

1

3,243,290

TANTALUM BASE ALLOY

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This invention relates to high strength tantalum base alloys and, more particularly, to precipitation- and solid-solution-hardened tantalum alloys having high strength in the temperature range of 2400 to 3000° F. and higher combined with good low temperature ductility.

Tantalum possesses very valuable properties in having a melting point second only to tungsten among the more readily available refractory metals (W, Ta, Mo, Cb), along with inherent low-temperature ductility to an extent unique among the body-centered-cubic refractory metals. In fact, it has been shown that tantalum of sufficient purity does not undergo a ductile-to-brittle transition even at temperatures as low as -418° F. These properties, in spite of tantalum's high density, make the metal very attractive as a base for alloy systems to be characterized generally as having high tensile strength and creep resistance at elevated temperatures while still retaining good ductility at room temperature and lower in a worked, annealed, coated, or welded condition.

Other alloys (for example, many of the existing molybdenum-base, tungsten-base and columbium-base compositions) are not suitable for all desired applications in the temperature range of 2400 to 3000° F. due to low strength levels or difficulties in fabricating and welding, among other factors. Moreover, presently known tantalum base alloys also lack the proper combination of hot strength and low temperature ductility for certain applications.

Many studies have been made on the properties of various tantalum base alloys, and perhaps the most thoroughly investigated and best known of these is tantalum alloyed with 10% tungsten (all percentages given in this specification are by weight unless indicated otherwise). This alloy has been shown to have a 0.2% offset yield strength at 3000° F. of about 11,800 p.s.i. in a rolled condition. It is greatly desired to have tantalum base alloys with yield strength at 3000° F. of over 20,000 p.s.i. Furthermore, short time tensile tests are generally not determinative of the ultimate value of alloys for sustained use at high temperatures where creep can be a serious problem. Dispersion-hardenable alloys having fine and well distributed particles are generally more creep resistant than alloys hardened by solid solution means to the same levels of short time strength.

An object of this invention is to provide a tantalum base alloy of improved high-temperature strength combined with good low-temperature ductility; said alloy being hardenable by heat treatment as well as by working and resulting in a more readily fabricatable alloy with improved strength in the temperature range of 2400 to 3000° F. and higher.

Another object is to provide a tantalum base alloy which can be strengthened by heat treatment after working, annealing, coating, or welding, while still retaining good ductility at room temperature and lower.

Still another object is to provide a tantalum base alloy with improved strength and creep resistance at elevated temperatures without using any of the rare and more expensive noble metals including Re, Os, Ir, Ru and others.

These and other objects will become apparent from a reading of the present specification.

Briefly stated, in accordance with one aspect of this invention, a tantalum base alloy is provided including al-

2

loying elements of tungsten, carbon and at least one of the elements zirconium and hafnium in which the carbon content is about 0.01-0.5% but preferably about 0.02-0.2%, by weight, the Zr:C or Hf:C atomic ratio is between about 0.2:1 and 2:1, the zirconium or hafnium content is about 0.08-2.0%, and the tungsten content is about 8-12%.

It has been found that previously unknown strength levels at 3000° F. can be obtained in improved tantalum base alloys by the addition of critical amounts and proportions of zirconium or hafnium and carbon to a Ta-10W alloy. The resulting alloy bodies can be precipitation hardened by appropriate heat treatments regardless of the prior thermal and mechanical history of the body within the limits of reasonable and normal procedures. More specifically, they can be heat treated to develop high temperature strength after fusion welding, high-temperature coating procedures, or annealing. Generally, a dispersion hardening mechanism also allows the use of the alloys at higher sustained stress levels than are possible with solid-solution-hardened alloys of comparable room temperature strength. It has been found that dispersion hardening and solution hardening can be superimposed in tantalum base alloys containing about 10% tungsten with unexpected results apparently of a synergistic nature; that is, alloys of the present invention have better high temperature strength than would be expected by the simple addition of the properties of comparable alloys hardened by each of the mechanisms alone. Moreover, and also unexpectedly, the alloys of the present invention retained good ductility at low temperatures, even as low as -320° F.

