

Feb. 28, 1961

R. G. FRANK
COLUMBIUM BASE ALLOYS

2,973,261

Filed June 11, 1959

2 Sheets-Sheet 1

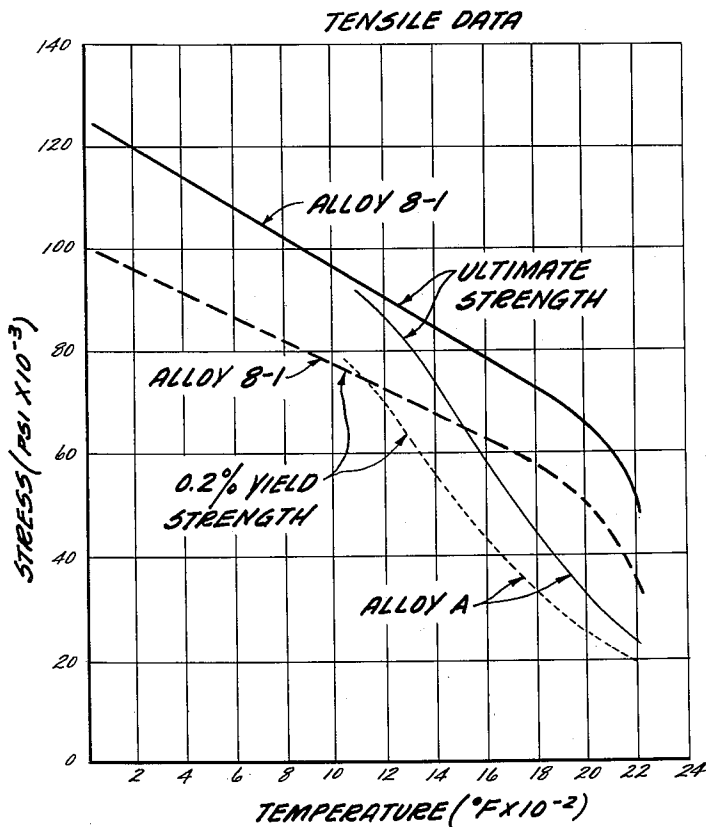


Fig 1

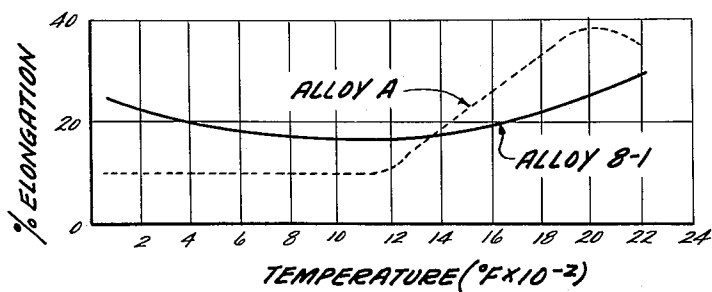


Fig 2

INVENTOR.
ROBERT G. FRANK
BY *Lee Hacks*
ATTORNEY-

Feb. 28. 1961

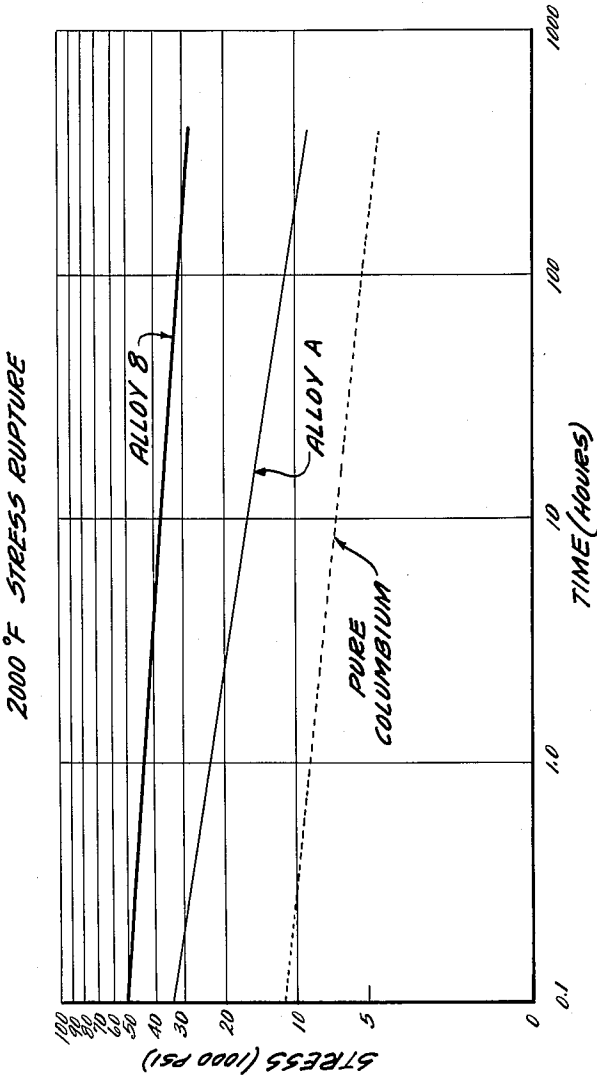
R. G. FRANK
COLUMBIUM BASE ALLOYS

2,973,261

Filed June 11, 1959

2 Sheets-Sheet 2

Fig. 3



INVENTOR.
ROBERT G. FRANK
BY *Lee H. Sachs*
ATTORNEY-

1

2,973,261

COLUMBIUM BASE ALLOYS

Robert G. Frank, Cincinnati, Ohio, assignor to General Electric Company, a corporation of New York

Filed June 11, 1959, Ser. No. 819,776

7 Claims. (Cl. 75-174)

This invention relates to columbium base alloys and more particularly to high strength columbium base alloys including zirconium as well as at least one of the elements tungsten and molybdenum.

Columbium base alloys represent a new class of materials which designers are studying in the selection of materials for applications in the temperature range of 1900-2500° F. The initial approach used by many in the study of columbium base alloys was to direct their work toward oxidation resistance believing that high temperature strength could be easily attained because of the high melting point of the alloy. However, such high temperature strength is not as easily attainable as was first anticipated because of unexpected detrimental effects on strength and/or ductility by elements which improve oxidation resistance of columbium base alloys.

A principal object of my invention is to provide a columbium base alloy including combined properties of both strength and oxidation resistance.

Another object is to provide a columbium base alloy including small amounts of zirconium as well as at least one of the elements tungsten and molybdenum.

