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DUCTILE COBALT-BASE ALLOY

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This invention relates to cobalt-base alloys and more specifically to high-strength, heat-resistant cobalt-base alloys with superior ductility after aging.

Various cobalt-base alloys containing chromium have been extensively used in the past under conditions of high stresses at high temperatures and it is well known that alloys of this class generally tend to lose ductility after prolonged exposure at high temperature. Many attempts have been made to improve cobalt-base alloys in this respect to thereby reduce or eliminate embrittlement after aging and it can be said that, up to the present, this problem has not been completely solved.

It is an object of this invention therefore to provide a cobalt-base alloy that will remain ductile after prolonged exposure in the temperature range between about 1400° F. and 1900° F.

Another object of this invention is to provide a superior oxidation-resistant cobalt-base alloy in the form of wrought products.

A further object of this invention is to provide cobalt-base alloys that have an optimum combination of high strength and resistance to embrittlement and oxidation. These and other objects were satisfied by the alloy in accordance with the present invention which consists essentially of about: 18 to 25 percent chromium, 11 to 15 percent tungsten, 16 to 25 percent nickel, 0.05 to 0.5 percent carbon, 0.001 to 0.025 percent boron balance cobalt and incidental impurities. The alloy of this invention may contain the usual impurities found in commercial alloys of this class, i.e. up to, about 5 percent iron, about 1.5 percent molybdenum, about 1 percent manganese, about 0.75 percent silicon; and about 0.15 percent total phosphorous, sulfur, hydrogen, oxygen, and nitrogen. Table 1 shows alloy ranges and specific compositions in accordance with the present invention.

TABLE 1.—ALLOYS OF THIS INVENTION

[Composition, in Weight Percent]

	Broad Range	Preferred Range	Typical Examples			
			Alloy A (60-238)	Alloy E (65-51)	Alloy G (71-2)	Alloy H (65-81-1)
Chromium	18 to 25	18.5 to 22	18.9	19.62	19.88	21.89
Tungsten	11 to 15	11 to 14	11.4	11.77	13.0	14.02
Carbon	.05 to .50	.05 to .35	.25	.15	.30	.11
Nickel	16 to 25	17 to 22	19.7	19.5	19.2	19.48
Manganese	Up to 1	.2 to .65	.48	.46	.64	.64
Boron	.001 to .025	.001 to 0.02	.008	.008	.018	.015
Cobalt and Incidental Impurities.	(1)	(1)	(1)	(1)	(1)	(1)

[1] Balance.

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There are many alloys commercially available and well known in the art that contain cobalt, chromium, tungsten, and/or molybdenum, nickel and iron and some of these alloys are shown in Table 2.

TABLE 2

Alloy No.	Nominal Composition, in Weight Percent								
	Cr	W	Mo	Fe	C	Co	Ni	B	Others
1	20	15		2	.10	Bal	10		1.5 Mn.
2	22	1	9	18	.10	2.5 max	Bal		

These alloys, often called "superalloys" are especially suitable for service at high temperature except that they tend to embrittle after prolonged use at temperatures above about 1400° F. Furthermore, while each alloy has certain outstanding individual characteristics, none by itself has the advantage of combined optimum characteristics of high strength, oxidation resistance and resistance to embrittlement. For example, Alloy 1 is known to have outstanding high temperature strength but its oxidation resistance is lower than that of Alloy 2. Alloy 2 has outstanding oxidation resistance but its high temperature strength is lower than that of Alloy 1. Up to the present such limitations had to be tolerated in the application of these superalloys.

The alloys of this invention on the other hand provide an optimum combination of all the advantageous properties generally associated with this class of "superalloys." As shown hereinbelow, the alloys of this invention have strengths equal to or higher than Alloy 1 and also have oxidation resistance characteristics approaching that of Alloy 2.

Although the exact mechanism of the strengthening effects of the elements proportioned within the scope of this invention is not completely understood, it is thought at this time to be a combination of solid solution and carbide dispersion hardening.

In accordance with the present invention, chromium, within the ranges shown in Table 1, provides oxidation resistance and contributes to high temperature strength; chromium contents below the indicated range are not sufficient to provide adequate oxidation resistance while chromium contents above the indicated range tend to yield alloys of decreased dutility at room temperature.

