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NIOBIUM-BASE ALLOYS

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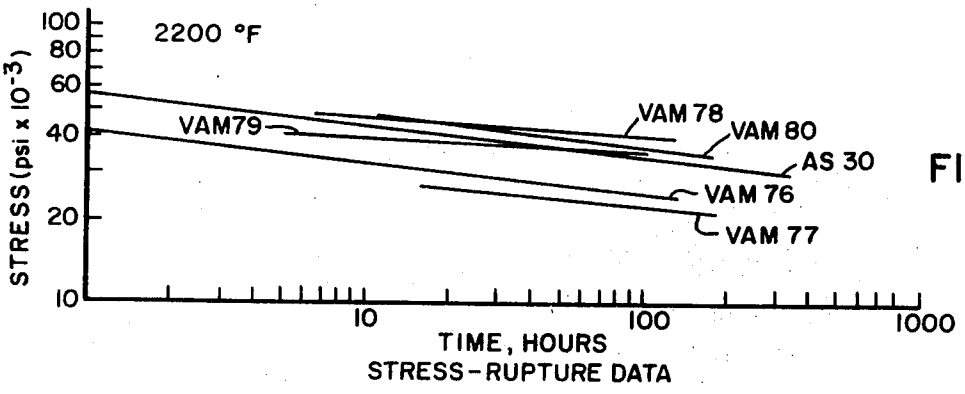


FIG. 1.

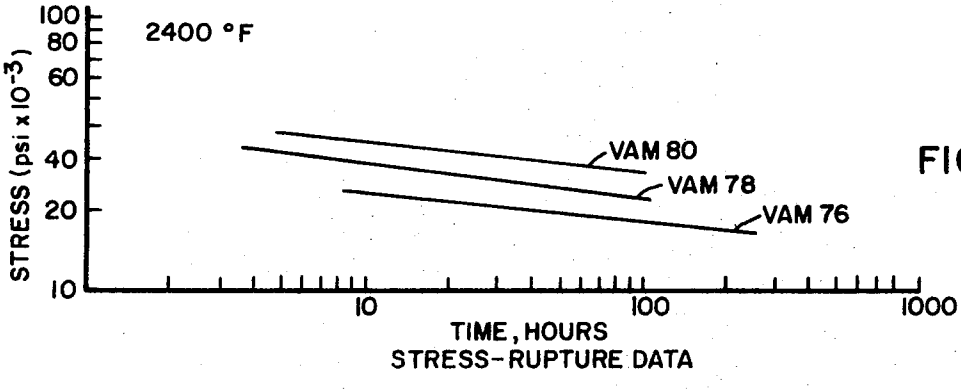


FIG. 2.

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NIOBIUM-BASE ALLOYS

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Continuation-in-part of application Ser. No. 529,088, Feb. 21, 1966. This application Oct. 4, 1968, Ser. No. 777,945

Int. Cl. C22c *27/00*

U.S. Cl. 75—174 3 Claims

ABSTRACT OF THE DISCLOSURE

A niobium-base alloy is described which is characterized by high strength and creep resistance. The alloy is composed of 27% hafnium and a carbon to hafnium atomic ratio of from 0.5 to 1.25 and the balance substantially niobium with incidental impurities.

This invention is directed to high strength and creep resistant niobium-base alloys particularly intended for service at elevated temperatures, and is a continuation-in-part of application Ser. No. 529,088 filed Feb. 21, 1966, now abandoned.

There is a requirement for high temperature structural materials as the result of higher operating temperatures contemplated in jet engines, missiles, nuclear reactors, other heat engines, power generation and propulsion systems. The element niobium has substantial potential as a base for high temperature alloys, since it has a high melting point (2460° C.), an intermediate density (8.56 g./cc.), a low ductile-brittle transition temperature and generally attractive high temperature properties.

This potential has been recognized in the art and a number of niobium-base alloys have been developed in recent years. These alloys are intended primarily for sheet and tubing applications in aerospace vehicles and high temperature liquid metal systems. For such applications, a high degree of fabricability and good weldability are vital prerequisites. However, there is also a need for niobium-base alloys having very high strength and good creep resistance for use in turbine blades, vanes, and discs in turbojet engines and in turboelectric space power systems. For these applications, a considerable sacrifice in fabricability can be tolerated in return for improved strength. Further, for such applications weldability is ordinarily not a necessary property.

