United States Patent Office 3,085,007 Patented Apr. 9, 1963

3,085,007

CHROMIUM BASE ALLOY POSSESSING HIGH-STRENGTH AT ELEVATED TEMPERATURES

Lewis R. Aronin, Lexington, and Arthur L. Geary, Arlington, Mass., assignors, by mesne assignments, to the United States of America as represented by the United States Atomic Energy Commission

No Drawing. Filed June 30, 1960, Ser. No. 40,123
1 Claim. (Cl. 75—176)

The present invention relates in general to chromium rich alloys and is specifically directed to alloys having superior strength at high temperatures combined with adequate hot workability.

Chromium, because of its high melting point and oxidation resistance, offers an attractive basis for high temperature alloys. Strengthening achieved by selected alloying elements should result in an alloy having useful strength as a structural material at temperatures well in excess of 1000° C. (1830° F.). While other metals such as molybdenum, tantalum and tungsten have higher melting points than chromium, the latter is superior to these in oxidation resistance.

In the search for strong, high temperature chromium alloys, the most satisfactory alloy has been reported as Cr–Fe–Mo in the range 60 w/o chromium, 15 to 20 w/o iron and 15–25 w/o molybdenum (Parke and Bens, "ASTM Symposium on Materials for Gas Turbines," 1946).

Sully and Brandes, "The Properties of Cast Chromium Alloys at Elevated Temperatures," Journal of the Institute of Metals, 81, 573 (1953), also investigated the strengths of cast chromium base alloys. Results of compression and creep tests at 900° C. (1650° F.) indicated that a Cr–10 w/o Fe–10 w/o W alloy containing either 5 or 10 w/o Ta was the most resistant to deformation when stressed at 10,000 p.s.i. Erratic results, however, were obtained in tensile stress-rupture tests, this behavior being attributed to defects in the cast structure which obscured the intrinsic creep resistance of the alloys.

Chromium base alloys containing 1 w/o Ti and up to 5 w/o W prepared by arc melting mixture of hydrogen-treated electrolytic chromium and high purity titanium and tungsten powders have been successfully forged, swaged and rolled (Henderson, Quass and Wain, "The Fabrication of Chromium and Some Dilute Chromium-Base Alloys," Journal of the Institute of Metals, 83, 126 (1954). Other workers report that Cr–5 w/o Mo and Cr–10 w/o W alloys fabricated by extrusion of arc-cast ingots, possess attractive creep and stress-rupture properties at 950° C. (1740° F.) (Wilms and Rea, "Preliminary Investigations on the Properties of Chromium and Chromium Alloys at Elevated Temperatures," Journal of the Institute of Metals, 87, 77 (1958).

It is the object of this invention to provide chromium alloys which have superior strength at high temperatures, are hot workable and extrudable.

These objects are obtained by alloying the chromium with small quantities of columbium, tantalum, and/or molybdenum. The alloys are distinguished from the prior art in that high-temperature strength is achieved with small alloying additions. Only two of the alloys of this invention have alloy contents as high as 7 w/o, while the majority have alloy contents substantially less than 5 w/o. The alloys can be hot worked and are extrudable into a wrought product.

FABRICATION OF ALLOYS

The alloys of the subject invention are fabricated by powder metallurgy techniques. Blended powders, compacted at 50,000 p.s.i. into 1-inch diameter by 2-inch high slugs, are sintered for 3½ hours in purified argon

at 2685–2730° F. (1475–1500° C.). The sintered slugs are enclosed in type 304 stainless steel containers and evacuated to 0.01 micron while heating at temperatures up to 800° F. (430° C.). After heating one hour at 2400° F. (1315° C.), the billets are extruded from a 2.800" liner of a 1000-ton press through 0.800 inch dies. The alloy core so produced is approximately .25 inch in diameter.

Alternatively, the slugs may be sintered in hydrogen. Slugs sintered in hydrogen are evacuated one hour at 1830° F. (1000° C.) to reduce residual hydrogen. In these alloys high purity chromium is used.

TESTING THE ALLOYS

In order to test the alloys at a temperature of 2300° F. (1260° C.) a conventional stress-rupture test machine was modified to permit use of an inert (argon) atmosphere. Specimens are placed in grips and inserted in a tubular furnace which is comprised of a Kanthal winding on a mullite tube. The latter is sealed, flushed with argon, after which the furnace is turned on. Within about 5 hours the specimen reaches the test temperature, 2300° F. (1260° C.). After soaking for half an hour at temperature, a load is applied to the specimen and the rupture life is measured to the nearest 0.1 hr. by an electric timer.

