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[54] **HIGH-TEMPERATURE OXIDATION-RESISTANT COBALT BASE ALLOYS**

3 Claims, No Drawings

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[50] **Field of Search** 75/171, 170; 148/32, 32.5

[56] **References Cited**

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ABSTRACT: Cobalt base alloys having improved high-temperature strength, ductility, and oxidation resistance consist essentially of, in percent by weight, chromium 20–35, carbon 0.05–1.5, tungsten 2–12, tantalum an effective amount of about 1 up to 7, iron 3–17, boron an effective amount of about 0.005 up to 0.1, yttrium 0.05–0.4, titanium an effective amount of about 0.1 up to 3, zirconium an effective amount of about 0.1 up to 3, with the remainder essentially cobalt except for impurities.

HIGH-TEMPERATURE OXIDATION-RESISTANT COBALT BASE ALLOYS

This invention relates to new and useful cobalt base alloys which are particularly characterized by improved high-temperature strength and ductility and have increased resistance to oxidation and hot corrosion at elevated temperatures.

Gas turbines and other equipment which depend upon the driving force of combustion gases operated more efficiently as the operating temperature rises. However, at such higher temperatures the strength of many alloys needed for both rotating and stationary parts often decreases rapidly, and the alloys become susceptible to oxidation caused by contact with the hot combustion gas stream. These conditions have precipitated a constant search for new and improved alloys and even relatively small improvements in high-temperature strength and oxidation resistance become very important. In gas turbines operating at temperatures of the order of about 1,600° F. with a peak of about 2,000° F., an improvement of only about 100° F. in the oxidation or corrosion resistance of the structural materials such as buckets, partitions, and other components represents a notable advance. For example, an increase in operating temperature of a typical gas turbine from about 1,500° to 1,600° F. produces an increase in power output of about 14 percent and an increase in efficiency of up to about 5 percent. The constant search for such high-temperature alloys will thus be appreciated, and it is a principal object of this invention to provide new and useful alloys which will permit the operation of equipment such as gas turbines at temperatures of up to about 1,900° to 2,000° F. or even higher. Another object of the invention is to provide improved materials of construction for high-temperature equipment in general which are subjected to oxidative atmospheres such as furnaces and the like.

Those features of the invention which are believed to be novel are set forth with particularity in the claims appended hereto. The invention will, however, be better understood and further objects thereof appreciated from a consideration of the following description.

Briefly, there are provided by the present invention economical, high-temperature, oxidation-resistant, cobalt base alloys which are also characterized by good room temperature and elevated temperature strength characteristics and good hot corrosion resistance which have a percent by weight composition of chromium 20–35, carbon 0.05–1.5, tungsten 2–12, tantalum an effective amount of about 1 up to 7, iron 3–17, boron an effective amount of about 0.005 up to 0.1, yttrium 0.05–0.4, titanium an effective amount of about 0.1 up to 3, zirconium an effective amount of about 0.1 up to 3, with the remainder essentially cobalt except for impurities such as manganese, silicon, sulfur, and phosphorus. Preferably, the manganese is kept below a maximum of about 1.2 percent, the silicon below about 1 percent, and the sulfur and phosphorus each below about 0.04 percent.

It has been found that alloys of the above precisely balanced composition are characterized by substantial improvements in oxidation resistance at elevated temperatures, at the same time retaining suitable strength, ductility, and other physical characteristics for operation at such temperatures. The alloys are also particularly useful in that they are adapted to precision investment casting techniques and other molding techniques which permit the precision formation of various shaped structures suitable for high-temperature apparatus such as buckets and such of the hot stages of gas turbines.

Those features of the invention which are believed to be patentable are set forth with particularity in the claims appended thereto. The invention will, however, be better understood and further advantages and objects thereof appreciated from a consideration of the following description.

It is to be particularly noted that the relatively high range of chromium of from about 20 to 35 weight percent is contrary to general prior art teaching that cobalt base alloys having a chromium content of over about 25 percent by weight show increased scaling or deterioration due to oxidative or corrosive influence at elevated temperatures. Such prior art teaching is set forth, for example, in *Journal of the Electrochemical Society*, Vol. 103, No. 8, by Pfalnikar et al. entitled "High Temperature Scaling of Cobalt-Chromium Alloys."