It is, accordingly, an object of this invention to provide niobium-base alloys having high strength at elevated temperatures and high resistance to creep deformation.

It is another object of this invention to provide niobium-base alloys which rely both on solid solution and dispersed phase strengthening for high strength.

Still another object of the invention is to provide niobium-base alloys having high strength at elevated temperatures and good resistance to creep deformation including, in predetermined amounts, the elements tungsten, hafnium and carbon.

Another object of this invention is to provide niobium base alloys having high strength at elevated temperatures including, in predetermined amounts the elements tungsten and hafnium.

Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter.

For a better understanding of the nature and objects

of this invention, reference should be had to the following detailed description and to the drawings, in which:

FIG. 1 is a graph showing curves for a number of alloys of this invention and for an alloy of the prior art of stress-rupture data at 2200° F. in which the stress is plotted against the time in hours.

FIG. 2 is a graph similar to FIG. 1 showing curves for several of the alloys of the invention at a temperature of 2400° F.

In accordance with the invention, niobium-base alloys having high strength at elevated temperatures and with good resistance to creep deformation comprise, by weight, from 18% to 30% tungsten, from 1% to 5% hafnium, and sufficient carbon to provide a carbon to hafnium atom ratio of from 0.5 to 1.25, and the balance essentially niobium.

A preferred alloy of the invention having high strength at elevated temperature and good resistance to creep deformation comprises, by weight, from 27% to 29% tungsten, from 1.5% to 2.5% hafnium, sufficient carbon to provide a carbon to hafnium atom ratio of 0.5 and the balance essentially niobium.

Other alloys of the invention having high strength at elevated temperatures comprise, by weight, from 18% to 26% tungsten, from 1% to 5% hafnium and the balance essentially niobium.

It should be understood that the operating temperature range which is of particular interest for the alloys of this invention is from 1800° F. (980° C.) to 2400° F. (1315° C.) and this temperature range is designated hereafter by the term "elevated temperature."

The high strength of the carbon-containing alloys of this invention arises in part from the solid solution of tungsten and hafnium in niobium and in part from the precipitation of complex carbide phases of niobium and hafnium during the thermal-mechanical processing treatments.

It is preferred to subject the alloy of the present invention to a heat treatment in order to obtain an optimum combination of elevated temperature strength combined with adequate room temperature ductility. In this respect a heat treatment at a temperature slightly in excess of the carbon solvus temperature is desired in order to dissolve all carbides within the matrix of the alloy for later reprecipitation at favorable sites. Further, it has been found that a recrystallized microstructure which is characterized by at least about 85% recrystallization from the original crystal texture is effective for producing excellent results. To this end, a heat treatment at a temperature within the range between about 1700° C. and about 1750° C. for a time period of about 30 minutes to 2 hours followed by cooling to room temperature has produced outstanding results. Such heat treatment temperature is selected so that the upper end of the range is employed where lower amounts of working have been effected to the alloy and lower temperatures within the range are employed where the alloy has been subjected to prior reductions amounting to at least 75% in the cross sectional area of the alloy. The recrystallization heat treatment can be preformed without encountering substantial grain growth.

Table I represents the low temperature tensile data obtained from certain of the alloys of this invention with various heat treatments. For purposes of comparison, tensile data on two prior art alloys are included. The specimens tested were .200 inch in diameter by one inch gauge length.

