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[54] **HAFNIUM BASE ALLOY (IRIDIUM)**
7 Claims, No Drawings

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[50] **Field of Search** 75/134.4, 172, 174, 177

[56] **References Cited**

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ABSTRACT: Hafnium base alloy containing between about 15 and about 35 weight percent tantalum and between about 2 and about 20 weight percent iridium. The alloy may also contain aluminum, silicon or chromium as additional alloying agents.

HAFNIUM BASE ALLOY (IRIDIUM)

This invention relates generally to hafnium base alloys, and more particularly it relates to hafnium-tantalum alloys having improved oxidation and corrosion resistance at elevated temperatures.

There has existed for some time a need for ductile structural metals and alloys which have good corrosion and oxidation resistance at elevated temperatures, e.g., above 2,200° F. In addition to corrosion resistance, a desirable metal should have good structural strength at temperatures above 2,200° F. and should be able to be fabricated and worked both before and after exposure to high temperature oxidation. The corrosion resistant metal should also be capable of being welded without embrittlement.

Hafnium is a ductile metal which has a melting point above 4,000° F. The ductility of hafnium is such that is does not possess good structural strength at elevated temperatures. The addition of between about 15 to about 60 weight percent tantalum to hafnium provides a hafnium-tantalum alloy which has sufficient strength at elevated temperatures to be useful in the manufacture of structural parts. Hafnium-tantalum alloys are also readily fabricated by hot working at 1,800° F. to 2500° F., and when the alloys contain relatively large amounts of tantalum, the alloys may be made cold workable by heat treatment and/or by the addition of minor amounts of molybdenum.

Hafnium oxidizes more slowly than does tantalum at temperatures above 2000° F. to form a stable dioxide, HfO_2. However, the hafnium-tantalum oxide surface scale layer which forms on the surface of hafnium-tantalum alloys upon oxidation at high temperatures affords limited protection against oxidation, principally because of the high oxygen mobility of hafnium-tantalum oxide, and the spalling of the hafnium-tantalum oxide surface scale layer due to the mismatch in the expansion coefficient of the hafnium-tantalum oxide scale as compared to the expansion coefficient of metallic hafnium-tantalum alloys substrate. Hafnium-tantalum oxide is also quite porous which permits diffusion of oxygen through the oxide layer to the metallic surface, resulting in further undesirable oxidation.

Hafnium-tantalum alloys containing between about 15 and about 35 weight percent tantalum have been found to have desired structural strength and fabricability both before and after high temperature oxidation. However, exposure of hafnium-tantalum alloys to oxidative corrosion at temperatures above 2,000° F. **results in extensive spalling of the protective oxide layer which forms on the surface of the alloy. This spalling is sufficiently severe that failure occurs after high temperature oxidation exposure of** 30 hours or less. Generally, the best oxidation resistance of the binary hafnium-tantalum alloys is obtained when the alloy contains between about 20 and about 25 weight percent tantalum. However, binary hafnium-tantalum alloys containing 20 to 25 weight percent tantalum do not exhibit useful lives greater than about 30 hours exposure to oxidation at 2500° F.

It is a principal object of the invention to provide improved hafnium base alloys. A further object is to provide hafnium-tantalum alloys having improved high temperature resistance to oxidation. A further object is to provide hafnium-tantalum alloys of good structural strength and fabricability which are able to withstand extended exposure to high temperature oxidative environments. Another object is to provide hafnium-tantalum alloys which are able to withstand cyclic temperature environments without excessive oxidation. Still another object is to provide hafnium-tantalum alloys which exhibit improved resistance to oxidation at high temperatures, and also exhibit resistance to oxidation at lower temperatures.

These and other objects of the invention will be more readily understood from the following detailed description.

Generally, the invention is directed to a hafnium base alloy which includes between about 5 and about 35 weight percent tantalum, and between about 2 and about 20 weight percent iridium. A preferred alloy may also include at least one additional alloying agent selected from aluminum, silicon and chromium. The additional alloying agents may be present in the hafnium-tantalum-iridium alloy in varying amounts, depending on the particular additional alloying agent, and the presence of other of the additional alloying agents. Aluminum may be present in an amount between 0 and 2.5 weight percent, and silicon may be present in an amount between 0 and about 1.6 weight percent. Chromium may be present in an amount between 0 and about 1.5 weight percent. The addition of substantially greater than about 1.5 percent chromium tends to cause spalling of the oxide scale, and for most purposes it is generally desirable to maintain the chromium content below about 1.5 percent. Particularly desirable alloys are those containing about 1.3 weight percent aluminum and about 0.8 weight percent silicon, and those containing about 1.3 weight percent aluminum, about 0.8 weight percent silicon and about 0.6 weight percent chromium.