These and other objects will become apparent from my description taken in connection with the accompanying drawings in which:

Figs. 1 and 2 are graphical comparisons of tensile properties for a form of my alloy and a known alloy.

Fig. 3 is a graphical comparison of stress rupture data for a form of my alloy with those of a known alloy and with pure columbium.

Briefly stated, in accordance with one aspect of my invention, I provide a columbium base alloy comprising in percent by weight about 4-20 of at least one of the elements tungsten and molybdenum, about 0.1-1.8 zirconium, up to about 1 titanium, up to about 0.3 carbon, up to about 0.25 oxygen with the balance essentially columbium.

From my studies to improve the high temperature strength of columbium base alloys, I found the addition of relatively large amounts of molybdenum or tungsten increases the strength of the matrix by solid solution and that the addition of small amounts of zirconium formed fine, well dispersed and thermodynamically stable particles of carbides and/or oxides within the matrix. In some instances I found that the addition of small amounts of titanium assisted the zirconium in the formation of such fine, well dispersed and stable particles.

In order to study the effects of molybdenum, tungsten, titanium, zirconium, carbon and oxygen on columbium base alloys, I melted a series of alloys by the consumable electrode vacuum process using columbium powder as a base. The columbium powder included an oxygen level of 0.08-0.12 percent by weight and a carbon level of about 0.06-0.1 percent by weight.

Table I includes typical examples of this series of alloys within the range in percent by weight of 4-20 Mo and/or W, 0.1 Ti, 0.0-1, Zr, up to about 0.3 C with

2

the balance essentially columbium and the oxygen level maintained below about 0.05.

