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TUNGSTEN-HAFNIUM-OXYGEN ALLOYS

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ABSTRACT OF THE DISCLOSURE

Tungsten-base alloys containing, by weight, 1–7% hafnium and 0.03–0.12% oxygen, along with optional elements, have been found to have useful strength properties. This unusual high oxygen content can be obtained by powder metallurgical processes not using carbon which would otherwise volatilize the oxygen content. Hafnium oxide dispersions strengthen these alloys.

The present invention relates generally to tungsten-base alloys useful in high temperature applications, and more specifically relates to such alloys containing both hafnium and oxygen in material amounts.

Previously known alloys of tungsten containing hafnium generally also include carbon in combination with the hafnium constituent. All alloys are subject to limitations on their utility due to their mechanical and metallurgical characteristics. In particular, the utilities of known tungsten-hafnium-carbon alloys have limits depending upon the fabricability of the metal, especially in the alloys containing larger amounts of hafnium and carbon, and also depending on such other factors as stability of hafnium carbides in the tungsten matrix. Each of these factors can be affected strongly by the contained amounts and proportions of alloying additives including and in addition to hafnium and carbon.

Although in certain cases one alloy system cannot be categorically stated to be superior to another, it often can be determined that certain properties of one type of alloy are significantly more useful in certain applications than are related properties of another type of alloy. Thus, it is desirable to provide different types of alloy systems that may be found to be superior in certain applications to known alloy systems.

Accordingly, it is an object of the present invention to provide tungsten-base alloys containing dispersoids, which alloys are different from and in some aspects superior to many known tungsten-base alloys in certain characteristics.

It is further the object of the invention to provide such alloys that are superior to many known tungsten-base alloys in workability and fabricability.

Still another object of the invention is to provide such alloys which are superior to many known tungsten-base alloys in applications at elevated temperatures.

Briefly stated, the present invention in one form provides tungsten-hafnium-oxygen alloys having desirable characteristics different from, and in some cases superior to presently known alloys. Alloys of the invention contain, by weight, about: 1–7% hafnium, 0.03–0.12% oxygen, not more than 10% of metal selected from the group consisting of columbium, molybdenum, tantalum, rhenium and mixtures thereof, not more than 2% of metal selected from the group consisting of zirconium, titanium and vanadium and mixtures thereof, and not more than 0.25% boron, the balance essentially all tungsten. Preferably, the oxygen content of the alloys of the invention is 0.06–0.09%. The elements specified in amount "not more than" certain percentages are entirely optional, and the term "not more than" is meant to include an amount of zero. Specifically preferred alloys of the invention include the preferred range of oxygen content along with hafnium in amounts of about 1%, 2.9 or 3%, and 6.6 or 7%. Percentages herein are given by weight except where specified otherwise.

By the use of large amounts of oxygen which, even in smallest amounts, was considered by the prior art to be deleterious and to render alloys unusable, the alloys of the present invention are provided with strengths and stabilities that are quite useful and in some cases superior to those previously generally known in tungsten-base alloys. While previously known alloys were considered to require that oxygen contents be no more than 50 or even 35 parts per million by weight (p.p.m.), I have found that the alloys of the invention beneficially contain oxygen within the limits of 300–1200 p.p.m., and preferably 600–900 p.p.m. oxygen.

Alloys of the invention have been prepared by mixing together freshly reduced tungsten metal powders and hafnium hydride powders according to predetermined nominal compositions, pressing them into compacts and sintering in vacuum. An analysis of the starting materials is presented in Table I below with the quantities given in p.p.m. except where expressed otherwise.

TABLE I.—ANALYTICAL DATA AND PARTICLE SIZE OF STARTING MATERIAL

Material	C	O	N	H	Mo	Zr	Fe	Ta	Particle Size
W	20	120	----	----	40	----	----	<200	4 microns.
HfH_3	<180	700	29	1.1%	20	3%	120	----	−325 mesh.

In addition to the impurities noted in the table, the tungsten contained less than 10 p.p.m. of other impurities. These materials were premixed in a twin shell blender, and then thoroughly blended for about four hours in a tungsten rod mill. Compacts were then made by hydrostatic pressing in a rubber sleeve at a pressure of about 35,000 p.s.i.