Tungsten is present in the alloy, within the indicated ranges, as a carbide former and in a solid solution matrix to provide high strength. Molybdenum is not substitutable for tungsten in the alloy of this invention, although molybdenum may be present as an unavoidable impurity up to not more than 1.5 percent by weight in the total alloy as previously noted.

Carcon is required in the alloy within the range as indicated in Table 1 as a solid solution strengthening element and as a carbide former to provide high strength and nickel must be present in the alloy within the indicated ranges to provide adequate post aging ductility, oxidation resistance, and high temperature strength. Alloys containing less than 15.5 percent nickel tend to embrittle after prolonged use at temperatures between about 1400° F. and 1900° F.

Manganese may be present in the alloy in amounts not exceeding about one percent and it appears that some metallurgical benefits are provided with manganese within the range 0.2 to 0.65 percent by weight.

Incidental impurities in amounts normally found in alloys of this type, may be tolerated as previously mentioned while zirconium, columbium, titanium and tantalum, often added in alloys of this class, are not required in the alloys of this invention. The combined total content in the final alloy of zirconium, columbium, titanium and tantalum must not exceed over one percent by weight, as impurities and residuals of prior processing steps, in order that the desired combination of properties be obtained.

In the course of experimentation, a series of alloys were prepared by a process commonly used in alloys of this class; however, other consolidating techniques could be used. In the technique employed, the alloy compositions were melted in an induction furnace, cast into ingots, forged and rolled into 0.063-inch thick sheet for testing purposes. Prior to testing, the alloys were annealed at 2150° F. for 15 minutes and fan cooled. Compositions of alloys prepared and tested are given in Table 3. The alloys of this invention described in Table 3 are in the range of about 19–20% Ni, 11–14% W, 19–22% Cr and 0.1–0.3% C. and will be seen to have an excellent combination of industrially useful properties. All of the alloys of Table 3, except alloy B, are in accordance with this invention. Tensile test results of these alloys, and prior are alloys, are shown in Table 4 while creep and stress-rupture test results are shown in Table 5.

In all tests, the alloys of this invention are seen to be superior, or at least comparable to, both alloys **1** and **2** of the prior art. For example, within the range 1400° F. to 1600° F. the average tensile strengths of the alloys of this invention are about 1.5 times the strengths of alloys **1** and **2**, in addition Table 6 shows that the alloys of this invention have much better oxidation resistance than alloy **1** of the prior art.

The oxidation tests of Table 6 were identical for all alloys tested. All oxidation test samples were nominally 0.07-inch thick sheet, 0.75-inch square and were uniformly polished to a 120-grit finish. One group of samples was exposed at 2000° F. for 100 hours continuously while another group was intermittently exposed at 2000° F. for eight 3-hour periods and four 19-hour periods for a total of 100 hours as indicated in Table 6. The oxidation rates were determined and are shown on the basis of mils penetration per year (m.p.y.). It is significant that the oxidation rates of the alloys of this invention closely approach those of alloy 2 which is generally recognized as the superior wrought oxidation-resistant alloy presently available in the metals industry.

TABLE 3.—COMPOSITION OF TESTED ALLOYS OF THIS INVENTION

	Code	Composition, in Weight Per cent											Total N,H,O
		Cr	W	Fe	C	Si	Co	Ni	Mn	B	P	S	
Alloy:													
A	60–238	18.91	11.37	2.05	.23	.06	Bal	19.68	.48	.008	.005	.023	
B	60–239	18.90	11.10	1.88	.11	.01	Bal	15.52	.50	.008	.003	.016	
C	64–218	19.42	12.68	2.15	.18	.01	Bal	19.4	.56	.005	.062	.014	.03
D	65–50	19.62	11.77	2.32	.15	.02	Bal	19.5	.46	.008			
E	65–51	19.62	11.77	2.30	.15	.2	Bal	19.5	.46	.008			
F	65–71–1	19.88	13.0	1.68	.19	.08	Bal	19.2	.64	.018			
G	65–71–2	19.88	13.0	1.68	.30	.08	Bal	19.2	.64	.018			
H	65–81–1	21.89	14.02	2.43	.11	.08	Bal	19.48	.64	.015			

