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HAFNIUM BASE ALLOY (CR-AI)

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3 Claims

ABSTRACT OF THE DISCLOSURE

Hafnium base alloy containing between about 15 and about 35 weight percent tantalum and between about 0.5 and about 5 weight percent chromium. The alloy may contain up to about 3.5 weight percent silicon and up to about 3.5 weight percent aluminum.

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 200° F. In addition to corrosion resistance, a desirable metal should have good structural strength at temperature above 2200° 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 4000° F. The ductility of hafnium is such that it 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 1800° 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, HfO₂. 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 alloy substrate. Hafnium-tantalum oxide is also quite porous which permits diffusion of oxygen through the oxide layer to the metallic surface.

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 2000° F. results in extensive

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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 15 and about 35 weight percent tantalum and between about 0.5 and about 5 weight percent chromium, the balance of the alloy being hafnium. Preferably, the hafnium alloy also includes minor amounts of at least one alloying agent selected from silicon and aluminum. Silicon may be present in amounts up to about 3.5 weight percent, and aluminum may be present in amounts up to about 3.5 weight percent.

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 15 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 15 weight percent tantalum, the resulting hafnium-tantalum alloy does not have desired structural strength or oxidation resistance. Generally, it has been determined that alloys containing between about 20 and about 30 weight percent tantalum provide the best combination of structural strength and resistance to high temperature oxidation.

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 improve the ability of the hafnium-tantalum alloy to withstand extended exposure to high temperature oxidation.

crease, 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.

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

Example	Alloy composition, weight percent (atomic percent)	Percent weight gain after exposure in—						
		1 hr.	5 hrs.	22 hrs.	40 hrs.	64 hrs.	80 hrs.	100 hrs.
1.....	Hf, 20 Ta.....	(1)						
2.....	Hf, 25 Ta.....	(1)						
3.....	Hf, 30 Ta.....	(1)						
4.....	Hf, 35 Ta.....	(1)						
5.....	Hf, 33.9 Ta, 3.3 Cr (10 Cr)	0.75	² 1.60	2.88				
6.....	Hf, 33.4 Ta, 4.9 Cr (15 Cr)	0.6	² 1.14					
7.....	Hf, 29.0 Ta, 3.3 Cr (10 Cr)	0.67	1.4	2.74	3.74	4.95	5.82	6.95
8.....	Hf, 28.5 Ta, 4.9 Cr (15 Cr)	0.6	² 1.0	1.33	1.40	3.28	3.94	4.15

¹ Fail.

² Scale cracked.

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 diffusions of oxygen to the alloy substrate surface and decreases the rate of corrosion. In addition, it has been found that 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.

The principal alloying agent which provides the improved resistance to high temperature oxidation is chromium. It is believed that in order to provide a hafnium-tantalum alloy which has improved resistance to corrosion at elevated temperatures, the hafnium-tantalum alloy should contain at least 0.5 weight percent chromium. The addition of chromium as an alloying agent causes a reduction in the size and regularity of the hafnium oxide platelets in the oxide scale layer.

When the chromium is the sole alloying agent, e.g., when the alloy is a ternary hafnium-tantalum-chromium alloy, at least about 3 weight percent chromium should be present in order to provide a desired degree of resistance to oxidative corrosion at high temperatures. If the hafnium-tantalum alloy contains, in addition to chromium, silicon and/or aluminum alloying agents, as discussed hereinafter, the chromium content of the alloy may be reduced to be as low as 0.5 weight percent without detrimentally affecting the high temperature corrosion resistance of the hafnium-tantalum 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 two 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 in-

crease. There is set forth in Table I the results of oxidation studies in static air at 2500° F. of hafnium-tantalum binary alloys and hafnium-tantalum-chromium ternary alloys. All of the hafnium-tantalum binary alloys failed to survive more than about 30 hours at 2500° F. and extensive spalling generally commenced after about 10-20 hours at 2500° F.

Examples 7 and 8 of Table I illustrate the substantially improved results and superior resistance to oxidation at elevated temperature which is obtained when at least about 3 weight percent chromium is added to a hafnium-tantalum alloy. If the hafnium-tantalum alloy contains only hafnium, tantalum and chromium, along with residual impurities normally associated with commercial grades of these materials, it has been found that the chromium content should be at least about 3 weight percent, preferably between about 3 and about 5 weight percent.

