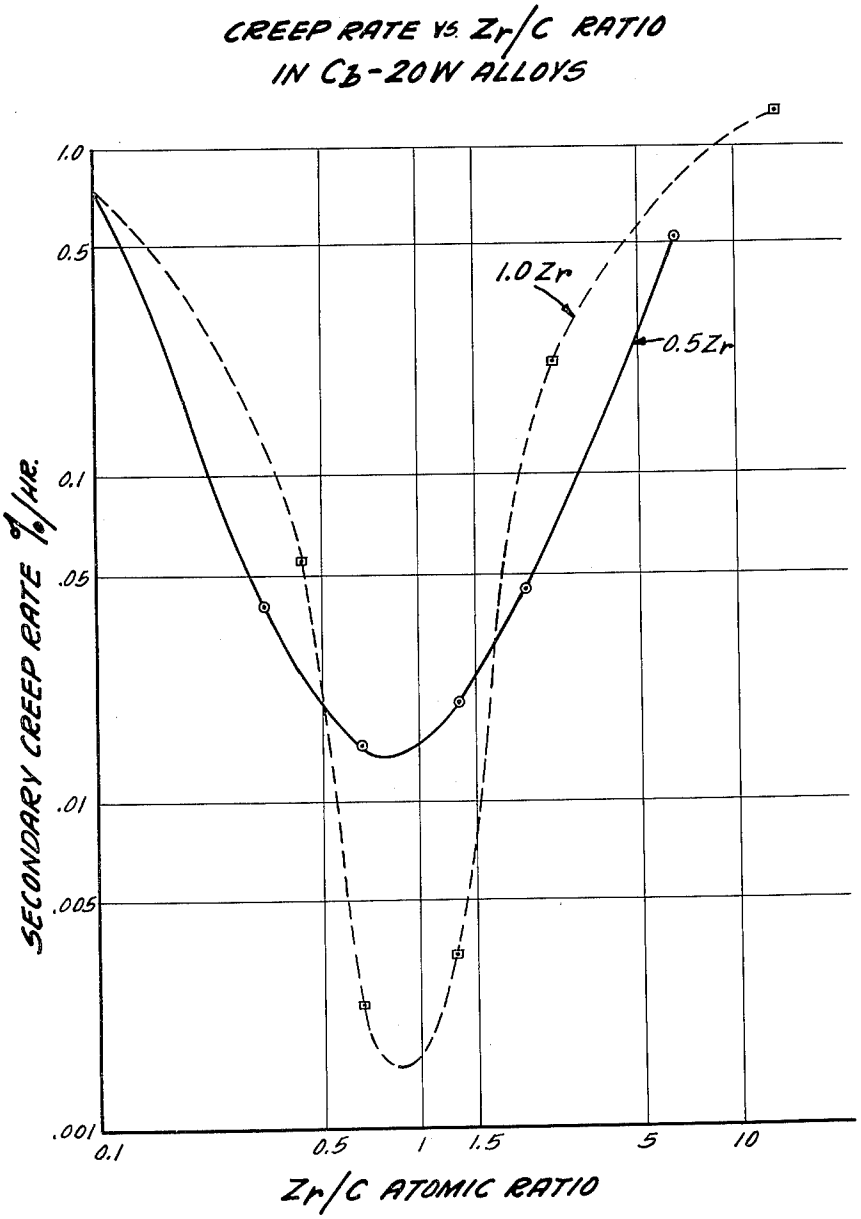
Oct. 2, 1962 J. W. CLARK 3,056,672

COLUMBIUM BASE ALLOY

Filed Dec. 1, 1960



INVENTOR.
JACK W. CLARK
BY
Lee H. Sachs
ATTORNEY—

United States Patent Office

3,056,672
Patented Oct. 2, 1962

3,056,672

COLUMBIUM BASE ALLOY

Jack W. Clark, Milford, Ohio, assignor to General Electric Company, a corporation of New York

Filed Dec. 1, 1960, Ser. No. 73,051
3 Claims. (Cl. 75—174)

This invention relates to fabricable oxidation resistant columbium base alloys and, more particularly, to oxidation resistant columbium base alloys having exceptionally high creep strength and good low temperature ductility.

The high melting temperature of the metallic element columbium has, in recent years, made it an attractive basis for alloy development studies. Because the element itself has relatively poor oxidation resistance at temperatures in excess of about 2000° F. at which it would be attractive for use, many studies have been reported showing that the oxidation resistance of columbium can be improved by alloying additions of a large variety of metallic elements. However, many of the columbium base alloys thus produced were very brittle, lacking the strength and ductility necessary for practical fabrication and use as high temperature operating articles.

In co-pending application Serial Number 819,776—Frank, filed June 11, 1959, now U.S. Patent 2,973,261—Frank, issued on February 28, 1961, and assigned to the assignee of this application, it was shown that a careful selection of alloying additions to columbium can result in greatly improved strength and fabricability.