TABLE 4.—AVERAGE TENSILE PROPERTIES OF ALLOYS TESTED

	Yield Strength 0.2% Offset, 1,000 p.s.i.	Ultimate Tensile Strength, 1,000 p.s.i.	Elongation, Percent
At Room Temperature:			
Alloy 1	67.2	145.9	64
Alloy 2	52.2	114.0	43
Alloy A	80.3	156.8	49
Alloy B	81.4	152.1	44
Alloy D	64.9	140.4	58
Alloy E	61.8	138.8	62
Alloy G	67.7	149.4	47
Alloy H	59.9	138.1	59
At 1,400° F.:			
Alloy 1	37.7	66.0	12
Alloy 2	37.8	63.1	33.5
Alloy A	49.6	90.9	30
Alloy B	46.3	88.2	26
Alloy H	43.4	88.5	(1)
At 1,600° F.:			
Alloy 1	34.5	46.6	30
Alloy 2	25.7	36.5	28.5
Alloy A	41.6	58.1	46
Alloy B	40.2	55.9	73
Alloy C	35.8	62.8	35
Alloy D	34.4	55.6	21
Alloy E	32.8	55.2	13
Alloy G	39.5	56.6	20
Aloy H	33.7	64.7	(1)
At 1,800° F.:			
Alloy 1	23.1	34.4	41
Alloy 2	16.0	22.5	45
Alloy C	19.5	29.9	14
Alloy H	20.7	32.8	(1)
At 2,000° F.:			
Alloy 1	12.0	19.6	34
Alloy A	10.8	17.5	24
Alloy B	10.1	16.4	35
Alloy C	8.5	14.1	21
Alloy D	10.8	18.6	47
Alloy E	8.7	15.1	25
Alloy G	11.2	17.0	44
Alloy H	10.4	17.5	(1)

[1] Not determined, specimen broke outside of gage marks.

TABLE 5.—CREEP AND STRESS RUPTURE DATA

Test Temp., ° F.	Stress, 1,000 p.s.i.	Initial Elong., percent	Time for Total Elongation Percent, Hours				Total Elong., percent	Life, Hours
			0.5	1.0	1.5	2.0		
Alloy A:								
1,500	24	0.10	1.5	5.6	12.5	22.0	11.6	154.3
1,600	15	0.33	2.2	24.9	65.5	98.7	6.5	193.1
1,800	6.7	0.01	7.6	14.1	20.5	25.3	8.0	51.2
2,000	2.6	0.06	1.7	3.6	5.4	6.9	21.3	29.0
Alloy B:								
1,500	24	0.11	1.6	7.7	18.5	30.0	12.4	198.9
1,600	15	0.05	2.1	11.4	29.9	52.4	3.6	117.2
1,800	6.7	—	9.6	23.7	35.1	43.6	12.9	87.6
2,000	2.6	0.07	2.5	5.8	8.6	11.0	16.0	39.3
	2.6	0.0	1.4	3.0	4.4	5.9	24.9	34.2
Alloy C:								
1,400	30	0.10	4.4	9.8	17.2	27.4	7.4	118.8
	35	0.19	1.4	2.7	4.1	5.6	8.1	31.3
1,600	15	0.0	3.1	9.7	18.2	29.0	23.7	217.0
	15	0.05	1.8	5.6	12.1	17.8	17.0	104.8
1,850	8	—	—	—	—	—	20.0	5.3
Alloy D:								
1,600	15	0.25	0.5	2.4	6.6	12.5	9.6	69.9
	10	0.0	50.1	112.8	162.8	188.2	4.7	253.7
1,800	9	—	—	—	—	—	19.7	33.8
Alloy E:								
1,400	35	0.16	3.9	7.1	9.6	12.3	6.6	42.4
	30	0.0	7.9	14.5	21.6	30.5	6.6	118.2
1,600	15	0.13	1.0	3.3	7.4	12.0	13.0	68.9
1,800	9	—	—	—	—	—	28.8	4.1
Alloy G:								
1,500	22	—	—	—	—	—	17.4	33.0
1,600	10	0.0	47.8	134.7	194.2	240.2	13.3	615.9
	23	—	—	—	—	—	23.6	12.8
	23	—	—	—	—	—	19.5	12.4
1,800	9	—	—	—	—	—	25.1	18.6
1,850	8	—	—	—	—	—	20.3	16.3
Alloy H:								
1,400	35	—	—	—	—	—	32.1	117.2
1,500	24	0.03	1.7	4.1	7.6	12.3	23.8	168.9
1,600	15	0.0	1.7	3.8	6.9	10.9	41.1	242.7
1,800	7	0.0	2.7	6.2	10.0	14.2	33.6	201.9
2,000	2.6	—	—	—	—	—	18.6	116.3

TABLE 6.—OXIDATION TESTING AT 2,000° F.