The addition of chromium in amounts substantially in excess of 5 weight percent tends to cause spalling of the oxide scale, and for most purposes it is generally desirable to maintain the chromium content of the hafnium-tantalum alloy below about 5 weight percent in order to reduce spalling.

In addition, as can be seen from Examples 5 and 6, if the tantalum content of the alloy exceeds about 30 weight percent tantalum the improved oxidation resistance obtained through the addition of chromium as the sole alloying agent is diminished. Above about 35 weight percent tantalum additional chromium additions have been found ineffective in improving oxidation resistance.

Accordingly, a preferred composition is a hafnium-tantalum alloy containing between about 20 and about 30 weight percent tantalum and between about 3 and about 5 weight percent chromium. The chromium content of the alloy should be adjusted in proportion to the tantalum content with increased chromium content being desirable at higher tantalum contents.

Although the hafnium-tantalum chromium alloys exemplified by Examples 7 and 8 of Table I provide desirable oxidation resistance at elevated temperatures and are capable of surviving 100 hours exposure at 2500° F. in static air, the addition of additional alloying agents provides a further improvement in the oxidation resistance of hafnium-tantalum alloys and permits wider varia-

tions in the constituents of the alloy without sacrifice of oxidation resistant properties.

weight percent tantalum, between about 0.5 and about 5 weight percent chromium, and between about 0.5 and

TABLE II.—OXIDATION RATE OF HAFNIUM-TANTALUM-CHROMIUM SILICON ALLOYS IN STATIC AIR AT 2,500° F.

Example	Alloy composition, weight percent (atomic percent)	Percent weight gain after exposure in—						
		1 hr.	5 hrs.	22 hrs.	40 hrs.	64 hrs.	80 hrs.	100 hrs.
1	Hf, 20 Ta, 0.25 Si (1.5 Si)	0.98	1.75	¹ 3.9				
2	Hf, 24.6 Ta, 0.8 Si (5 Si)	0.56	1.11	2.38	¹ 3.64			
3	Hf, 24.2 Ta, 1.6 Si (10 Si)	0.47	0.94	2.12	¹ 3.4			
4	Hf, 24.1 Ta, 1.5 Cr, 0.3 Si (5 Cr) (2 Si)	0.56	1.05	¹ 2.05	2.69	3.28	3.6	3.9
5	Hf, 23.9 Ta, 1.5 Cr, 0.8 Si (5 Cr) (5 Si)	0.49	0.90	1.73	2.28	2.76	3.03	3.34
6	Hf, 24.2 Ta, 0.6 Cr, 1.1 Si (2 Cr) (7 Si)	0.42	0.73	1.64	2.18	2.8	3.04	3.3
7	Hf, 23.7 Ta, 1.5 Cr, 1.1 Si (5 Cr) (7 Si)	0.50	0.84	1.7	2.14	2.61	2.88	3.17
8	Hf, 28 Ta, 1.5 Cr, 1.1 Si (5 Cr) (7 Si)	0.45	0.86	1.58	2.06	² 2.48	2.78	3.04
9	Hf, 32 Ta, 1.5 Cr, 1.1 Si (5 Cr) (7 Si)	0.44	0.88	1.6	2.08	² 2.55	2.81	3.09
10	Hf, 23.5 Ta, 1.8 Cr, 1.1 Si (6 Cr) (7 Si)	0.49	0.95	1.78	2.27	2.77	3.02	3.33
11	Hf, 23.4 Ta, 2.1 Cr, 1.1 Si (7 Cr) (7 Si)	0.49	0.96	1.79	2.28	2.8	3.07	3.28
12	Hf, 23.2 Ta, 2.6 Cr, 1.1 Si (8 Cr) (7 Si)	0.47	0.94	1.78	2.28	2.79	3.06	3.34
13	Hf, 22.9 Ta, 3.0 Cr, 1.1 Si (10 Cr) (7 Si)	0.47	0.94	1.79	2.3	2.83	3.11	3.4
14	Hf, 22.9 Ta, 3 Cr, 1.3 Si (10 Cr) (8 Si)	0.46	0.93	1.78	2.3	2.82	3.10	3.4
15	Hf, 23.4 Ta, 2.1 Cr, 1.1 Si (7 Cr) (7 Si)	0.49	0.96	1.79	2.28	2.8	3.07	3.28
16	Hf, 23.6 Ta, 1.8 Cr, 1.1 Si (6 Cr) (7 Si)	0.49	0.95	1.78	2.27	2.77	3.02	3.32
17	Hf, 23.2 Ta, 2.6 Cr, 1.1 Si (8 Cr) (7 Si)	0.47	0.94	1.78	2.28	2.79	3.06	3.34
18	Hf, 22.9 Ta, 3.0 Cr, 1.1 Si (10 Cr) (7 Si)	0.49	0.94	1.79	2.3	2.83	3.11	3.4
19	Hf, 22.9 Ta, 3.0 Cr, 1.3 Si (10 Cr) (8 Si)	0.46	0.93	1.78	2.3	2.83	3.10	3.4