The invention employs a basic alloying system having high temperature strength and creep resistance which is ductile and fabricatable at room temperature and exhibits usable ductility at the temperatures of liquefied gases such as might be encountered in some extreme applications. The desired results make it necessary to eliminate low-melting constituents from consideration. Molybdenum as a substitute for either all or part of the tungsten in a 10% tungsten alloy has a deleterious effect on weld ductility and most probably also on high temperature creep.

Rhenium and other like metals are rare and very expensive in comparison to tantalum, zirconium and hafnium. Although such metals do offer interesting possibilities for improving the 2400-3000° F. strength of tantalum base alloys, the present invention demonstrates that their use as alloying constituents appears not to be required and therefore uneconomical in this temperature range.

Other elements such as columbium, vanadium, hafnium, zirconium, and titanium are undesirable as major alloying additions for solid-solution strengthening purposes due primarily to their melting temperatures being much lower than that of tantalum. Large differences in melting temperature and high vapor pressure of alloy constituents result in serious interdendritic- and macro-segregation on melting and seriously objectionable micro-segregation as a result of fusion welding. Also, lower melting metals such as molybdenum serve to increase atomic mobility in tantalum base alloys, thereby directly lowering high temperature creep resistance.

For these reasons, only tungsten was considered as a major alloying addition in the experimental work leading to this invention. Additions of tungsten much greater than 10%, such as greater than about 12%, are known to lead to marginal low temperature ductility. However, tungsten additions much below 10% contribute less to the alloy's strength and, at low enough levels, such as below about 8%, would not possess strength-to-weight ratios much better than those of existing columbium base alloys.

Therefore, the tantalum-10% tungsten alloy was selected for studies in the superimposing of dispersion hardening mechanisms on solid-solution strengthening in tantalum base alloys. This is considered to be the binary solid-solution alloy of this system having the maximum strength and strength-to-weight ratio compatible with optimum weld ductility and fabricability.

Patent 3,056,672—Clark, patented October 2, 1962, and assigned to the assignee of this application, shows that a very critical relation exists in the atomic ratio of zirconium to carbon in a columbium base alloy containing 20% tungsten and 2%, 1% or 0.5% zirconium. The present invention concerns a different alloying system, namely tantalum rather than columbium and provides useful strength at much higher temperatures than do the alloys of Patent 3,056,672. As is well known, properties of complex alloys, such as high temperature strength and fabricability, cannot be accurately predicted from one alloy system to another. Strength, ductility and fabricability are not presently susceptible of theoretical prediction, although analysis after the fact often is possible. The mechanisms operable in columbium base alloys at 2000–2200° F. are not considered to be fundamentally analogous to the mechanisms operable in tantalum alloys in the temperature range of 2400–3000° F. Evidence of one such difference is presented in the data of Example II below which shows good properties in an alloy having a Zr:C atomic ratio of only about 0.23. The data in Example I also tends to show improved properties when the Zr:C ratio exceeds unity. According to Patent 3,056,672, such a ratio as 0.23 would not produce the desired results in a Cb-20W-Zr-C alloy.

Dispersion hardening mechanisms generally can be classified in two groups: (1) permanent solid particle dispersion, and (2) precipitation hardening. Precipitation hardening is the reversible one of these two modes, and it allows the use of procedures in which the metal is worked in a relatively soft condition and then hardened by heat treatment. The time and temperature combinations encountered in some of the more complex coating and welding procedures demand alloys the strengths of which can be adjusted after severe heat treatment without the necessity of further metal deformation.

A group of tantalum alloys containing about 10% tungsten has been discovered, which alloys can be hardened by a precipitation mechanism after various thermal and mechanical histories. Conversely, of course, the alloys can be softened for further malleability or ductility by solution heat treatments after various prior treatments. Optimum creep resistance occurs with a uniform, fine dispersion of ZrC, (Zr,Ta)C, HfC, (Hf,Ta)C, or a combination of these.