As indicated, the base metal of the improved alloy composition is hafnium. Generally, the hafnium should be of high purity, but minor amounts of those impurities normally associated with hafnium, such as zirconium can be tolerated. It is to be understood that use of the term "hafnium" is intended to include those impurities normally associated with commercial grades of hafnium.

The alloy may include between about 5 percent and about 35 weight percent tantalum, which may be any commercial grade of tantalum along with the impurities normally associated therewith. It has been determined that if the tantalum content exceeds about 35 weight percent, the high temperature oxidation resistance of the resulting alloy is reduced. Below about 5 weight percent tantalum, the resulting hafnium-tantalum alloy does not have desired structural strength or oxidation resistance. When the alloy is a ternary hafnium-tantalum-iridium alloy, the tantalum content is preferably between about 20 and about 30 weight percent to provide the best combination of structural strength and resistance to high temperature oxidation. When the alloy contains the described additional alloying agents, higher or lower tantalum concentration can be permitted without detrimentally affecting the properties of the alloy.

As indicated, the surface oxide scale layer which is formed on binary hafnium-tantalum alloys when exposed to oxidative environments at high temperatures, e.g., 2500° F., is relatively porous and friable, which permits excessive oxygen mobility through the oxide scale to the metal substrate. Further, the expansion mismatch between the oxide scale layer and the alloy substrate results in extensive spalling upon extended exposure to oxidation at high temperatures.

It has been determined that the addition of specific alloying agents to hafnium-tantalum alloys substantially improved the ability of the hafnium-tantalum alloy to withstand extended exposure to high temperature oxidation. The addition of the alloying agents decreases the porosity and modifies the structure of the oxide scale layer formed during high temperature oxidation. This lessens diffusion of oxygen to the alloy substrate surface and decreases the rate of corrosion. In addition, it has been found the addition of certain alloying agents modifies the metal plus oxide subscale layer which exists between the outer fully oxidized surface scale layer and the alloy substrate.

Hafnium-tantalum alloys improved resistance to high temperature oxidation may be obtained through the addition of a minor amount of iridium, desirably between about 2 and about 20 weight percent.

For most purposes, the iridium content of the alloy is desirably between about 2 and about 15 weight percent, further additions of iridium not providing corresponding increases in oxidation resistance. Preferred alloy compositions are those containing between about 5 and about 10 weight percent iridium.

Although the ternary hafnium-tantalum-iridium alloys have good resistance to high temperature oxidation and are sufficient for most purposes, it has been found that the addition of

certain additional alloying agents improves and enhances the high temperature oxidation resistance of the described hafnium-tantalum-iridium alloys. Specifically, the addition of aluminum or silicon, and to a lesser extent, the addition of chromium, substantially provides desirable improvements in the oxidation resistance of the alloys.

Aluminum is particularly desirable because of the minimal growth and weight gain of the alloy during oxidation, as compared to alloys which do not contain aluminum. Examination of oxidized alloys containing aluminum show that the addition of aluminum to the hafnium-tantalum-iridium alloy produces a dense nonporous surface oxide layer and a subscale layer which is a dispersion of metal and oxide phases, resulting in a much slower oxygen diffusion rate than with alloys which do not contain aluminum.

The aluminum content of the alloy is between 0 and about 2.5 weight percent, preferably between about 0.5 and about 2 weight percent for most purposes. Increasing the aluminum content above about 2.5 weight percent does not provide increased oxidation resistance, and may, in some instances, act to reduce to oxidation resistance of the alloy.

Improved oxidation resistance may also be obtained through the addition of silicon to the alloy in an mount between 0 and about 1.6 weight percent, preferably between about 0.5 and about 1.0 weight percent, and through the addition of chromium in an amount between 0 and about 1.5 weight percent. For best results and lowest weight gain these additional alloying agents are combined with aluminum. Chromium does not provide significant improvements over alloys which do not contain chromium, but the presence of chromium in amounts below about 1.5 weight percent does not detract from the oxidation resistance of the alloy.

