iron and manganese in amounts up to about 2.5% in addition to small amounts of zirconium and boron. However, the absence or presence of these additional elements is not critical or necessary to the alloys of the invention.

The superior sulfidation resistant cobalt-bast alloys as disclosed herein may be used for a number of varied purposes. The alloy may be cast, rolled into sheets or prepared as bars or tubing for any uses where superior resistance to sulfur attack as well as oxidation is desired.

What is claimed is:

1. A cobalt-base alloy comprising a major amount of cobalt, at least about 5% by weight chromium and at least about 1% by weight aluminum and a metal selected from the group consisting of scandium, lanthanum and a lanthanide series metal in combination, the amount of chromium, aluminum and said metal being effective to increase the sulfidation resistance of the cobalt-base alloy.

2. The composition of claim 1 wherein the amount of aluminum is up to about 6.0% by weight and the amount of said metal is up to about 3.0% by weight.

3. The composition of claim 1 wherein the amount of said metal is at least about 0.05% by weight.

4. The composition of claim 1 which contains one or more metals selected from the group consisting of tungsten, tantalum, molybdenum and columbium wherein the total amount of the group is between about 3% and about 20% by weight of the total composition.

5. The composition of claim 4 wherein the respective individual amounts of tungsten and tantalum are between about 4 and 10%, the amount of molybdenum is up to about 10% and the amount of columbium is up to about 2% by weight.

6. The composition of claim 1, which contains up to about 30% by weight chromium.

7. The composition of claim 1 which contains up to about 0.5% by weight carbon.

8. The composition of claim 1 wherein said lanthanide series metal is selected from the group, consisting of cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, holmium and ytterbium.

References Cited

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RICHARD O. DEAN, Primary Examiner

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,589,894 Dated June 29, 1971

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

Column 1, line 28, "oils" should read --oil--. Column 2, line 42, before "sulfidation" insert --0.05% is insufficient to obtain substantial increase in the--. Column 4, line 41, in Example II, Alloy 6, under heading "Ce", "1.0" should read --0.1--. Column 5, line 20, in Table II, composition (L), after "0.1%", "Ge" should read --Ce--.

Signed and sealed this 14th day of March 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
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Commissioner of Patents