It has been discovered that carbon limits of 0.01–0.2% are preferable for optimum creep resistance in the temperature range of 2400 to 3000° F. Certain small amounts of carbon are soluble in the basic solid-solution alloy, but the solubility limit of carbon in tantalum at 3000° F. is not definitely known. For precipitation hardening, there must be enough carbon present above the solubility limit to react with the active metals and form carbides. On the other hand, for good weldability, the carbon content should be the minimum imparting the required strength at the intended use temperature. This means that the carbon content should be substantially but not excessively above the amount soluble at the intended use temperature. The amount of carbon soluble at 2400° F. is thought to be below 0.01%, at 3000° F. in the region of 0.04% and at 3500° F. in the region of 0.1–0.2%. Therefore, about 0.01% carbon is the minimum used in alloys of this invention. Carbon contents above 0.5% are considered to be high enough to lead to interdentritic carbide precipitation in the fusion zones of weldments, thereby vitiating the effect of any heat treatment used to minimize possible weld embrittlement. This consideration

establishes about 0.5% as the upper limit of carbon in alloys of the invention.

Carbides of the Group IV–A metals (Ti, Zr, Hf) have a significantly higher thermodynamic stability than carbides of the Group V–A metals such as tantalum. This factor makes IV–A metal-carbide precipitation hardening of tantalum base alloys possible. If carbon and Group IV–A metals are present in the proper ratios in a tantalum base alloy, mono-metal carbides will form preferentially rather than the lower melting di-metal carbides which would generally form massive deposits. Assuming good homogeneity, TiC, ZrC, HfC or complex mono-metal carbides, i.e., $(Ta_{1-x}Zr_x)C$, will precipitate as uniform fine dispersions not preferentially oriented or segregated as in Widmanstätten patterns or in the grain boundaries. Complex mono-metal carbides such as $(Ta_{1-x}Zr_x)C$, which has an exceptionally high melting point, may form and aid in strengthening the alloys.

It should be noted that titanium, zirconium, and hafnium, added in small amounts for carbide precipitation, behave in a manner far different from that of the same elements used in larger quantities as major solid solution hardeners; however, the melting point of titanium is too low, and its vapor pressure too high for it to be a practical addition to melted tantalum alloys.

Table I presents the approximate melting temperatures of various metals and compounds along with metal vapor pressures at the melting point of tantalum.

TABLE I

Metal	Melting Point (° F)	Vapor Pressure (mm.Hg) 5,425° F	Carbide	Melting Point (° F)
Ti	3,035	200	TiC	5,700
Zr	3,365	1	ZrC	6,415
Hf	4,035	1	HfC	7,030
Mo	4,730	0.4	MoC	4,875
W	6,170	0.001	WC	5,195
			TaC	6,870
Ta	5,425	0.006	Ta ₂ C	6,150
			TaC-ZrC	7,110

It is important to avoid the formation of large di-metal carbide particles such as Ta₂C and $(Ta_{2-x}Zr_x)C$ which do not strengthen the alloy. For this reason, the zirconium or hafnium levels in alloys of the invention should be sufficient to react with residual nitrogen and oxygen and have enough left over to cause formation of the mono-metal carbides rather than the di-metal carbides.

The ratio of Group IV–A metals to carbon appears critical. It must be large enough to allow the formation of significant amounts of mono-metal carbides for strengthening but not substantially larger than this. The presence of too much IV–A metal would be deleterious to strength at elevated temperatures and also to homogeneity after melting or welding. Example II below shows that a Zr:C atomic ratio as low as 0.23:1 is satisfactory in alloys of the invention, and Example I shows improved properties at Zr:C ratios near 1.5:1 in such alloys. A ratio of much over 2:1 would leave too much IV–A metal in solid solution. Therefore, the Zr:C or Hf:C atomic ratio in alloys of the invention is from about 0.2:1 to about 2:1.

Table II indicates some of the approximate weight percentages of Zr and Hf established by the above carbon content and ratio limitations.

TABLE II

Atomic Ratio Zr:C or Hf:C	C (wt. percent)	Zr (wt. percent)	Hf (wt. percent)
0.2	0.01	0.015	0.028
	0.2	0.31	0.59
	0.5	0.76	1.49
2.0	0.01	0.15	0.23
	0.2	3.1	5.9
	0.5	7.6	14.9

Regardless of the maximum levels set by Table II, it is believed that the practical maximum limit of Group IV—A metal determined by the solid-solution criterion expressed above is about 2% for zirconium and 4% for hafnium. Mixtures of Zr and Hf within these maximum levels can also be used.