TABLE I.—LOW TEMPERATURE TENSILE DATA

Specimen No.	Temperature (° C.)	Temperature (° F.)	0.2% yield strength (p.s.i.)	Ultimate strength (p.s.i.)	Elongation (percent) Uniform	Elongation (percent) Total	Reduction in area (percent)	Initial heat treatment
Nb-22W-2Hf:								
76-L-1	R.T.	R.T.	90,900	105,800	21.5	36.4	62.7	A
76-L-2	−73	−100	108,300	[1] 154,500	----	21.6	19.9	A
76-L-3	−129	−200	125,000	[1] 128,000	----	0.5	1.9	A
Nb-18W-2Hf; 77-L-1	R.T.	R.T.	75,000	91,200	19.2	35.3	73.4	A
Nb-22W-2Hf-0.13C:								
78-L-1	R.T.	R.T.	91,200	[1] 107,000	----	2.0	2.5	B
78-L-2	R.T.	R.T.	139,200	[1] 160,000	----	2.55	3.02	C
Nb-22W-2Hf-0.067C:								
79-L-1	R.T.	R.T.	86,000	[1] 109,200	----	6.0	6.7	B
79-L-2	R.T.	R.T.	142,200	[1] 163,500	----	3.35	4.04	C
Nb-28W-2Hf-0.067:								
80-L-2	R.T.	R.T.	121,200	[1] 136,500	----	1.78	1.93	A
T-33	R.T.	R.T.	119,300	137,300	----	11.3	8.8	D
Nb-5V-5Mo-1Zr (B-66)	R.T.	R.T.	88,200	111,800	----	33	----	[2].
Nb-20W-.9Zr-.1C (AS-30)	R.T.	R.T.	143,000	171,500	----	21	----	[3].

[1] True stress at fracture.
[2] Recrystallized 1,370° C.–1,480° C.
[3] Wrought and stress relieved.

NOTE.—A=Swaged and recrystallized 1 hour at 1,600° C.; B=Swaged and S.H.T. 2 hours at 2,000° C. helium quench; C=S.H.T. 2 hours at 2,000° C. helium quench and swaged plus 1 hour at 1,100° C.; D=Swaged and recrystallized 1 hour at 1,700° C. helium quench.

From the above table, it can be seen that the solid solution alloys and the carbon-containing alloys have essentially the same matrix strength at room temperature; i.e., from 85,000 to 90,000 p.s.i., but the solid solution alloys have much higher ductilities.

However, it should be understood that the low temperature properties of these alloys are not of over-riding importance, since the operating conditions the alloys must withstand particularly include an elevated temperature environment. The low temperature properties are of interest principally in that the relative workability of the alloys can be gauged.

The stress-rupture properties of the alloys of this invention are set forth in the following Table II together with properties of two prior art alloys.

TABLE II.—STRESS-RUPTURE DATA

Specimen No.	Temperature ° C.	Temperature ° F.	Stress (p.s.i.)	Rupture time (hours)	Minimum creep rate (percent/hour)	Transition time[1] (hours)	Reduction in area (percent)	Elongation (percent)	Initial heat treatment
Nb-22W-2Hf (VAM-76):									
76 T-1	1,205	2,200	30,000	22.3	0.042	4.2	76.8	27.3	A
76 T-2	1,205	2,200	35,000	1.0	7.90	0.4	76.8	26.7	A
76 T-3	1,205	2,200	28,000	27.1	0.028	5.0	78.2	22.0	A
76 T-4	1,095	2,000	45,000	1.1	2.83	0.5	79.8	20.7	A
76 T-5	1,205	2,200	25,000	93.8	0.014	30.0	81.8	16.7	A
76 T-6	1,095	2,000	37,000	25.8	0.0263	10.2	67.8	18.0	A
76 T-7	1,315	2,400	23,000	11.8	0.308	3.6	77.5	24.7	A
76 T-8	1,315	2,400	17,650	168.4	0.0255	30.0	85.6	38.7	A
76 T-9	1,205	2,200	31,000	2.2	----	----	----	----	A
Nb-18W-2Hf (VAM-77):									
77 T-1	1,205	2,200	25,000	39.7	0.034	12.5	85.0	18.7	A
77 T-2	1,205	2,200	22,000	127.6	0.009	44.0	88.4	32.0	A
Nb-22W-2Hf-.13C (VAM-78):									
78 T-1	1,205	2,200	40,000	97.7	0.018	83.5	----	4.0	B
78 T-2	1,205	2,200	45,000	21.6	0.066	16.0	----	2.98	B
78 T-3	1,095	2,000	58,400	54.1	0.0234	41.0	8.8	6.0	B
78 T-4	1,095	2,000	54,500	98.2	0.0120	85.0	12.9	4.0	B
78 T-5	1,315	2,400	33,000	4.4	0.3785	2.2	10.9	5.6	B
78 T-6	1,315	2,400	25,000	39.7	0.0666	23.5	10.9	6.0	B
78 T-7	1,205	2,200	45,000	4.3	0.976	1.4	36.2	16.0	C
78 T-8	1,205	2,200	40,000	8.7	0.4853	3.2	50.5	14.6	C
78 T-9	1,205	2,200	28,000	43.5	0.1152	10.0	75.9	26.0	C
Nb-22W-2Hf-.067C (VAM-79):									
79 T-1	1,205	2,200	40,000	8.3	0.189	7.7	12.3	3.3	B
79 T-2	1,205	2,200	37,000	46.4	0.0431	22.2	24.2	6.7	B
79 T-3	1,095	2,000	49,000	773.	0.0191	67.0	14.1	4.6	B
79 T-4	1,095	2,000	41,500	170.0	0.00653	126.0	14.0	3.3	B
79 T-6	1,205	2,200	40,000	1.95	----	----	----	----	B
79 T-7	1,315	2,400	25,000	32.8	0.0620	7.5	24.2	10.0	B
79 T-9	1,205	2,200	40,000	4.3	1.276	1.7	76.1	20.0	C
79 T-10	1,205	2,200	35,000	9.1	0.594	3.0	77.5	22.6	C
79 T-11	1,205	2,200	21,000	94.0	0.0801	16.0	80.5	26.6	C