Resistance to high temperature oxidative corrosion is determined by exposure of 15 gram arc melted buttons of the various alloys to high temperature oxidation for varying periods of time. In all of the tests set forth herein the alloy buttons were annealed at 2500° F. for 2 hours prior to oxidation. During the oxidation tests the buttons were supported in high purity alumina boats in the ambient atmosphere. The samples were considered to fail when one or more of the following effects were observed; (1) excessive spalling, (2) extensive cracking of the surface oxide scale layer, or (3) high weight gain.

Generally, cracking of the surface oxide scale is not considered to be a failure unless accompanied by one of the other effects. However, in most tests if cracking of the oxide scale layer occurred, the test was terminated after the next exposure cycle. The oxidation rate of each of the alloy buttons was measured in terms of weight increase, as compared to original weight. Measurement of percent weight gain is an accurate method of comparing the oxidation resistance of alloys of similar composition and size, but should not be used to quantitatively compare the oxidation resistance of alloys containing widely varying alloying agents due to the differences in rate of oxidation and affinity for oxygen of the different alloying agents.

There is set forth in table I the results of oxidation studies in static ambient air at 2500° F. of hafnium-tantalum alloys containing iridium as the sole alloying agent and hafnium-tantalum alloys containing iridium and various combinations of the additional alloying agents. Each of the examples of table I illustrate the substantially improved results and superior resistance to oxidation at elevated temperature which is obtained when the hafnium-tantalum alloy contains the disclosed alloying agents. Without the addition of such alloying agents, the hafnium-tantalum alloys fail to survive more than 30 hours exposure to high temperature oxidation.

The significant improvement in oxidation resistance of hafnium-tantalum alloys containing iridium and at least one additional alloying agent is further illustrated by extended oxidation studies at 2500° F. for up to 500 hours. The oxidation studies were carried out in accordance with the test procedures outlined herein except that the tests were extended from 100 hours to 500 hours. The results of these studies, using samples similar to those of tables I confirm that such alloys are capable of withstanding 500 hours exposure to oxidation in static air at 2500° F. without failure. This represents a significant improvement over previously known structural alloys.

It can readily be seen that hafnium-tantalum alloys containing iridium, with or without additional alloying agents, have good oxidation resistance at temperatures above 2200° F. However, such alloys which do not contain aluminum exhibit rapid oxidation at lower temperatures, e.g., 1200° F. to 1800° F. It is believed that the susceptibility of the alloys to low temperature oxidation is due primarily to the inability of the outer oxide scale layer to be self healing at lower temperature. That is, the cracks which form in the oxide layer are not effectively sealed at low temperatures. It is also possible that at lower temperatures the subscale layer is not sufficiently formed or is absent so that the expansion mismatch between the substrate and the oxide layer is not buffered.

Oxidation studies at temperatures between 1200° F. and 1800° F. have shown that the presence of aluminum as the sole alloying agent in a hafnium-tantalum alloys provides substantial protection against oxidative corrosion within this temperature range. However, hafnium-tantalum alloys containing aluminum as the sole alloying agent are susceptible to rapid oxidation at temperatures of 2500° F. with the resulting failure of the alloy.

The low temperature oxidation resistance of hafnium-tantalum alloys containing iridium may be substantially improved if aluminum is employed as an additional alloying agent. The aluminum provides low temperature resistance to oxidation, and the combination of iridium and aluminum, as discussed herein, provides excellent high temperature oxidation resistance.

The low temperature oxidation resistance of hafnium-tantalum alloys containing iridium can also be improved by preoxidation, that is, by exposure of the alloy to elevated temperatures about 2200° F. prior to exposure at lower temperatures. It is believed that preoxidation causes the formation of

TABLE I.—OXIDATION RATE OF HAFNUIM-TANTALUM ALLOYS IN STATIC AIR AT 2,500° F.

