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IITRI-B6099-4
(Final Report)

DEVELOPMENT OF OXIDATION-RESISTANT HAFNIUM ALLOYS

Naval Air Systems Command
Department of the Navy
Washington, D.C. 20025

Contract No. N00019-70-C-0120

~~THIS DOCUMENT IS SUBJECT TO SPECIAL EXPORT CONTROLS AND EACH TRANSMITTAL TO FOREIGN GOVERNMENTS OR FOREIGN NATIONALS MAY BE MADE ONLY WITH THE APPROVAL OF THE NAVAL AIR SYSTEMS COMMAND.~~

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FOREWORD

This report, IITRI-B6099-4, covers work performed on the project entitled "Development of Oxidation-Resistant Hafnium Alloys," under Contract No. N00019-70-C-0120. The period covered is 1 September 1969 to 31 August 1970.

Personnel contributing to this program include V. L. Hill, Manager of Coatings Research, as the IITRI Project Manager; H. R. Nichols, Associate Metallurgist, as the Project Engineer; and Mr. I. Machlin of the Naval Air Systems Command as the Project Monitor.

Experimental data reported herein are recorded in IITRI Logbooks No. C19455, C19610, and C19725.

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DEVELOPMENT OF OXIDATION-RESISTANT HAFNIUM ALLOYS

ABSTRACT

The objective of this program was to investigate oxidation resistant hafnium-base alloys as cladding for columbium- and tantalum-base alloys. Oxidation behavior of other combinations of Group IVB-VB alloys was also studied.

Clad composites consisting of Cb-752 and Ta-10W clad with Hf-Ta-Cr-B-Al and Hf-Ta-Cr-Si alloys were exposed at 2200°, 2500°, and 2700°F. Oxidation life varied from about 100 hr at 2200°F to 25 hr at 2700°F. Failure of the composites generally occurred at edges between the picture frame and substrate. The Hf-Ta-Cr-B-Al alloy indicated greater tolerance to surface defects than the Hf-Ta-Cr-Si alloy.

Oxidation studies of modified Group IVB-VB alloys at 2000°-2500°F showed that oxidation resistance could be developed in several systems. The minor alloying additions employed were chromium, boron, columbium, silicon, yttrium, vanadium, and combinations of these elements. Chromium-silicon additions were the most effective in improving oxidation resistance in nearly all systems, although Cr-Al-Si combinations were also effective in Cb-Ti alloys.

X-ray diffraction examination of oxides developed in oxidation-resistant hafnium-base alloys suggested that the oxide structures, probably a complex Hf-Ta oxide, were similar for all alloys. Similar oxides were also developed on zirconium-base systems, but a different complex oxide was developed on titanium-base systems. A model for the oxidation resistance obtained in modified Hf-Ta alloys based on occupancy of specific lattice sites by the minor alloying elements is proposed.

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DEVELOPMENT OF OXIDATION-RESISTANT HAFNIUM ALLOYS

I. INTRODUCTION

The objective of the previous programs on hafnium-base alloys at IITRI was to develop alloys capable of operating in oxidizing environments at temperatures above 2200°F. These alloys were to be used either as structural oxidation-resistant materials or as oxidation-resistant cladding for columbium- or tantalum-base alloys. The work reported here was a continuation of these investigations of hafnium-base alloys for both applications. However, efforts were concentrated on the use of hafnium-base alloys as oxidation-resistant cladding.

The materials to be developed as structural alloys are expected to have useful strength above 2500°F, oxidation resistance under both static and cyclic conditions to 2500°F, and fabricability. Cladding alloys are expected to provide oxidation resistance greater than that of current silicide coatings or improved reliability in environments. Claddings based on the Hf-Ta-Cr-Si and Hf-Ta-Cr-B-Al systems developed in previous work can provide either or both of the above requirements.