Several alloy compositions have been evaluated and unexpectedly good results have been obtained. For a clearer understanding of the invention, specific examples are given below. These examples are merely illustrative of the invention and do not define its limits, which are set forth in the appended claims.

Example I

Tantalum-10% tungsten alloys with varying amounts of zirconium and carbon were melted by consumable electrode techniques to approximately 500 gram ingots in a water cooled crucible. Following melting, the ingots were turned on a lathe to clean up the side walls, then homogenized by heating in vacuum to 3,750° F. for one hour. This heat treatment substantially dissolved the carbides, thereby promoting increased fabricability and allowing precipitation strengthening later in the processing schedule. The ingots, which were 1 inch diameter, were impact extruded to $\frac{3}{16}$ " diameter rods. The rods were machined to about $\frac{1}{2}$ " diameter and then swaged to about $\frac{1}{4}$ " diameter in a temperature range of 2,200 to 2,050° F. in argon. The swaged rod was centerless-ground into conventional button-head specimens which were heat treated at 2,000° F. for one-half hour in vacuum.

Table III presents the compositions and the hardness and tensile data obtained with the specimens. In the tables, testing temperatures are given in degrees Fahrenheit, UTS stands for ultimate tensile strength in thousands of pounds per square inch, YS is the 0.2% offset yield strength also measured in thousands of pounds per square inch, the elongation is measured over a three-quarter inch gage length, percent RA is percent reduction in area, and

Example II

A 44-lb. ingot having a nominal percentage composition of Ta-10W-1.3Zr-0.075C was mixed, pressed, pre-sintered and triple melted by electron beam technique. Analysis of the melted alloy was Ta-9.4W-0.08Zr-0.046C (Zr:C atomic ratio 0.23:1) with interstitial levels of oxygen at 22 ± 10 p.p.m., nitrogen at 5 p.p.m. and hydrogen at 2 p.p.m. The cast ingot had an average grain size of 180 grams per square centimeter and a hardness of 257 ± 5 VHN, as an average of 5 readings. Short time tensile properties of the cast material are shown in Table IV.

TABLE IV

Test Temp. (° F.)	TS	YS	Percent EL	Percent RA
75.....	88.9	70.5	8.2	18.4
2,200.....	39.8	28.8	20.4	36.4
2,950.....	25.3	21.4	9.65	-----

After machining the ingot to 3.5 inch diameter it was canned in molybdenum with a $\frac{1}{16}$ " wall thickness and extruded to a rectangular bar at 1725° C. (3,137° F.) with the heating being done in an argon atmosphere. The extrusion ratio was approximately 3.0 to 1. After extrusion, the molybdenum jacket was removed and the billet was annealed at 1350° C. (2,462° F.) for one hour. The billet was then jacketed in a steel can $\frac{1}{8}$ " thick and rolled at 1,100° C. (2,012° F.) using an argon atmosphere for heating and a reduction of about 20% per pass for a total reduction of approximately 60%. The rolled alloy was then annealed at 1,350° C., re-jacketed in steel and rolled another 60% total reduction to approximately 0.310" thickness at 1,000° C. (1,832° F.) with heating being done in an argon atmosphere. Final rolling was done without cladding to a finish size of 0.100" at 650° C. (1,202° F.) with heating still being conducted in argon.

Tensile tests performed on this sheet are presented in Table V wherein ReX stands for recrystallized.

TABLE V

Test Temp. (° F.)	TS	YS	Percent EL	Remarks
-320 (Liquid nitrogen).....	178.6	167.9	28.0	(Annealed at 2,200° F., $\frac{1}{2}$ hr.).
75.....	113	93	27.5	Rollled.
3,000.....	21.4	16.7	83.0	
3,500.....	11.4	10.3	18.0	(ReX at 3,900° F., 1 hr.).
	11.8	10.2	42.0	(ReX at 2,950° F., $\frac{1}{2}$ hr.).

VHN stands for Vicker's Hardness Number which is given in both the as-cast and the homogenized conditions (3,750° F./one hour).