¹ Scale cracked. ² Scale spalled.

There is illustrated in Table II the results of oxidation studies in static air at 2500° of hafnium-tantalum alloys

about 3.5 weight percent silicon. Preferably, the tantalum content is between about 20 and about 30 weight percent.

TABLE III.—OXIDATION RATE OF HAFNIUM-TANTALUM-CHROMIUM-SILICON ALLOYS IN STATIC AIR AT 2,500° F.

Example	Alloy composition weight percent (atomic percent)	Percent weight gain after exposure in—						
		100 hrs.	200 hrs.	245 hrs.	292 hrs.	365 hrs.	400 hrs.	465 hrs.
1	Hf, 23.4 Ta, 2.1 Cr, 1.1 Si (7 Cr) (7 Si)	3.28	4.43	4.8	5.14	5.61	6.0	7.6
2	Hf, 23.6 Ta, 1.8 Cr, 1.1 Si (6 Cr) (7 Si)	3.32	4.38	4.76	5.1	5.5	5.96	6.26
3	Hf, 23.2 Ta, 2.6 Cr, 1.1 Si (8 Cr) (7 Si)	3.34	4.4	4.77	5.12	5.64	5.96	¹ 6.32
4	Hf, 22.9 Ta, 3.0 Cr, 1.1 Si (10 Cr) (7 Si)	3.4	4.55	4.94	5.3	5.79	¹ 6.2	6.63
5	Hf, 22.9 Ta, 3.0 Cr, 1.3 Si (10 Cr) (8 Si)	3.4	4.5	4.9	5.26	5.74	¹ 6.17	

¹ Scale cracked.

containing chromium and silicon alloying agents. It is readily seen from Examples 1 to 3 of Table II that the addition of silicon to hafnium-tantalum alloys in the absence of added chromium does not provide oxidation resistance. However, as seen from Examples 4 to 19 of Table II (if silicon and chromium are both present as alloying agents, the resulting hafnium-tantalum alloy has good oxidation resistance. The oxidation resistance of hafnium-tantalum alloys containing chromium and silicon alloying agents is generally superior to alloys which contain only chromium as an alloying agent.

Several of the alloy buttons of Examples 4 to 19 of Table II were cut in half and examined. It was found that the surface oxide scale layer of the hafnium-tantalum alloy containing both chromium and silicon alloying agents is thinner than the metal plus oxide subscale layer. This indicates a denser surface oxide layer is formed when the alloy contains both chromium and silicon alloying agents.

Hafnium-tantalum alloys containing both chromium and silicon alloying agents have the further advantage that they have good oxidation resistance over wider tantalum concentrations, e.g., between about 15 and about 35 weight percent, than the alloys containing chromium as the sole alloying agent. Further, when silicon is also present as an alloying agent, the amount of chromium may be reduced to as low as 0.5 weight percent without detracting from the oxidation resistance of the hafnium-tantalum alloy. Accordingly, improved hafnium-tantalum alloy containing chromium and silicon alloying agents include between about 15 and about 35

The significant improvement in oxidation resistance of hafnium-tantalum alloys containing chromium and silicon alloying agents is further illustrated by the examples of Table III. The oxidation studies reported in Table III were carried out in accordance with the test procedure outlined herein except that the tests were extended from 100 hours to 465 hours. The results of Table III show that hafnium-tantalum alloys containing chromium and silicon alloying agents are capable of withstanding 465 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 chromium, or chromium and silicon, alloying agents have good oxidation resistance at temperatures above 2200° F. However, such alloys exhibit rapid oxidation at lower temperatures, e.g., 1200° F. to 1800° F., particularly if they have been previously exposed to high temperature oxidation. 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 addition of aluminum to hafnium-tantalum alloys provides substantial protection against oxidative corrosion within this temperature

range. However, hafnium-tantalum alloys containing aluminum alloying agents, in the absence of added chromium and silicon, are susceptible to rapid oxidation at temperatures of 2500° F. with the resulting failure of the alloy.