See footnotes at end of table.

TABLE II—Continued

Specimen No.	Temperature ° C.	Temperature ° F.	Stress (p.s.i.)	Rupture time (hours)	Minimum creep rate (percent/hour)	Transition time [1] (hours)	Reduction in area (percent)	Elongation (percent)	Initial heat treatment
Nb-28W-2Hf-.067C (VAM-80):									
80 T-4	1,205	2,200	35,000	172.7	0.0112	143.0	12.0	4.0	B
80 T-5	1,205	2,200	40,000	52.2	0.0295	37.0	9.9	4.0	B
80 T-1	1,205	2,200	48,000	8.3	0.1138		1.1	1.33	B
80 T-2	1,315	2,400	30,000	44.7	0.0483	34.0	9.9	4.6	B
80 T-3	1,315	2,400	37,000	6.5	0.2420	4.8	12.0	4.0	B
B-66 Nb-5V-5Mo-1Zr	1,095	2,000	35,000	2.20					[2].
B-66 Nb-5V-5Mo-1Zr	1,095	2,000	25,000	14.2		4.0		47.0	[2].
AS-30 Nb-20W-.9Zr-.1C	1,095	2,000	53,000	10.0					[3].
	1,205	2,200	42,000	10.0					[3].
	1,095	2,000	43,000	100.0					[3].
	1,205	2,200	34,000	100.0					[3].

[1] Time to 3rd stage.
[2] Swaged and recrystallized 1370–1480° C.
[3] Wrought and stress relieved.

NOTE.—A=Swaged plus 1 hour at 1,600° C.; B=Swaged plus 2 hours at 2,000° C.-helium quench; C= 2/2,000° C., helium quench plus swaged plus 1 hour at 1,100° C.

From the above table and from FIGS. 1 and 2, it can be seen that the carbon-containing alloys of the invention are particularly resistant to creep deformation. The solid solution alloys (VAM–76 and VAM–77), while not as creep resistant as the carbon-containing alloys, are usefully resistant to creep deformation at temperatures as high as 2200° F. under stress of over 20,000 p.s.i. The advance achieved in the alloys of the invention, particularly with the carbon-containing alloys, can be measured against the prior art alloy AS–30 in FIG. 2 where heats VAM–78, VAM–79 and VAM–80 clearly show superiority over AS–30.

It is also seen from the data that the "B" heat treatment; i.e., swaging, followed by two hours at 2000° C., followed by quenching in helium, yielded better high temperature properties than the other heat treatments attempted.