Following a vacuum pre-sintering treatment at 1050° C. for two hours, the ingots were finally sintered at 2800° C. for two hours in a dynamic vacuum of less than 10^{-5} torr. Above the dissociation temperature of hafnium hydride of about 600° C., the small amounts of tungsten oxide on the surface of the tungsten metal powder continued to evaporate and react with the nascent hafnium surfaces, thus resulting in a significant pickup of oxygen by hafnium during sintering. Since material quantities of carbon were not present in the compacts, the oxygen became usefully associated with the hafnium rather than being volatilized out of the compact. The hafnium oxide dispersoid particles thus formed perform a useful function in greatly strengthening the alloys while also allowing them to be worked at elevated temperatures. Subsequent to the sintering operation, the alloys were analyzed, and the results of these tests are presented in Table II below. The values are in p.p.m. except for hafnium which is expressed in percentages.

TABLE II.—ALLOY COMPOSITIONS AND ANALYSES

	Analysis				
	Hf	C	O	N	H
Nominal Composition:					
W-1Hf	1.0	<10	610	6	1
W-3Hf	2.9	<10	695	3	1
W-7Hf	6.6	20	860	4	2

The sintered ingots were from 92–95% of theoretical density. They were machined to cylinders one inch in diameter by 2.5 inches long with a 45° chamfered nose. The cylinders were extruded at a 10:1 ratio to 0.350 inch diameter rods in a high energy rate extrusion apparatus. Hardness and grain size measurements were taken on the

as-extruded alloys and are presented in Table III below. VPH stands for Vickers pyramid hardness.

TABLE III.—HARDNESS AND GRAIN SIZE

	Extrusion Temp., ° C.	Grain Size, microns	VPH, kg./mm.²
Nominal Composition:			
W-1Hf	2,050	27	378
W-3Hf	2,100	7	477
W-7Hf	2,310	9	517

Tensile tests in vacuum were performed on button-head specimens ground from the extruded rods. These specimens had a gauge diameter of 0.160 inch and a gauge length of one inch. The specimens were tested at a strain rate of 8.3×10^{-4} per second at a pressure of less than 10^{-5} torr. Table IV below presents the results of this testing in comparison with similar testing done on unalloyed tungsten. UTS stands for ultimate tensile strength, K s.i. stands for thousand pounds per square inch, and 0.2% YS stands for the 0.2% offset yield strength.

TABLE IV.—HIGH TEMPERATURE TENSILE DATA

	Temperature, ° C.	UTS, K s.i.	0.2% YS, K s.i.	Elongation, percent
Nominal Composition:				
W	1,649	15.4	8.3	65.1
	1,927	8.9	4.9	36.8
	2,206	6.0	3.4	32.4
W-1Hf	1,649	48.2	30.4	36.2
	1,927	26.9	18.1	38.6
	2,206	12.6	11.1	12.7
W-3Hf	1,649	63.7	47.5	20.5
	1,927	41.4	36.1	19.9
	2,206	21.0	18.5	13.8
W-7Hf	1,649	49.1	30.1	19.5
	1,927			
	2,206			

It can be seen from the table that these alloys are significantly stronger than unalloyed tungsten at elevated temperatures. In addition, the alloy containing 7% hafnium is considerably stronger than most previously known tungsten-base alloys.

It is contemplated by the appended claims to cover any such modifications as fall within the true spirit of the scope of this invention.

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

1. A sintered tungsten-base alloy consisting essentially of about, by weight: 1–7% hafnium, 0.03–0.12% oxygen, not more than 10% of metal selected from the group consisting of columbium, molybdenum, tantalum, rhenium and mixtures thereof, not more than 2% of metal selected from the group consisting of zirconium, titanium and vanadium and mixtures thereof, and not more than 0.25% of boron, the balance essentially all tungsten, said alloy containing hafnium oxide dispersoid particles therein.

2. A sintered tungsten-base alloy consisting essentially of about, by weight: 1–7% hafnium, 0.06–0.09% oxygen, not more than 10% of metal selected from the group consisting of columbium, molybdenum, tantalum, rhenium and mixtures thereof, not more than 2% of metal selected from the group consisting of zirconium, titanium, and vanadium and mixtures thereof, and not more than 0.25% of boron, the balance essentially all tungsten, said alloy containing hafnium oxide dispersoid particles therein.

3. A sintered tungsten-base alloy consisting essentially of about, by weight: 1% hafnium, 0.06–0.09% oxygen, the balance essentially all tungsten, said alloy containing hafnium oxide dispersoid particles therein.

4. A sintered tungsten-base alloy consisting essentially of about, by weight: 2.9% hafnium and 0.06–0.09% oxygen, the balance essentially all tungsten, said alloy containing hafnium oxide dispersoid particles therein.

5. A sintered tungsten-base alloy consisting essentially of about, by weight: 6.6% hafnium and 0.06–0.09% oxygen, the balance essentially all tungsten, said alloy containing hafnium oxide dispersoid particles therein.

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