TABLE IV.—OXIDATION RATE OF HAFNIUM-TANTALUM-CHROMIUM-ALUMINUM-SILICON ALLOYS IN STATIC AIR AT 2,500° F.

Example	Alloy composition weight percent (atomic percent)	Percent weight gain after exposure in—						
		1 hr.	5 hrs.	22 hrs.	40 hrs.	64 hrs.	80 hrs.	100 hrs.
1	Hf, 24.6 Ta, 1.13 Al, 0.59 Cr (7 Al) (2 Cr)	1.18	2.26	2.98	4.60			
2	Hf, 23.2 Ta, 0.9 Al, 1.1 Si, 1.5 Cr	0.42	0.82	1.88	2.46	3.08	3.42	3.81
3	Hf, 23 Ta, 1.3 Al, 1.1 Si, 1.5 Cr (8 Al) (7 Si) (5 Cr)	0.40	0.83	1.72	2.27	2.86	3.28	2.76
4	Hf, 24.5 Ta, 0.31 Si, 0.59 Cr, 1.13 Al (2 Si, 2 Cr, 7 Al)	0.74	1.5	2.96	3.96			
5	Hf, 24.5 Ta, 0.31 Si, 1.50 Cr, 1.13 Al (2 Si, 5 Cr, 7 Al)	0.77	1.62	3.25	4.34	1.624		
6	Hf, 24.5 Ta, 0.79 Si, 1.5 Cr, 1.13 Al (5 Si, 5 Cr, 7 Al)	0.69	1.33	2.6	3.48	1.4.6		
7	Hf, 23 Ta, 0.79 Si, 1.5 Cr, 1.13 Al (5 Si, 5 Cr, 8 Al)	0.65	1.33	2.62	3.45	1.4.62		
8	Hf, 23 Ta, 0.79 Si, 1.5 Cr, 1.3 Al (5 Si, 5 Cr, 8 Al)	0.56	1.21	2.37	3.11	3.84	4.25	4.65
9	Hf, 23 Ta, 0.79 Si, 0.15 Cr, 1.3 Al (5 Si, 0.5 Cr, 8 Al)	0.69	1.34	2.66	3.56	1.6.1		
10	Hf, 23.3 Ta, 1.1 Si, 1.5 Cr, 0.36 Al (7 Si, 5 Cr, 1.5 Al)	0.62	1.22	2.43	3.15	3.84	4.2	4.57
11	Hf, 23.1 Ta, 1.1 Si, 1.5 Cr, 0.92 Al (7 Si, 5 Cr, 5 Al)	0.67	1.4	2.96	4.06	5.17	6.33	7.62
12	Hf, 24.5 Ta, 1.1 Si, 0.59 Cr, 1.13 Al (7 Si, 2 Cr, 7 Al)	0.63	1.32	2.61	3.46	4.34	4.93	5.9
13	Hf, 24.5 Ta, 1.1 Si, 1.5 Cr, 1.13 Al (7 Si, 5 Cr, 7 Al)	0.54	1.16	2.33	3.08	1.3.68		
14	Hf, 24.5 Ta, 1.1 Si, 1.5 Cr, 1.3 Al (7 Si, 5 Cr, 8 Al)	0.55	1.16	2.35	3.4	1.3.42		

¹ Spalled.

There is set forth in Table IV the results of oxidation studies of hafnium-tantalum alloys containing chromium, silicon and aluminum alloying agents. These alloys have good resistance to oxidation at elevated temperatures and, in addition, exhibit improved resistance to corrosion at lower temperatures. Desirable alloy compositions having good resistance to oxidation over extended temperature ranges are obtained when the alloy contains between about 0.3 and about 3.5 weight percent aluminum.