One object of this invention is to provide a columbium base alloy of improved high temperature creep strength combined with good oxidation resistance to result in an alloy readily fabricable with greater improved high strength and oxidation resistance at temperatures of at least 2200° F.

Another object is to provide a columbium base alloy of improved high temperature strength without sacrifice of low temperature ductility.

Still another object is to provide a columbium base alloy including relatively small but significantly particular amounts of zirconium and carbon along with a substantial alloying addition of tungsten.

These and other objects will become apparent from my description taken in connection with the accompanying drawing which is a graphical representation of creep rates of alloys both within and without the scope of this invention.

Briefly stated, in accordance with one aspect of this invention, there is provided a columbium base alloy including alloying additions of tungsten, carbon and at least one of the elements zirconium and hafnium in which the Zr or Hf to C atomic ratio is about 0.5–3.0, the zirconium or hafnium content is 0.5–3 weight percent and the tungsten content is 5–25 weight percent. In another more preferred form of the alloy the zirconium or hafnium content lies between 0.5–2.0 weight percent while the tungsten is about 20 weight percent.

It was found unexpectedly that although improved strength and ductility can be achieved in a columbium base alloy including the elements zirconium and carbon, there exists an unexpectedly significant relationship between the elements zirconium or hafnium and carbon at a relatively small zirconium or hafnium addition of up to about 3 weight percent.

There are two major factors which contribute to the significant strength improvement of alloys of the type to which this invention relates. The first and most significant is the combined control of the atomic amounts of the carbide forming elements zirconium or hafnium and of the interstitial element carbon employed in dispersion strengthening of columbium base alloys. It was found that this control must be exercised over significantly

narrow composition ranges in order to optimize ductility and dispersion strengthening by zirconium carbide or hafnium carbide. Of the two elements zirconium and hafnium, zirconium may be more desirable because of its ready availability and lower cost. However, hafnium forms a carbide of higher thermal and thermodynamic stability. Except for its high cost, testing has shown that hafnium is very desirable in some forms of the alloy of this invention. As will be shown more particularly in connection with Table II, at an atomic ratio of less than about 0.5, too much free carbon is available and the ductility of the alloy is drastically affected. On the other hand above an atomic ratio of about 3, too much free hafnium or zirconium is available with similar detrimental effects on the strength of the alloy. Therefore this invention recognizes that a particularly significant zirconium or hafnium to carbon atomic ratio exists between about 0.5–3.

The second factor contributing to strength improvement is the choice of the primary solid solution alloying addition or additions. Because the elevated temperature creep rate is controlled by the rate of dislocation climb around barriers, such as dispersed carbides, which rate in turn is controlled by the rate of vacancy diffusion, the most creep resistant alloy would be the one in which atomic (or vacancy) mobility in the matrix is a minimum. Since it is an experimental fact that the rate of atomic mobility in metals decreases as the melting point increases, the most effective alloying element for improving creep resistance through solid solution effects was found to be the one which raises the melting point to the greatest extent. Of the elements which are completely soluble in columbium, tungsten raises the melting point by 9.7° C. per atomic percent added, tantalum by 5.8° C., and molybdenum by 2.0° C. On the other hand vanadium decreases the melting point by about 5.6° C. per atomic percent and titanium by 7.2° C. It was found that tungsten is by far the most potent alloying addition in this respect. As shown in the following table of two columbium base alloys, one including by weight 15% W and 5% Mo, and the other including 20% W and no Mo, the creep rate of the 20% W alloy within the range of this invention is significantly better, particularly at 2200° F. Note that the stresses for the 20% W-Cb alloy are higher at the given temperatures than those of the 15% W—5% Mo-Cb alloy.

TABLE I

Composition in Wt. percent (balance Cb)	Creep Rupture Properties		
	Temp. (° F.)	Stress (p.s.i.)	Hours to Fail
15 W—5 Mo—1 Zr—.11 C	2,000	35,000	162
15 W—5 Mo—1 Zr—.11 C	2,200	25,000	20
20 W—1 Zr—.11 C	2,000	40,000	250
20 W—1 Zr—.11 C	2,200	30,000	120

Thus it can be seen that in the alloy of this invention, the elements tungsten and molybdenum are not equivalents as they sometimes are found to be in other columbium base alloys having lower creep rates.

It is very important that, in order to achieve optimum creep rates coupled with good ductility at room temperature, the level and atomic ratio of Hf or Zr and C must be controlled, preferably within the range of about 0.5–1.5. The following Table II, representative of a number of alloys melted within the range of this invention, gives the data for a 20 weight percent tungsten-columbium base alloy including the elements zirconium and carbon in varying amounts to produce a significant variation in creep rate and rupture life over a relatively

narrow range of variations in composition. Tests were conducted in vacuum of at least 5×10^{-4} mm. Hg and all alloys were in the warm worked (swaged) condition.