TABLE I

Alloy No.	Composition (percent by weight)						
	Mo	W	Ti	Zr	O	Cb	C ₁
1	7.6		0.3	0.1	0.23	Bal.	0.033
2		5.2	0.74	0.32	0.22	Bal.	0.024
3			0.72	0.33	0.27	Bal.	0.018
4	13.8			1.3	0.05	Bal.	0.025
5		9.4		0.47	0.05	Bal.	0.025
8	4.7	13.1		0.88	0.04	Bal.	0.049

Alloys 1, 2 and 3 include a relatively large amount of carbon as compared with alloys 4, 5 and 8. Alloy 3 contains no molybdenum or tungsten and alloy 8 contains both molybdenum and tungsten.

Two tests generally conducted on alloys to determine some of their mechanical properties are called "ultimate tensile" and "yield tests," the results of such tests being generally reported as "ultimate tensile strength" and "yield strength."

"Ultimate tensile strength," shown in the tables as U.T.S. is the value in pounds per square inch obtained when the maximum load recorded during the plastic straining of a specimen is divided by the cross sectional area of the specimen before straining.

The term "0.2% yield strength," shown in the table as 0.2% Y.S., is the stress at which a material exhibits 0.2% deviation from the proportionality of stress to strain. This figure, sometimes referred to as "0.2% offset" is commonly used as the basis of design strength of articles.

Another tensile test which is a measure of the permanent deformation before fracture by stress in tension is a tensile ductility test reported in the table as "percent elongation": the amount of permanent extension in the fracture area in the tension test.

The strongest commercially produced columbium base alloy that I know of and which I will designate as alloy A includes in percent by weight about 10 Ti and 10 Mo with the balance essentially Cb. Tensile data for alloy A is compared graphically in Figs. 1 and 2 with pure columbium and with an alloy within my novel composition range. Thus the improved strength of my alloy is easily recognized.

Table II represents some of the tensile data obtained from forms of my alloy after swaging and vacuum annealing for about one hour at about 2000° F. The specimens tested which were from 0.350 inch diameter bar stock were 0.160" diameter by 1. inch gage length and were tested in a vacuum.

TABLE II
Tensile properties

Alloy	Temp., F.	U.T.S., 1,000 p.s.i.	0.2% Y.S., 1,000 p.s.i.	Percent Elongation
1	2,000	54.3	45.0	18
	2,200	34.8	18.4	46
2	2,000	54.5	30.4	19
	2,200	32.2	25.2	32
3	2,000	37.9	35.3	14
	2,200	23.2	20.2	18
4	2,000	65.3	49.8	19
	2,200	49.0	44.3	16
5	2,000	55.5	54.5	19
	2,200	44.4	36.7	19
8	2,000	51.1	47.5	20
	2,200	42.6	37.1	22

Alloys 1, 2, 4, 5 and 8 exhibited relatively good tensile properties, with alloys 4, 5 and 8 being the strongest in that respective order. Alloy 3, which had the same composition as alloy 2 and is similar to alloy 1 except

that it included neither molybdenum nor tungsten, exhibited much lower strength characteristics. Thus molybdenum and tungsten are important strengtheners in my alloy.

In order to study further the variation in composition of alloys 4, 5 and 8, additional alloys were melted. One of these, a variation on alloy 4 is shown in Table III.

TABLE III

Alloy	Percent By Weight				
	Mo	Zr	C	O ₂	Ob
4-1	15.2	-----	.054	.064	Bal.
4-2	13.5	0.75	.043	.056	Bal.
4-3	13.9	1.84	.049	.086	Bal.
4-5	12.4	0.60	.131	.039	Bal.
4-6	10.5	0.53	.067	.258	Bal.

The series of alloys of Table III represent a composition range in percent by weight of about 10-15 Mo, up to about 1.8 Zr, about 0.04-0.13 C, about 0.03-0.26 O₂ with the balance essentially columbium. Alloy 4-1 which included no zirconium was difficult to work and fractured during swaging. Alloy 4-3 which included 1.84 percent by weight zirconium was just barely workable; it could not be swaged but was double extruded. Thus the useful range of zirconium in my alloy was established to be about 0.1-1.8 percent by weight. The tensile data obtained from alloys 4-2, 4-5 and 4-6 are shown in the following Table IV.