Examination of the results of a number of oxidation studies tends to indicate that the degree of spalling that occurs is somewhat dependent upon the relative proportion of chromium and aluminum present in the alloy. When the alloy contains both chromium and aluminum alloying agents it is generally considered preferable to adjust the aluminum and chromium content of the alloy in an inverse relationship, so that at low chromium content higher concentrations of aluminum are employed, and at high chromium content, lower concentrations of aluminum are employed.

In addition, it has been found that when aluminum is employed as an alloying agent the amount of chromium alloying agent may be reduced to as low as 0.15 percent by weight.

It has been further determined that the susceptibility of hafnium-tantalum-chromium-silicon alloys to oxidation at low temperatures, e.g., 1200 to 1600 may be improved by preoxidation of the alloy at 2500° F. for 5 to 20 hours. However, hafnium-tantalum-chromium-aluminum alloys which are resistant to oxidation at 1600° F. without prior exposure to elevated temperatures have substantially reduced oxidation resistance if exposed to pre-oxidation at 2500° F.

In addition to the static air oxidation corrosion studies, the results of which are set forth in Tables I to IV, oxidation studies were also conducted under cyclic conditions. The cyclic oxidation studies were carried out by using herein described 15 gram arc melted buttons supported in alumina boats. The samples were heated to 2500° 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 one hour followed by cooling to room temperature constituted one thermal cycle.

TABLE V.—CYCLIC OXIDATION BEHAVIOR OF Hf-Ta ALLOYS AT 2,500° F. IN STATIC AIR

Example	Alloy composition weight percent (atomic percent)	Exposure test method	Percent weight gain in given time (hr. cycles)													
			1	2	5	10	15	20	22	25	30	35	40	45	100	
1	Hf, 23.7 Ta, 1.5 Cr, 1.1 Si (5 Cr) (7 Si)	(Cyclic*)	0.46	0.60	0.88	1.17	1.46	1.73	1.80	1.90	2.08	2.21	2.39	2.51		
		(Static)	0.50	0.80	0.84				1.70				2.14		3.1	
2	Hf, 24.6 Ta, 1.13 Al, 0.59 Cr (7 Al) (2 Cr)	(Cyclic*)	0.56	0.74	1.06	1.42	1.71		2.01	2.13	2.33	2.52	2.66	2.81		
		(Static)			1.18				2.26				2.98		4.6	

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 cor-

ners 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. Table V also includes comparable static oxidation data showing the generally comparable results obtained under cyclic oxidation and static oxidation.

The results of Table V illustrate that the susceptibility of the described hafnium-tantalum alloy to increased oxidation and corrosion at relatively 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.

The oxidation resistance of substrates clad with the described hafnium-tantalum alloys was tested by sandwiching a pure tantalum substrate between various hafnium-tantalum alloy cladding materials containing the described alloying agents. The sandwich assemblies were hot rolled air at 2500° F. to a total reduction in area of 65 percent. Excellent bonding of the cladding material to the tantalum substrate was achieved.

Exposure of clad tantalum substrates to 2500° F. for periods up to 150 hours showed that the hafnium-tantalum alloy cladding containing the described alloying agents sufficiently protected the tantalum substrate which remained soft and ductile. The cladding material was, in some instances, completely converted to oxide scale and subscale, but even in these instances prevented oxygen or interstitial element contamination of the tantalum substrate.

It will be seen that desirable hafnium-tantalum alloy compositions have been disclosed which have substantially improved resistance to oxidation at elevated temperatures. The hafnium-tantalum alloys have good ductility and workability and may be readily fabricated. 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.

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What is claimed is:

1. A hafnium base alloy having improved resistance to oxidation at high temperatures consisting of, between about 15 and about 35 percent by weight tantalum, between about 0.5 and about 5 percent by weight chromium, and at least one alloying agent selected from the group consisting of between 0.5 and about 3.5 percent by weight silicon, and between 0.3 and about 3.5 percent by weight aluminum, the balance being hafnium.
2. A hafnium base alloy in accordance with claim 1 comprising between about 20 and about 30 weight percent tantalum and between about 3 and about 5 percent by weight chromium.
3. A hafnium base alloy in accordance with claim 1 comprising between about 15 and about 35 percent by

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weight tantalum, between about 0.15 and about 5 percent by weight chromium, and between about 0.3 and about 3.0 percent by weight aluminum, the amount of aluminum being inversely proportional to the amount of chromium.

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