Finally, sheet samples were annealed at various temperatures for one hour, and furnace cooled. Hardness tests were then made. The VHN results are presented

TABLE III

[PROPERTIES OF TANTALUM ALLOYS]

Composition (Wt. percent)	M/C Ratio ^a	Test Temp. (°)	Tensile Properties ^b				Hardness Cast	(VHN) Homog.
			UTS (k.s.i.)	0.2% YS (k.s.i.)	Elong. (percent)	R.A. (percent)		
10 W, 0.6 Zr, 0.058 C.....	1.37	75	175	154	16	36	318	302
		2,200	104	95	>4	>8		
		3,000	29	21	40	41		
		75	171	169	3	5		
10 W, 0.6 Zr, 0.093 C.....	0.85	2,200	92	69	6	7	355	310
		3,000	21	16	48	50		
		75	183	176	10	21		
		2,200	145	136	9	13		
10 W, 1.2 Zr, .109 C.....	1.45	3,000	102	96	24	45	372	335
		75	145	136	9	13		
		2,200	102	96	24	45		
		3,000	>30	25	-----	-----		

^a Atomic ratio of reactive-metal: carbon.

^b Nominal strain rate of 0.01 in./in./min.

^c Annealed 3,000° F. prior to test. All others annealed 2,000° F. $\frac{1}{2}$ hr.

in Table VI. Longitudinal tests are those made on the flat surface of the sheet, and transverse tests are those made on the sheet ends.

TABLE VI

Temperature ° F.	1,830	2,200	2,550	2,900	3,270	3,630	4,000
Longitudinal.....	334	298	246	256	297	311	267
Transverse.....	332	300	243	258	290	300	279

Metallography on these hardness test samples showed the one hour 50% recrystallization temperature of the material in this condition to be about 2,550° F. The hardness data indicate no significant directionality. Also, strengthening has occurred as a consequence of annealing in the temperature range of 3,270–3,630° F. This can be attributed to aging (precipitation) either at temperature or during furnace cooling. The lower hardness after annealing at 4,000° F. may have resulted from some decarburization. These data indicate that the material can be strengthened by precipitation heat treatment after working, annealing at high temperatures, or fusion welding. It is significant to note that this alloy is near the low end of the zirconium and carbon ranges of alloys of the invention. It can be assumed that alloys with different amounts of zirconium or hafnium and carbon could be aged at different temperatures. Also, of course, different heat treatment can be used to age harden such alloys.

These examples have shown that alloys of the present invention have exceptional strength and ductility at –320° F., very high ductility at room temperature and quite significant retention of strength at temperatures up to 3,000° F. and higher.

Examples I and II show that alloys of the invention can be fabricated into sheet and rod forms and that they have unexpectedly good mechanical properties at both high and low temperatures. The data suggest that high-temperature properties can be substantially improved by appropriate heat treatment.

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

What we claim as new and desire to secure by Letters Patent of the United States is:

1. An improved tantalum base alloy consisting of, by weight: about 8–12% W; about 0.01 to 0.5% C; at least one Group IV–A metal selected from the group consisting of Zr in an amount less than 2% and Hf in an amount less than 4%, with the atomic ratio of Group IV–A metal to carbon being between about 0.2:1 and 2:1, the balance being Ta and incidental impurities.

2. An improved tantalum base alloy characterized by a 0.2% offset yield strength of over 20,000 p.s.i. at 3,000° F.; and consisting of, by weight: about 8–12% W; about 0.1–1.5% Zr; about 0.05 to 0.15% C; the atomic ratio of Zr:C being between 0.5:1 and 2:1, with the balance Ta and incidental impurities.

3. An improved tantalum base alloy consisting of, by weight: about 10% W; about 0.05–0.1% Zr, about 0.02–0.05% C; with the balance Ta and incidental impurities.

4. An improved tantalum base alloy consisting of, by weight: about 10% W; about 0.6% Zr; about 0.06% C; with the balance Ta and incidental impurities.

5. An improved tantalum base alloy consisting of, by weight: about 10% W; about 1.2% Zr; about 0.11% C; with the balance Ta and incidental impurities.

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