II. BACKGROUND

A. Previous Work

Oxidation-resistant hafnium-base alloys were investigated previously under Contracts NOw 65-0301-f and NOw 66-0212-d.(1,2) These investigations were concerned primarily with evaluating the oxidation behavior of hafnium-tantalum and hafnium-columbium alloys and with improving the oxidation resistance afforded by alloying additions. Subsequently, investigations of both oxidation resistance and elevated temperature strength were conducted under Contracts N00019-67-C-0403 and N00019-68-C-0362.(3,4) During screening studies, oxidation evaluations were conducted in static air at 2500°F for periods up to 100 hr on a variety of alloys and clad composites. Also, the oxidation behavior of selected alloys was evaluated at 1200°-2500°F and under cyclic conditions.

Oxidation screening tests were performed in static air at 2500°F on numerous binary and complex Hf-Ta and Hf-Cb alloys. The alloying additions studied were B, Al, Si, Cr, Mo, W, Ir, Pt, Y, and Ti in hafnium-base alloys containing up to 50 w/o Ta and 30 w/o Cb. The results of the screening studies are summarized as follows:

1. Hf-Ta base alloys were more oxidation-resistant than comparable Hf-Cb alloys.
2. Hf-Ta alloys in the range of 20-30 w/o Ta had the highest oxidation resistance and best response to alloying additions.
3. Complex alloys containing combinations of B, Al, Cr, Si, and Ir had the highest oxidation resistance.
4. The initial goal of 100 hr life at 2500°F was obtained in a variety of complex Hf-Ta alloys.

The most oxidation-resistant Hf-Ta alloys were the Hf-Ta-Cr-Al, Hf-Ta-Cr-Si, Hf-Ta-Cr-B, and Hf-Ta-Ir-Al-Si systems. These alloys contained 20-30 w/o Ta; the total concentration of the other alloying elements was less than 20 a/o. Oxidation samples of the latter three alloy systems survived exposures up to 450 hr at 2500°F without failure. Of these, the Hf-Ta-Ir-Al-Si alloys had considerably lower weight gains up to 300 hr, but the oxidation rate increased after this exposure time apparently because the protective oxide cracked. Alloys containing appreciable aluminum additions (~1 w/o) did not exhibit growth during oxidation exposure.

Evaluation of the tensile properties of binary and ternary Hf-Ta alloys revealed that the binary alloys had very low strength at 2500°F in the annealed condition. Exposure in air at 2500°F increased the tensile strength, but resulted in severe embrittlement of the alloy at room temperature. The observed effects were apparantly due to the high solubility of interstitial oxygen and, probably, to the effect of oxygen on the transformation kinetics of the α-β transition.

More recent data on hafnium-base alloys(3,4) show that the alloys with the greatest oxidation resistance are the Hf-Ta-Cr-B, Hf-Ta-Cr-B-Al, and Hf-Ta-Cr-Si systems. Effort on the Hf-Ta-Ir-Cr-Si system was discontinued because of the high cost of iridium, the poor workability of the alloys, and only minor improvement in oxidation behavior over the other systems was developed. Thus, work during Contract N00019-68-C-0362(4) concentrated on the three remaining (Cr-B, Cr-B-Al, Cr-Si) oxidation-resistant systems.

These efforts on hafnium-base alloys (including the Hf-Ta-Cr-B, Hf-Ta-Cr-Si, and Hf-Ta-Cr-B-Al compositions) generated the following information:

1. Both oxidation resistance and strength properties are controlled by the α-β transition.
2. Low-temperature degradation can be minimized by preoxidation at 2500°F.
3. Cyclic oxidation does not reduce the life of Hf-Ta-Cr-B, Hf-Ta-Cr-Si, or Hf-Ta-Cr-B-Al alloys at 2200°-2700°F.
4. High strength cannot be obtained at 2200°-2500°F with small additions of refractory metals or interstitials in alloys which can be cold rolled at 2500°-2650°F.

B. Current Program

These results of previous work suggested that further work should be conducted on hafnium-base alloys in two major areas. (1) an investigation of oxidation-resistant alloys as cladding materials for high-strength columbium and tantalum alloys, and (2) an evaluation of the influence of refractory metal additions, at concentrations greater than those employed to date, on the α-β transition. These efforts should enable a full definition of the potential for the hafnium-base alloys that have already been developed. Emphasis in this program was on clad composite systems.