The present compositions represent a carefully balanced formulation of constituents, each of which contributes in the amounts stated to the desirable end results obtained. Deviations in the amounts of materials destroy this critical balance resulting in materials which have been found to be lacking in one or more desired characteristics. For example reduction of the chromium content below that prescribed results in a detrimental loss of oxidation resistance while excessive amounts of chromium produce precipitation of a cobalt plus chromium-rich sigma phase intermetallic compound, which precipitation embrittles the alloy during service and further renders it brittle at room temperature. When the carbon is lowered beyond that indicated, undesirable weakening occurs, whereas increasing the carbon content above that set forth results in an embrittling tendency due to excessive precipitation of metal carbides at the alloy grain boundaries. Lesser amounts of tungsten than those stated result in weakening, as tungsten substitutionally solid-solution strengthens the alloy matrix lattice. Amounts greater than those set forth again result in embrittlement, as tungsten enhances precipitation of sigma phase. Tantalum, titanium and zirconium are necessary as strengthening constituents through formation of the cubic carbide structure, previously enriched in tantalum but also containing titanium and zirconium. In excess of the prescribed ranges of these elements, an undesirable amount of MC carbide precipitator creates an imbalance with the second major strengthening carbide, chromium-rich $Cr_{23}C_6$. Furthermore, an undesirable reaction occurs between the MC carbide and the ceramic mold when the molten alloy is poured during the casting operation.

It is to be noted here that it has been the practice in the prior art to use nickel as a matrix stabilizer. However, it is a critical finding of this invention that iron, which is much less expensive than nickel, effectively stabilizes the alloy matrix. That is, an equal percentage substitution of iron for nickel more effectively inhibits transformation of the matrix crystallographic structure from the high-temperature face centered cubic polymorph to the low-temperature, less ductile hexagonal closely packed polymorph. Further, nickel is in worldwide short supply while iron is widely available, which increases the practicality of this alloy immensely while at the same time sharply decreasing the price. Greater amounts of iron than those set forth, however, unduly weaken the alloy.

In the prescribed range, boron strengthens the alloy through precipitation of metal borides and creation of thermodynamic grain boundary perfection. In excess amounts, however, metal boride precipitation at the alloy grain boundaries severely embrittles the alloy. Yttrium is particularly critical to the oxidation and hot corrosion resistance of these alloys, by the manner in which properties of the predominant oxide, Cr_2O_3, are improved. Adherence of this scale, particularly under thermal cycling conditions, is markedly improved due to the mechanical keying of scale to alloy substrate afforded by the presence of yttrium-rich oxide particles formed near the oxidizing surface. These same particles inhibit the free flow of chromium atoms to the surface, thereby reducing the rate at which the alloy oxidizes. Greater amounts of yttrium, however, lead to formation of an yttrium- and cobalt-rich intermetallic compound, which embrittles the alloy. As a practical matter, furthermore, it is quite difficult to retain greater amounts of yttrium during the casting operation because of its extreme reactivity and subsequent loss to the slag. Amounts of manganese and silicon over those prescribed result in unwanted embrittlement and weakening as a result of sigma phase formation, or of other intermetallic compounds whose formation is enhanced in particular by silicon.

The following examples will illustrate the practice of the invention, it being realized that they are exemplary only and not to be taken as limiting in any way.

EXAMPLE 1

There was prepared by vacuum induction melting techniques an alloy consisting of by weight percent: chromium 24, carbon 0.65, tungsten 7, tantalum 3.5, iron 10, boron 0.015, yttrium 0.15, titanium 0.2, zirconium 0.5, manganese 0.3, silicon 0.1, sulfur 0.015, and phosphorus 0.015, with the remainder essentially cobalt except for other incidental impurities. This alloy was poured into ceramic molds to prepare test bars 3 inches long by 0.252 inch diameter. A first heat, heat No. 1, had a casting temperature of 2,850° F., a mold temperature of 1,500° F., and was cooled in the enclosed mold. Heat No. 2 had a casting temperature of 2,680° F., a mold temperature of 1,800° F., and again was cooled in the enclosed mold. Heat No. 3 had a casting temperature of 2,680° F., a mold temperature of 1,800° F., and was cooled in air, the mold being broken open after solidification of the melt.

EXAMPLE 2

There was prepared by vacuum induction melting techniques an alloy consisting of, by weight percent, chromium 24.8, carbon 0.68, tungsten 6.6, tantalum 3.64, iron 9.0, boron 0.015, yttrium 0.22, titanium 0.2, zirconium 0.5, manganese 0.1, silicon 0.1, sulfur 0.015, and phosphorus 0.015, with the remainder essentially cobalt except for other incidental impurities. Test bars 3 inches long by 0.25 inches in diameter were prepared by vacuum induction melting and investment casting techniques.

Shown in table I are the high-temperature stress-rupture properties of the examples of the alloy claimed as compared with a typical prior art alloy, specifically Mar M-509.

The Larsen-Miller parameter (constant =20) is a well-known numerical value which combines time and temperature to allow comparison of the capabilities of alloys on a normalized basis, such that at any given temperature the parameter gives a direct comparison of rupture strength value.