TABLE II

Effect of Zr/C *Atomic Ratio on* 20W-Cb *Basic Alloy*

Example	Alloy Addition, Wt. percent	Zr/C Atomic Ratio	Rupture Life (2,000 F./35,000 p.s.i.), hrs.	Creep Rate (percent/hr.)
AS 21	.01 C	0	5	1.0
AS 22	.01 C, 0.5 Zr	6.6	8	0.52
AS 25	.03 C, 0.5 Zr	2.2	80	0.045
AS 26	.05 C, 0.5 Zr	1.35	140	0.020
AS 27	.10 C, 0.5 Zr	0.67	210	0.015
AS 28	.20 C, 0.5 Zr	0.34	83	0.040
AS 23	.01 C, 1.0 Zr	13.3	5	1.25
AS 29	.05 C, 1.0 Zr	2.7	20	0.22
AS 30	.10 C, 1.0 Zr	1.35	790	0.0034
AS 31	.20 C, 1.0 Zr	0.67	1100	0.0024
AS 32	.30 C, 1.0 Zr	0.45	77	0.055
AS 24	.02 C, 2.0 Zr	13.3	26	0.20
AS 65	.10 C, 2.0 Zr	2.7	40	0.11

Examples AS 26, 27, 30 and 31, within the preferred range of Zr/C atomic ratio of this invention, clearly show the unexpected increase in high temperature rupture life and decrease in creep rate over similar alloys outside the range of this invention. Similarly alloys As 25, 28, 29, 32 and 65 show improvement over the creep rate of alloys outside the range of this invention although the combination of improved rupture life and creep rate is not as significant as is the preferred range. It is easily seen from Table II that in order to achieve good rupture life and creep rate where the intended use dictates such characteristics, the Zr/C atomic ratio must be kept within the critical preferred range of about 0.5–1.5.

In addition, the Zr or Hf content has a marked effect on ductility at low temperatures. Where room temperature ductility is a problem there should be sufficient Zr not only to combine with the added C, but also to reduce the embrittling effect of residual oxygen and nitrogen. Room temperature ductility testing of Cb-20W alloys at C levels of 0.01 to 0.20C and Zr levels of 0–2.0 proved that the best balance between creep behavior and low temperature ductility is obtained at a Zr level of 1–2% and a Zr/C atomic ratio slightly greater than the unity.

Although the preferred weight percent of zirconium in the alloy of this invention lies between 0.5 and 2.0, the maximum allowable amount of zirconium lies at about 3 weight percent because at that point a two phase alloy is formed which is undesirable from a fabricability point of view.

Although the alloying addition of tungsten is preferred to be between about 5–20 weight percent and is specifically preferred at about 20 weight percent, a higher percentage such as up to about 25 weight percent can be included. A slightly stronger alloy can result at 25 weight percent tungsten; however, although it will have significantly lower

ductility, it can be useful as a material for articles in which low ductility is not a problem.

The following Tables III and IV show some of the specifically preferred forms of the alloys of this invention and the unusually high elevated temperature stress rupture and tensile strength properties obtainable.

TABLE III

Example	100 Hr, Stress Rupture Strength (p.s.i.)	
	2,000° F.	2,200° F.
AS 26	36,000	22,000
AS 27	37,000	24,000
AS 30	43,000	31,000
AS 31	47,000	

TABLE IV

Example	Wt. percent (Cb—Bal.)	Zr/C	Tensile Strength (p.s.i. @ 2,000° F.)
AS 66	20W—2 Zr—0.2C	1.35	73,200
AS 30	20 W—1 Zr—0.1C	1.35	67,200

The alloy shown as Example AS 66 in Table IV and which includes 2Zr and 0.2C, has the best tensile strength properties without impairment of room temperature ductility.

Although this invention has been described in connection with specific examples, it will be readily understood by those skilled in the art of metallurgy the modifications and variations of which this invention is capable.

What is claimed is:

1. A columbium base alloy consisting essentially of, by weight, about 20% tungsten; 0.5–2% of at least one of the elements selected from the group consisting of zirconium and hafnium; 0.01–0.2% carbon; with the balance columbium, the atomic ratio of the elements of said group to carbon being in the range of 0.5–1.5.

2. A columbium base alloy consisting essentially of, by weight, about 20% tungsten; 0.5–2% zirconium; 0.05–0.2% carbon; with the balance columbium, the Zr/C atomic ratio being in the range of 0.5–1.5.

3. A columbium base alloy consisting essentially of, by weight, about 20% tungsten; 1–2% zirconium; 0.1–0.2% carbon; with the balance columbium, the Zr/C atomic ratio being in the range of 0.5–1.5.

References Cited in the file of this patent

UNITED STATES PATENTS

2,822,268	Hix	Feb. 4, 1958
2,838,395	Rhodin	June 10, 1958
2,881,069	Rhodin	Apr. 7, 1959
2,973,261	Frank	Feb. 28, 1961