The amount of tungsten in the alloys is determined by the requirement for high strength while avoiding excessive brittleness. At least 18% tungsten is required to achieve a strength of the order required while a tungsten content in excess of 30% will lead to excessive brittleness. The primary function of the hafnium in the alloy is to tie up the carbon as carbides which tend to pin dislocations in the material and thereby increase resistance to creep deformation. However, hafnium contents in excess of the upper limit of 5% will cause embrittlement of the alloys at room temperature.

Partial substitution of tantalum and rhenium for tungsten on a weight-for-weight basis has also been undertaken. Thus, alloys of the following compositions have been made and tested with results essentially equivalent to the unsubstituted alloys:

Nb-20W-2Re-2Hf-0.13C
Nb-22W-6Ta-2Hf-0.13C
Nb-26W-4Re-2Hf-0.067C

Up to 10% tantalum and up to 5% rhenum may be so employed. Generally from 1 to 10% weight of tantalum and from 1 to 5% by weight of rhenium will be used and these substitute elements may be used individually or in combination.

As indicated previously, the presence of carbon is extremely important in certain of the alloys of this invention. When the hafnium content is 2%, by weight, in these alloys and carbon is present in the stoichiometric proportion, the carbon content is 0.133%, by weight. The preferred amount of carbon, i.e., one-half the stoichiometric proportion, is 0.067%, by weight. Up to 0.05% by weight of nitrogen may be substituted for a like weight of carbon, if desired. Thus, a heat having the composition Nb-22W-2Hf-0.035C-0.04N was made and tested with results quite comparable to an alloy heat having carbon alone (VAM–79—0.067% C.).

In an application such as gas turbine buckets, the critical strength parameter is resistance to creep deformation at high stresses, for moderate times of the order of 100 hours.

The alloys were prepared in the form of two inch diameter double arc melted ingots. All alloys with intentional carbon additions had residual oxygen levels below 75 p.p.m., while the heats having no carbon additions had over 150 p.p.m. oxygen.

As mentioned above, the alloys of the invention are prepared employing a double consumable arc melting process. In this process, pure metal strips of tungsten, hafnium and niobium are tack welded together to form an electrode and this electrode is vacuum arc melted into a $1\frac{5}{16}$ inch diameter mold. Graphite cloth is used where additions of carbon are required. Ingots formed in this way are welded together to form an electrode and then remelted into a 2 inch diameter mold.

The as-melted ingots are lathe conditioned, cut in half, fitted with molybdenum nose plugs and plasma sprayed with molybdenum prior to extrusion. All the ingots are heated to a temperature in the range of 1200° C. to 1500° C. and then extruded in a high energy extrusion "Dynapak" press using an extrusion ratio of 5 or 6 to 1. The extruded bars are cropped and then surface conditioned by centerless grinding. The bars are swaged at from 1000° C. to 1270° C. from approximately 0.8 inch diameter to 0.44 inch diameter. Heating is accomplished in an argon purged retort between successive reductions of 25 to 40 mils per pass.

There have been disclosed niobium-base alloys having high strength at elevated temperatures and preferred alloys having both high strength at elevated temperatures and exceptionally high resistance to creep deformation.

It will be understood by those skilled in the art that although the present invention has been described with particular emphasis on selected alloy compositions, modifications and variations may be employed without departing from the underlying spirit and scope of the invention.

What we claim is:

1. A workable niobium-base alloy for use at elevated temperatures consisting essentially of, by weight, from about 27% to 29% tungsten, from about 1.5% to about 2.5% hafnium, carbon, sufficient to provide a carbon to hafnium atomic ratio of from 0.5 to 1.25, and the balance essentially niobium with incidental impurities, the alloy being characterized by high resistance to creep deformation and excellent strength at elevated temperatures within the range between 1800° F. and 2400° F.

2. The alloy of claim 1 wherein up to 0.05% by weight of nitrogen is substituted for an equal weight of carbon.

3. A heat treated article having a composition as set forth in claim 1 and which has been given a treatment including heating to a temperature within the range be-

tween about 1700° C. and about 1750° C. for a time period of from 30 minutes to 2 hours.

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CHARLES N. LOVELL, Primary Examiner

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