Alloy	Average Oxidation Rates, MPY	
	Continuous 100 hrs.	Eight 3-hr. periods plus four 19-hr. periods
1	51.5	131.5
2	22.5	22
C	23	34
	23.5	43
D	23	52
E	31	—
H	23	47

Alloys of this invention may be readily hot- and cold-rolled into thin sheet and wire, they are cold-formable into desired finished products. Table 7 shows Ericksen cup test data for two typical alloys within the scope of the invention, Alloy G and Alloy H. These data show excellent cold-formable properties for cold-rolled sheet 0.063-inch thick.

TABLE 7.—ROOM-TEMPERATURE ERICKSEN CUP TEST DATA

[.063-inch thick sheet]

Alloy	Load at Rupture, 1,000 p.s.i.	Cup Depth, inch	Cup Depth, mm.
G	19.8	0.382	9.7
H	19.7	0.464	11.8

To obtain best results with the present invention, it appears that the nickel content should be substantially the same amount by weight as chromium, i.e. within about 5 percent.

In a series of further tests it was found that the minimum content of nickel must exceed about 16 percent in the alloy in order to retain the desired ductility after prolonged exposure at 1500° F. Samples of Alloy A and Alloy B, described in Table 3, were processed under similar conditions. The two alloys are similar except that the nickel content of Alloy B is outside the range of the present invention; Alloy A contains 19.68 percent nickel and Alloy B contains 15.52 percent nickel. The respective alloys were rolled into test specimens (0.063 inch thick sheet, ⅝ inch in width and 2 inches in length) and exposed at 1600° F. for various time periods in air atmosphere to simulate prolonged use at high temperature. Free bend tests were performed on the specimens to evaluate ductility properties after aging. The following results were obtained:

Time at 1,600° F.	Bend Angle, Degrees	Radius of Bend, Inch	Result
Alloy A:			
25 hours	180	1/16	Passed, No Failure.
	180	3/32	Do.
50 hours	180	3/16	Do.
	180	1/8	Do.
100 hours	180	1/8	Do.
	180	1/8	Do.
Alloy B:			
25 hours	180	3/16	Fractured.
	180	3/16	Do.
50 hours	180	1/4	Do.
	180	1/4	Do.
100 hours	135	(1)	Do.
	120	(1)	Do.

[1] Bend not completed due to failure.

In a further test for ductility after aging, two sample specimens each of Alloy G of this invention and Alloy 1 in the form described above were exposed in air at temperatures and for time periods as follows:

Alloy G:
- 984 hours at 1600° F.
- 310 hours at 1500° F.

Alloy 1:
- 26 hours at 1600° F.
- 140 hours at 1500° F.

The sample specimens were given a free bend test, as described above, after aging for the times and temperatures shown above. Both samples of Alloy G were successfully bent to 180 degrees angle about a radius of about 3/32 inch. Both samples of Alloy 1 fractured before they were bent 90 degrees.

What is claimed is:

1. A cobalt base alloy characterized by high temperature strength, oxidation resistance and resistance to em-

brittlement after exposure to elevated temperatures, said alloy consisting essentially of about:

	Percent
Chromium	18–25
Tungsten	11–15
Carbon	0.05–0.5
Nickel	16–25
Boron	0.001–0.025

balance cobalt and incidental impurities.

2. An alloy in accordance with claim 1 wherein:

	Is about, percent
Chromium	18.5–22
Tungsten	11–14
Carbon	0.05–0.35
Boron	0.001–0.02
Nickel	17–22

3. An alloy in accordance with claim 1 wherein:

	Is about, percent
Chromium	19–22
Tungsten	11–14
Carbon	0.1–0.3
Boron	0.005–0.018
Nickel	19–20

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