One other aspect of alloys containing hafnium and other Group IVB elements was investigated. Hafnium-rich alloys containing columbium were investigated in earlier programs,(1,2) but the work was discontinued because of the superior oxidation resistance obtained in the hafnium-tantalum system. However, the oxidation resistance for hafnium-columbium alloys at 2500°F was significantly better than that obtained for current columbium alloys; oxidation exposures up to 100 hr at 2500°F were possible. In addition, the hafnium-columbium alloys were more ductile than comparable hafnium-tantalum alloys after oxidation exposure. Work conducted to date was limited to hafnium-rich alloys. An advantage with the columbium alloys is that Group IVB additions afford strengthening by precipitation of their carbides or oxides. Thus, it may be possible to develop high-strength alloys with moderate to good oxidation resistance with columbium alloys containing Group IVB additions. Accordingly, a study of these alloys was included in the current program, particularly those with compositions approaching the most oxidation resistant Hf-Ta alloys.

Supplemental studies conducted during the program included X-ray diffraction examination of the oxides developed during exposure and siliconizing of Hf-Ta-Cr-B and Hf-Ta-Cr-Si alloys.

III. EXPERIMENTAL PROCEDURE AND RESULTS

A. Clad Composites

The protective capability of oxidation-resistant hafnium-base alloys as cladding for columbium- and tantalum-base alloys was investigated in this phase. Cb-752 and Ta-10W were selected for the substrate alloys as typical columbium and tantalum-base alloys of current usage. The hafnium-base claddings selected were Hf-24.5Ta-1.2Cr-0.66B-0.12Al and Hf-23.5Ta-1.8Cr-1.1Si because these compositions provide the best overall oxidation resistance in hafnium-tantalum alloys. The objective of this effort was to compare the oxidation resistance of clad composites to that of the cladding alloys in air at 2200°-2700°F.

1. Fabrication

Previously, Hf-Ta alloys were hot rolled in air at 2500°-2600°F to minimize edge and surface cracking caused by continuous interruption of the surface oxide during multiple rolling passes in air. Furthermore, considerable surface preparation of the surfaces after rolling was often required to remove surface contamination. IITRI-B6090-4$^{(4)}$ demonstrated that hot rolling at 2000°-2100°F in cans is possible due to the low strength and high ductility of annealed material. A preliminary rolling study was conducted to investigate the workability of canned alloys. Canning of the alloys was expected to permit lower rolling temperatures and require less surface preparation after rolling to remove surface defects. This was particularly important in this program since the alloys were to be fabricated into sheet material nominally 0.040 in. thick for fabrication of composites. The ability to roll the alloys in cans at 2000°-2100°F and, thus, to minimize surface preparation after rolling conserved considerable material. Furthermore, it was also planned to subsequently fabricate picture-frame composites by roll cladding in cans.

Accordingly, small samples of arc-melted Hf-Ta-Cr-Si and Hf-Ta-Cr-B-Al alloys were canned in 0.105 in. thick 410 stainless steel. Austenitic stainless steel was not used because of possible melting interaction of nickel and hafnium at 2100°F. The canned alloys were rolled at 2000°F with multiple passes of 15 to 20 mils per pass. After about a 75% reduction to 0.100 in. thick sheet, both cans fractured. The alloys were removed, replaced in new cans, and then hot rolled to about 0.01 in. thick sheet at 2000°F using 20 mil reductions per pass. Both alloys had an excellent surface condition after rolling and could be removed from the cans without difficulty. Edge cracking was minimal in spite of the probability of some localized oxidation following failure of the first cans.