The properties of unalloyed chromium and 23 chromium-base alloys have been investigated in stress-rupture tests at 2300° F. (1260° C.). Results for unalloyed chromium and for chromium alloys are set forth below in Table I and Table II respectively:

Table I.—Results of Stress-Rupture Tests at 2300° F. (1260° C.) Unalloyed Chromium

Atmosphere	Stress (p.s.i.)	Elongation (percent)	Reduction in area (percent)	Rupture life (hr.)
COMPACTED POWDERS EXTRUDED TO 0.18-INCH DIAMETER				
Argon	2,000	48.4	31.2	3.8
Helium	2,000	82.0	55.0	1.3
Do	1,500	61.0	47.0	5.2
Argon	1,000	37.5	32.0	15.0
Do	1,000	36.0	30.0	19.9
Helium	1,000	66.0	33.0	16.5
SINTERED POWDERS EXTRUDED TO 0.18-INCH DIAMETER				
Argon	1,720	81.2	68.7	5.8
Do	1,220		55.3	18.2
COMPACTED POWDERS EXTRUDED TO 0.25-INCH DIAMETER				
Argon	2,720	43.8	48.8	0.6
Do	2,220	46.6	32.4	1.0
Do	1,720	29.8	22.3	1.8
Do	1,720	36.6	23.3	1.7
Do	1,720	31.2	29.2	1.7
Do	1,720	26.6	19.4	2.9
Do	1,220	37.5	25.9	5.4
Do	920	34.4	17.2	12.6
COMPACTED POWDERS EXTRUDED TO 0.25-INCH DIAMETER; HEAT TREATED 2 HOURS IN HYDROGEN AT 2,460° F. (1,350° C.)				
Argon	1,720	60.9	45.2	2.5
Do	1,220	42.2	35.0	5.4
Do	920	39.1	36.7	14.3
SINTERED POWDERS EXTRUDED TO 0.25-INCH DIAMETER				
Argon	3,220	77.9	93.8	0.3
Do	2,220	62.5	50.6	1.8
Do	1,720	106.2	79.4	5.8
Do	1,220	46.9	43.1	24.3

Table II.—Results of Stress-Rupture Tests in Argon at 2300° F. (1260° C.) Chromium-Base Alloys Materials Sintered and Extruded to 0.25-Inch Diameter Unless Otherwise Noted