Alloy composition, weight percent (atomic percent)	Percent weight gain after exposure in hours						
	1	5	22	40	64	80	100
Example:							
1. Hf-21.8Ta-5Ir-1.3Al (8Al)	0.47	0.90	1.77	2.35	2.9	3.3	[1] 4.35
2. Hf-19.4Ta-10Ir-1.3Al (8Al)	0.42	0.78	[1] 1.58	2.2	2.78	3.15	3.7
3. Hf-20.7Ta-7Ir-0.79Si (5Si)	0.54	1.11	2.18	2.8	3.4	3.74	4.12
4. Hf-20.7Ta-7Ir-1.6Si (10Si)	0.48	1.52	[1] 4.85				
5. Hf-19.3Ta-10.8Ir-1.5Cr (5Cr)	0.66	1.13	[1] 2.2	2.92	3.9	4.7	6.0
6. Hf-21.5Ta-5Ir-1.3Al-0.8Si (8Al) (5Si)	0.37	0.78	1.53	[1] 2.27			
7. Hf-20.6Ta-7Ir-0.9Al-0.8Si (5Al) (5Si)	0.36	0.63	1.35	1.76	2.24	2.64	3.08
8. Hf-20.5Ta-7Ir-1.3Al-0.8Si (8Al) (5Si)	0.34	0.62	1.34	1.73	2.14	2.38	2.62
9. Same as above	0.36	0.74	1.41	1.81	[2] 2.47	3.03	3.42
10. Hf-23.5Ta-7Ir-1.3Al-0.8Si (8Al) (5Si)	0.36	0.72	1.4	1.8	[2] 2.52	2.86	3.76
11. Hf-28Ta-7Ir-1.3Al-0.8Si (8Al) (5Si)	0.37	0.73	1.39	1.8	2.23	2.45	2.70
12. Hf-20.2Ta-7Ir-1.3Al-0.8Si-0.6Cr (8Al) (5Si) (2Cr)	0.35	0.70	[1] 1.34	1.72	2.13	2.35	2.58
13. Hf-23.7Ta-7Ir-1.3Al-0.8Si-1.5Cr (8Al) (5Si) (5Cr)	0.39	0.79	1.54	[2] 1.97	2.92	3.62	

[1] Scale cracked.
[2] Scale spalled.

oxide and subscale layers which aid in preventing oxidation when the alloy is exposed to temperatures of 1200° F. to 1800° F.

In addition to the static air oxidation corrosion studies, the results of which are set forth in table I, oxidation studies were also conducted under cyclic conditions. The cyclic oxidation studies were carried out using herein described 15 gram arc melted buttons supported in alumina boats. The samples were heated to 2500° F. for one hour and then removed from the furnace and cooled to room temperature. Upon reaching room temperature the samples were replaced in the furnace and heated to 2500° F. for another hour. Heating to 2500° F. for 1 hour followed by cooling to room temperature constituted one thermal cycle.

The weight gain during thermal cycling oxidation studies is generally comparable to the weight gain during static oxidation at 2500° F. Cracks were observed on the surface of the samples subjected to thermal cycling and these cracks were generally concentrated at the edges and corners of the samples. However, none of the cracks which occurred resulted in accelerated oxidation and microscopic examination showed that the cracks were limited to the surface oxide scale layer and did not propagate to the alloy substrate.

The results of the thermal cycling studies illustrate that the susceptibility of the described hafnium-tantalum alloy to increased oxidation and corrosion at relative low temperatures, e.g., 1200° to 1800° F., does not occur under conditions of thermal cycling from room temperature to higher temperatures, e.g., above 2200° F. Thus, it would be possible to utilize the disclosed alloys in environments which include thermal cycling between room temperature and elevated temperatures without fear of excessive oxidation.

It will be seen that desirable hafnium-tantalum alloy compositions have been disclosed which have substantially improved resistance to oxidation at elevated temperatures. Further, the hafnium-tantalum alloy compositions are corrosion resistant under both static conditions and cyclic conditions.

Although certain features of the invention have been described with particularity, alternative embodiments within the skill of the art, are contemplated.

Various of the features of the invention are set forth in the following claims:

What is claimed is:

1. A hafnium base alloy having improved resistance to corrosion at elevated temperatures comprising, between about 5 and about 35 weight percent tantalum, between about 2 and about 20 weight percent iridium, up to about 2.5 weight percent aluminum, up to about 1.6 weight percent silicon, and up to about 1.5 weight percent chromium, and the balance hafnium.

2. A hafnium base alloy in accordance with claim 1 comprising between about 20 and about 30 weight percent tantalum.

3. A hafnium base alloy in accordance with claim 1 comprising between about 0.5 and 2.5 weight percent aluminum.

4. A hafnium base alloy in accordance with claim 1 comprising between about 0.5 and about 1.6 weight percent silicon.

5. A hafnium base alloy in accordance with claim 1 comprising between about 0.5 and about 2.0 weight percent aluminum and between about 0.5 and about 1.0 weight percent silicon.

6. A hafnium base alloy in accordance with claim 2 comprising about 1.3 weight percent aluminum and about 0.8 weight percent silicon.

7. A hafnium base alloy in accordance with claim 6 comprising about 0.6 weight percent chromium.

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