TABLE I.—STRESS-RUPTURE TESTS

Alloy	Temp., ° F.	Stress, K s.i.	Life, hours	Percent elongation	Percent reduction in area	Larsen-Miller parameter (C=20)
Heat 1	1,600	25	101.6	19.4	49	45.3
	1,800	15	40.8	18.4	34	48.8
	2,000	9	11.4	23.9	43	51.8
Heat 2	1,600	25	59.5	27.4	52	44.8
	1,800	15	27.2	41.3	72	48.5
	2,000	9	4.8	39.9	70	50.9
Heat 3	1,600	25	249.5	28.7	69	46.2
	1,800	15	79.3	35.3	79	49.5
	2,000	9	19.7	56.2	84	52.4
Prior art (typical)	1,600	25	205.0	15.0	25	46.0
	1,800	15	80.0	15.0	25	49.5
	2,000	9	35.0	8.0	15	53.0

From the above table it will be seen that the materials of the present invention have about two times the ductility of the prior art material as measured by reduction in area. The stress-rupture test results in table I indicated that the stress-rupture strength of present alloys using the Larsen-Miller parameter indicated has a strength comparable to the prior art alloys at high stresses.

Shown in table II is the hot corrosion resistance of the present exemplary alloy as compared to the above prior art alloy. In this test, disc-shaped test pieces of the above example and the prior art material were placed in the combustion gas stream flow in a simulated gas turbine burner apparatus at the temperatures indicated using natural gas as a fuel at an air-to-fuel weight ratio of 50 to 1. THe specimens were thermal cycled every 50 hours to simulate gas turbine shutdown, this procedure being particularly rigorous as it evaluates the adherence properties of the protective scale. After the times indicated, the surface loss and maximum penetration were measured metallographically for each sample in terms of mils per side.

TABLE II

Ex.	Heat	Fuel	Temp., ° F.	Time, hrs.	Maximum penetration, mils	Surface loss, mils
1	1	Natural gas	1,800	630	3.3	1.2
		do	2,000	620	9.9	4.7
2	1	Natural gas	1,800	606	4.0	0.6
		do	[1] 1,900	606	6.3	2.0
		do	[1] 2,000	619	10.5	7.1
		Diesel oil and Sea salt	1,600	628	2.1	0.5
			1,800	617	5.5	0.6
(2)		Natural gas	1,800	600	4.	1.
		do	1,900	600	8.	1.
		do	2,000	600	18.	9.
		Diesel oil and Sea salt	1,600	600	2.2	0.5
			1,800	600	4.8	1.4

[1] Average of 2 tests.

[2] Prior art alloy, average results.

The oxidation resistance of the prior art alloy, while acceptable at 1,800° F. in natural gas, rapidly worsens with increasing temperature. The present exemplary alloy, therefore, is distinctly more resistant at the higher temperatures. In diesel oil plus sea salt combustion products, the two are virtually equivalent at both 1,600° and 1,800° F., this being superior to most contemporary cobalt base alloys.

From the above table it will be quite evident that the present alloys which are characterized by much improved rupture ductility at elevated temperatures have far and away superior oxidation resistance at elevated temperatures to the prior art alloy; such oxidation resistance combined with the naturally excellent hot corrosion resistance of cobalt alloys make these alloys very useful for operation under high-temperature oxidation conditions which are experienced in gas turbine and similar apparatus. The alloys are considered as particularly attractive for gas turbine bucketing where such high strength is mandatory, usually preserved for nickel-base alloys.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A cobalt base alloy characterized by good high-temperature strength and ductility and corrosion resistance consisting essentially of about, by weight, chromium 20–35 percent, carbon 0.05–1.5 percent tungsten 2–12 percent, tantalum an effective amount of about 1 percent up to 7 percent, iron 3–17 percent boron an effective amount of about 0.005 percent up to 0.1 percent yttrium 0.05–0.4 percent titanium an effective amount of about 0.1 percent up to 3 percent, zirconium an effective amount of about 0.1 percent up to 3 percent, with the remainder essentially cobalt except for impurities.

2. A cobalt base alloy as in claim 1 characterized by good high-temperature strength and ductility and corrosion resistance consisting essentially of about, by weight, chromium 24 percent, carbon 0.65 percent, tungsten 7 percent, tantalum 3.5 percent, iron 10 percent, boron 0.015 percent, yttrium 0.15 percent, titanium 0.2 percent, zirconium 0.5 percent, with the remainder essentially cobalt except for impurities.

3. A cobalt base alloy as in claim 1 characterized by good high-temperature strength, ductility and corrosion resistance consisting essentially of, by weight, chromium 24.8 percent, carbon 0.65 percent, tungsten 6.6 percent, tantalum 3.64 percent, iron 9.0 percent, boron 0.015 percent, yttrium 0.22 percent, titanium 0.2 percent, zirconium 0.5 percent, manganese 0.1 percent, silicon 0.1 percent, sulfur 0.015 percent, and phosphorus 0.015 percent, with the remainder essentially cobalt except for incidental impurities.

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