Composition (a/o)	Stress (p.s.i.)	Elongation (percent)	Reduction in area (percent)	Rupture life (hr.)
Cr–1.0 Cb	2,220	46.9	36.0	15.1
	1,720	37.5	29.3	23.4
	1,220	37.5	26.0	56.4
	1,220	37.5	26.0	57.7
	920	40.6	36.3	195.3
Cr–2.0 Cb	2,220	28.1	20.7	13.6
	1,720	18.7	13.6	21.1
	1,220	25.0	19.2	48.6
Cr–1.0 Ta	2,220	21.9	19.0	14.1
	1,720	15.6	12.1	18.2
	1,220	18.8	8.7	35.5
	1,220	18.8	14.6	46.5
	920	15.6	6.1	39.4
	920	21.9	16.0	75.4
Cr–2.0 Ta [1]	2,000	15.4	12.1	20.7
Cr–2.0 Ta	1,720	14.1	8.5	20.4
	1,220	6.3	4.9	41.0
Cr–1.0 Ti [2]	2,220	53.1	50.8	1.6
	1,720	50.0	42.4	5.0
	1,220	31.2	32.5	11.2
	920	28.1	29.5	17.1
Cr–1.0 Ti	2,220	46.9	23.4	1.1
	1,720	34.4	28.9	4.5
	1,220	18.8	5.2	10.0
	1,220	18.8	10.9	6.7
	920	6.3	6.3	14.5
Cr–2.0 Ti	2,220	15.6	13.6	3.9
	2,220	15.6	11.1	4.1
	1,920	15.6	9.8	5.7
	1,720	15.6	12.1	10.6
	1,220	14.1	10.9	15.4
	920	12.5	8.6	25.3
Cr–4.0 Ti	2,220	25.0	15.3	5.5
	1,720	23.4	16.8	15.4
	1,220	25.0	18.0	23.0
	1,220	18.8	15.9	30.1
	920	37.5	25.8	[3]<66.2
Cr–1.0 Cb–0.1 Mo	2,720	37.5	32.0	7.3
	2,220	34.4	28.0	15.5
	1,720	47.5	26.9	33.8
	1,220	34.4	21.7	111.5
Cr–1.0 Cb–1.0 Mo	2,220	28.1	17.0	13.1
	1,720	18.8	12.4	30.7
	1,220	21.9	10.0	55.3
Cr–1.0 Cb–0.1 Ta	2,220	39.1	28.8	15.4
	1,720	18.8	31.6	24.1
	1,720	39.1	22.5	[4]36.4
	1,220	34.4	30.8	80.1
	920	18.8	12.1	[5]>121.0
Cr–1.0 Cb–1.0 Ta	2,220	12.5	5.1	5.0
	1,720	10.9	7.4	11.3
	1,220	12.5	11.1	22.2
	920	18.8	7.9	68.4
Cr–2.0 Cb–0.1 Mo	2,220	28.1	11.1	10.1
	1,720	21.9	15.8	[4]15.3
	1,220	15.6	12.3	[4]30.5
	920	28.1	14.0	58.9
Cr–1.0 Ta–0.1 Cb	2,220	25.0	13.3	13.0
	1,720	25.0	19.4	33.5
	1,720	21.9	14.6	16.3
	1,220	25.0	16.8	37.6
	920	21.9	24.9	[6]<88.5
Cr–1.0 Ta–0.1 Mo [1]	2,000	25.0	18.0	13.4
Cr–1.0 Ta–0.1 Mo	2,220	27.4	20.3	16.9
	1,720	25.0	26.0	32.6
	1,220	29.7	21.5	68.5
	920	23.4	10.9	85.1
Cr–1.0 Ta–0.1 Cb–0.1 Mo	3,220	12.5	13.3	2.5
	2,220	15.6	12.1	9.1
	1,720	25.0	9.8	14.0
	1,220	17.2	15.6	21.6
	920	21.9	14.5	44.2
Cr–2.0 Ta–0.1 Mo	2,220	17.2	10.9	12.1
	1,720	25.0	12.1	50.1
	1,220	15.6	8.7	79.4
Cr–2.0 Ta–0.1 Cb–0.1 Mo	2,220	21.9	15.6	10.4
	1,220	21.9	12.1	73.9
	920	15.6	9.9	142.0
Cr–1.1 Ti–1.0 Cb	2,220	5.1	9.3	2.5
	1,720	15.6	7.5	6.7
	1,220	17.2	7.5	13.4
	920	18.8	7.8	27.2
Cr–1.1 Ti–1.0 Mo	2,220	17.2	7.5	8.2
	1,720	25.0	7.5	17.5
	1,220	25.0	8.7	35.9
	920	12.5	8.7	44.1
Cr–1.1 Ti–1.0 Ta	2,220	14.6	7.4	3.5
	1,720	12.5	5.1	6.0
	1,220	14.6	5.2	12.5
	920	12.5	8.7	44.1
Cr–0.6 Zr–1.0 Cb	2,220	28.1	12.2	5.5
	1,720	25.0	12.1	[4]9.5
	1,220	25.0	11.1	18.8
	920	37.5	11.1	38.2
Cr–0.6 Zr–1.0 Mo	2,220	18.8	9.9	6.3
	1,220	21.9	8.8	20.8
Cr–0.6 Zr–1.0 Ta	2,220	18.8	6.2	5.5
	1,720	23.4	11.1	10.6
	1,220	18.8	8.7	22.5
	920	21.9	8.7	37.9

[1] Blended powders extruded to 0.18 inch diameter core and heat treated in argon for 72 hours at 2190° F. (1200° C.).
[2] Blended powders extruded to 0.18-inch diameter core.
[3] Temperature below 2300° F. for approximately 5 hours.
[4] Specimen fractured at shoulder.
[5] Furnace winding burned out. Elongation and reduction in area determined for unfractured specimen.
[6] Temperature below 2300° F. for approximately 7 hours.

It will be noted from the foregoing tables that insofar as pure chromium is concerned, sintering has a pronounced effect on its performance. However, none of the chromium samples had a stress-rupture life of 100 hours at 2300° F. as required for certain contemplated uses.

From Table II it is seen that among the elements investigated as binary alloys, Cb accomplishes the most significant increase in strength. Rupture lives of Cr–Cb alloys are approximately 3 to 5 times that of unalloyed chromium, and improved strength is evident at all stress levels.

Ta also increases the strength of chromium but to a lesser extent than Cb. The degree of strengthening varies with stress, being greater at the high stresses than at the low. The stress-rupture data, however, indicate that Cr–Ta alloys would continue to possess strengths greater than Cr down to very low stress levels.

Ti at the lower concentrations, unlike Cb and Ta, decreases the strength. Rupture lives of the 1 and 2 a/o alloys are less than those of chromium. It is not until the 4 a/o level that strengthening is evident, and then only to a slight extent.

The binary alloy data, although indicating the more promising base compositions, cannot be used to predict the performance of ternary and quaternary alloys. Strengths of these alloys depend, in a complex manner, upon the specific elements and their concentrations. Comparison with strengths of the corresponding binary alloys, rather than with unalloyed chromium, more clearly reveals the effect of the alloying additions. This comparison is given below for the better ternary and quaternary alloys.

With respect to alloys based on Cr–1 a/o Cb, the addition of 0.1 a/o Mo significantly increases the strength; the addition of 1.0 a/o, however, does not. Ta additions do not appear beneficial. The 0.1 a/o addition is without effect, whereas the 1.0 a/o addition resulted in a shorter rupture life.