Based on the initial results, fabrication of 0.040 in. sheet material from 150 g arc-melted buttons of Hf-Ta-Cr-Si and Hf-Ta-Cr-B-Al alloys was conducted using 410 stainless steel cans. Hot rolling of the alloys required two canning operations for the complete reduction from 0.350 in. to 0.040 in. thick material. Reductions during hot rolling were nominally 20 mils per pass. A photograph of typical 0.040 in. material after hot rolling at 2000°F is shown in Figure 1. This photograph shows that edge cracking is minimal and no surface cracking occurs.

It was found that edge cracking of the 150 g arc-melted ingots could be completely eliminated by increasing the rolling temperature to 2100°F. No problems in surface interactions were encountered at the higher rolling temperature. Consequently, the rolling temperature was raised to 2100°F after hot rolling the first 150 g ingots of both alloys. A total of about 100 in.^{2} of 0.040 in. thick sheet of each alloy was prepared for fabrication of clad composites. In addition, approximately 20 in.^{2} of 0.125 in. thick sheet was hot-rolled for the edge plates of the composites. Sufficient cladding material was produced to fabricate 10 composites with Hf-Ta-Cr-Si cladding and 8 composites with Hf-Ta-Cb-B-Al cladding. For each cladding material, one-half of the composites had a Cb-752 substrate; the remaining composites had Ta-10W as the substrate alloy.

The components of the composites prior to assembly are shown in Figure 2. Each 1½ x 1½ in. composite had two compartments containing the substrate alloy. This permitted sectioning of the initial composite with two completely encapsulated, individual cladding-substrate composites after hot rolling. Thus,

Neg. No. 37516 X1/2

Fig. 1 - Surface Appearance of Hot Rolled $Hf-24.5Ta-1.8Cr-1.1Si$ After 85% Reduction by Hot Rolling at 2000°F.

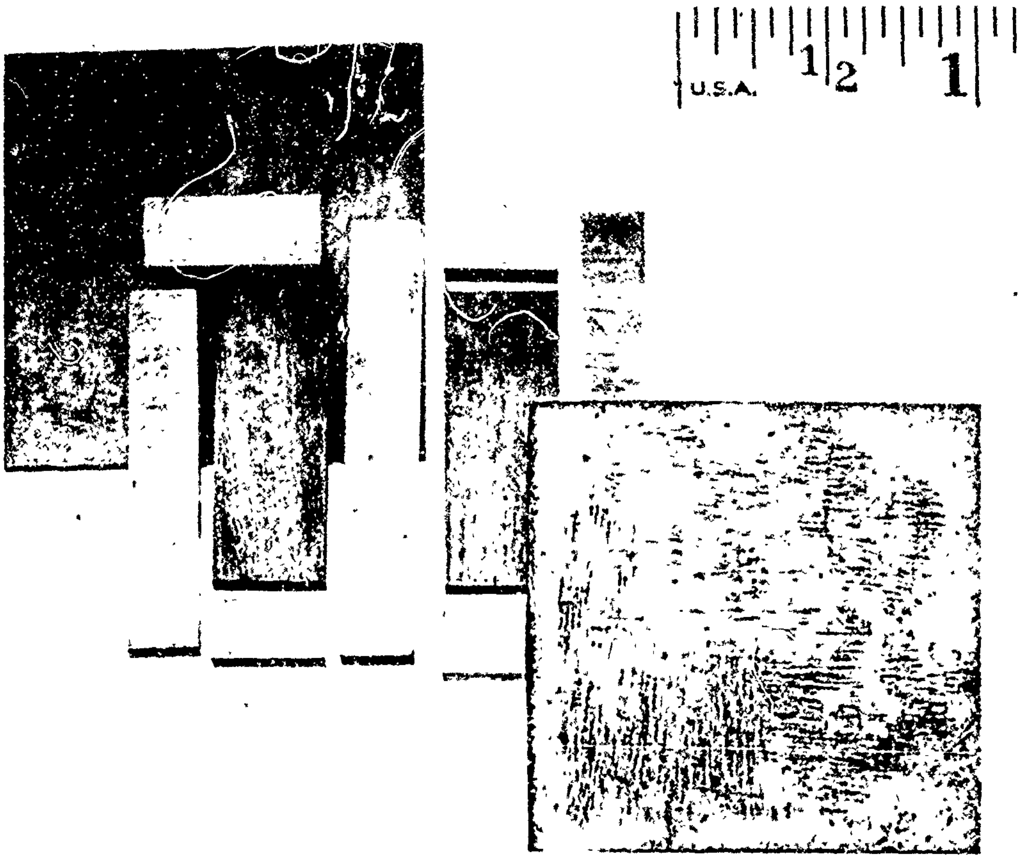

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Fig. 2 - Components of Clad Composite Prior to Assembly and Edge Welding.