TABLE IV
Tensile properties

Alloy	Temp., ° F.	U.T.S., 1,000 p.s.i.	Elongation, percent
4-2	2,000	49.3	23.2
	2,200	39.4	30.0
4-5	2,000	47.3	18.1
	2,200	37.8	25.4
4-6	2,000	52.7	29.5

Although alloy 4-5 included a relatively large amount of carbon which resulted in a coarse secondary phase, it exhibited satisfactory tensile properties. However the increased carbon at such high levels is not effective as a strengthener or a means to increase recrystallation temperature. Carbon would probably be detrimental to workability in amounts greater than about 0.3% by weight. The effect of high oxygen content in alloy 4-6 resulted in higher tensile strength at the 2000° F. testing temperature.

Alloy 8 and its variations, for example alloy 8-1 of Figs. 1 and 2, which I have found to have the preferable composition in percent by weight of about 0.04-0.12 carbon, about 0.03-.06 oxygen, about 4-6 molybdenum, about 13-17 tungsten, about 0.5-1.25 zirconium with the balance essentially columbium, offers the best combination of strength and oxidation resistance.

A test which I conducted and which shows the excellent strength of my alloy at elevated temperatures is sometimes called a "stress rupture" test. The result of this test, reported as "stress rupture strength," which is the

value in pounds per square inch (load on a specimen divided by the cross-sectional area of the specimen before straining) of a specified amount of resistance to deformation and/or fracture that the specimen can withstand for a specified length of time.

The presence of a fine, well dispersed phase within the matrix of a metal alloy is most effective in inhibiting motion of dislocations and thereby slip during long time constant load stress-rupture tests. Stress rupture data for my alloy 8 which is compared with that of alloy A and pure columbium in Fig. 3, shows again the improved strength of my alloy over pure columbium or the strongest commercially produced columbium base alloys. Along with its high level of strength, my alloy 8 has good oxidation resistance and is representative of other forms of my alloy. As measured by metal loss in mils per side, alloy 8 loses only about 8 mils per side after 24 hours at 2000° F. and only about 13 mils per side after 24 hours at 2200° F. in air.

Although I have described my invention in connection with specific examples, such examples are illustrative of rather than limitations on my invention. It will be understood by those skilled in the art, the modifications and variations of which my invention is capable.

What I claim is:

1. A columbium base alloy consisting essentially of by weight at least one element selected from the group consisting of tungsten and molybdenum, the molybdenum content being selected from the range 4-13.5% and the tungsten content being selected from the range 5.2-17%, about 0.1-1.8% zirconium, with the balance essentially columbium.

2. The alloy of claim 1 including by weight up to about 0.25% oxygen, up to about 1% titanium, and up to about 0.3% carbon.

3. The alloy of claim 2 including 0.02-0.25% by weight oxygen.

4. A columbium base alloy consisting essentially of by weight 5.2-17% tungsten, 0.3-1.3% zirconium, up to about 1% titanium, 0.04-0.12% carbon, with the balance essentially columbium.

5. A columbium base alloy consisting essentially of by weight 4-13.5% molybdenum, 0.1-1.8% zirconium, up to about 1% titanium, 0.04-0.13% carbon with the balance essentially columbium.

6. A columbium base alloy consisting essentially of by weight 10-13.5% molybdenum, 0.5-1.3% zirconium, 0.04-0.13% carbon, with the balance essentially columbium.

7. A columbium base alloy consisting essentially of by weight 13-17% tungsten, 4-6% molybdenum, 0.5-1.25% zirconium, 0.04-0.12% carbon, 0.03-0.06% oxygen, with the balance essentially columbium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,822,268	Hix	Feb. 4, 1958
2,838,396	Rhodin	June 10, 1958
2,883,282	Wainer	Apr. 21, 1959

FOREIGN PATENTS

201,297	Austria	Dec. 27, 1958
---------	---------	---------------