As for alloys based on Cr–1 a/o Ta, it is noted that strength is increased by the addition of 0.1 a/o Mo, but is not affected by addition of 0.1 a/o Cb. Additions of 1.0 a/o Cb or 0.1 a/o Cb plus 0.1 a/o Mo decrease the strength.

Alloys based on Cr–2 a/o Ta are strengthened by additions of 0.1 a/o Mo or 0.1 a/o Cb plus 0.1 a/o Mo.

In order to determine which alloys have a stress-rupture life of 100 hours or more at 1000 p.s.i. and at a temperature of 2300° F., Table III has been compiled by interpolation and extrapolation of log-lot plots of rupture life vs. applied stress. While such extrapolations assume that chemical and metallurgical instabilities do not alter the slope of the curve, over short distances such assumptions are valid, and the data summarized in Table III is deemed to be correct within reasonable limits.

Table III.—Life at 1000 p.s.i. and Stress to Rupture in 100 Hours at 2300° F. Unalloyed Chromium and Chromium-Base Alloys

Alloy composition (a/o)	Life at 1,000 p.s.i. (hr.)[1]	100 hour rupture stress (p.s.i.)[1]
Cr-2.0 Ta-0.1 Mo	(250)	(1,270)
Cr-1.0 Cb-0.1 Mo	220	1,260
Cr-1.0 Cb	130	1,100
Cr-1.0 Cb-0.1 Ta	130	1,100
Cr-2.0 Ta-0.1 Cb-0.1 Mo	122	1,070
Cr-1.0 Ta-0.1 Mo	(104)	(1,020)
Cr-1.0 Cb-1.0 Mo	(103)	(1,020)
Cr-2.0 Cb	68	830
Cr-1.0 Ta	64	800
Cr-1.0 Ta-0.1 Cb	64	800
Cr-2.0 Ta	(63)	(800)
Cr-1.1 Ti-1.0 Mo	(54)	(770)
Cr-4.0 Ti	50	840
Cr-2.0 Cb-0.1 Mo	48	551
Cr-1.0 Cb-1.0 Ta	48	770
Cr-1.0 Ta-0.1 Cb-0.1 Mo	35	550
Cr-0.6 Zr-1.0 Cb	33	590
Cr-0.6 Zr-1.0 Mo	33	590
Cr-0.6 Zr-1.0 Ta	33	590
Cr-1.1 Ti-1.0 Cb	23	510
Cr-2.0 Ti	23	510
Cr-1.1 Ti-1-0 Ta	23	510
Cr-1.0 Ti	12	320
Unalloyed chromium:		
Compacted, 0.18-inch core	(17)	(600)
Compacted, 0.18-inch core and tested in helium	17	600
Sintered, 0.18-inch core	(33)	(710)
Compacted, 0.25-inch core	10	450
Compacted, 0.25-inch core and heat treated	10	450
Sintered, 0.25-inch core	(71)	(910)

[1] Doubtful values enclosed in parentheses.

From Table III it will be seen that appropriate additions of Cb, Ta and Mo have resulted in rupture lives 3 to 5 times that of unalloyed chromium. Quantitatively, the rupture lives of certain of these alloys substantially exceed the desired 100 hour rupture life at 1000 p.s.i. and at a temperature of 2300° F. Of particular interest is the alloy Cr–1 a/o Cb–0.1 a/o Mo which appears to be the strongest alloy tested except perhaps the Cr–2 a/o Ta–0.1 a/o Mo as to which the data is scattered so that its life at 1000 p.s.i. cannot be precisely stated.

A number of other alloys successfully meet the desired conditions. These include (in atomic percent) Cr–1.0 Cb; Cr–1.0 Cb–0.1 Ta; Cr–2.0 Ta–0.1 Cb–0.1 Mo; Cr–1.0 Ta–0.1 Mo; and Cr–1.0 Cb–1.0 Mo.

From the foregoing it is seen that new and useful alloys of chromium have been produced by the addition of small amounts of selected alloying elements whereby the strength of chromium has been substantially increased at stresses of about 1000 p.s.i. and temperatures of about 2300° F.

We claim:

An alloy of chromium characterized by high strength at temperatures of about 2300° F. that consists of chromium-1 atomic percent columbium, and 0.1 atomic percent molybdenum.

References Cited in the file of this patent

Kubaschewski et al.: Journal Inst. Metal., vol 75, pp. 407–413 and 419, 1949.

Sully: Chromium, Butterworths Scientific Publication, London, 1954, p. 239.

Abrahamson et al.: "Brittle to Ductile Transition Temperature of Binary Chromium-Base Alloys," A.S.M. Transaction, vol. 50, 1958, pp. 709 and 711.

Hansen: Constitution of Binary Alloys, McGraw-Hill Book Co., Inc., New York, 1958, p. 541.