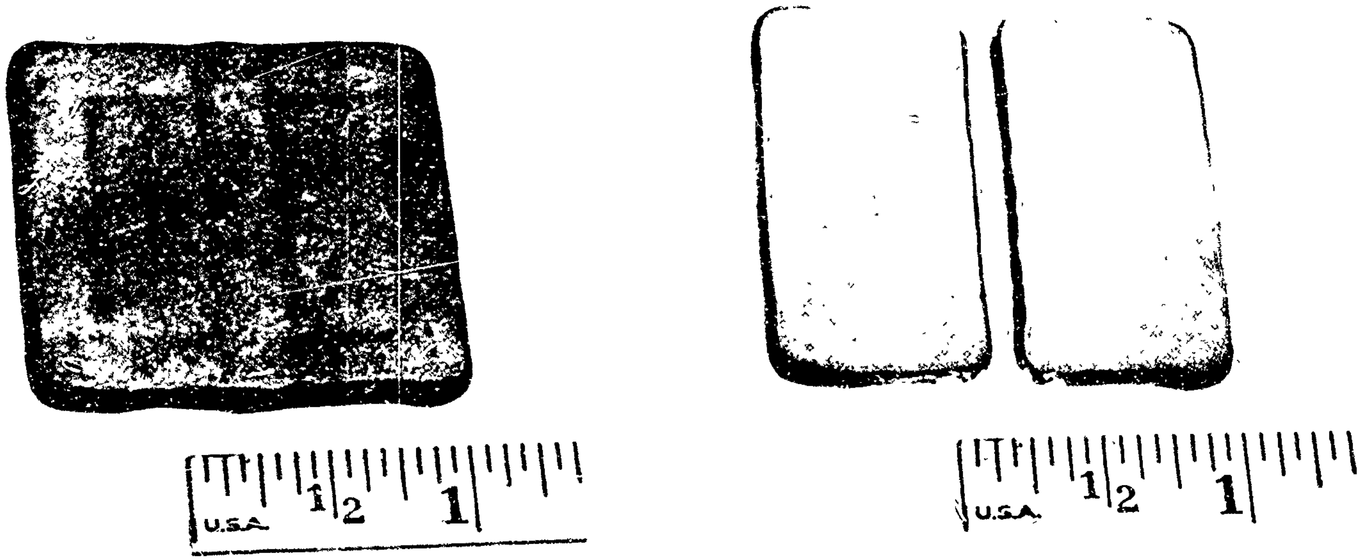
the number of composites available for oxidation testing was doubled after surface grinding and sectioning.

The method of composite fabrication was as follows:

1. Assemble duplex composite and seam-weld in inert atmosphere.
2. Can in evacuated 410 stainless steel cans, and roll clad at 2200°F to about a 5% reduction.
3. Surface grind cladding to a nominal thickness of 10 or 20 mils.
4. Section duplex composite through center rib.
5. Seam-weld sectioned edges to assure sealing of the composite.

The roll cladding reduction of 5% was established by a preliminary rolling study. In this study, it was found that higher reductions caused a separation of the substrate alloy from the picture frame. This resulted in hot tears in the cladding at this point. It was found that good bonding of the substrate was obtained after a 5% reduction without hot tears. Accordingly, all composites were fabricated using this reduction. Seam welding of the sectioned center rib was precautionary, since excellent bonding of the cladding to the center rib was generally obtained.

Photographs of a composite after hot rolling and surface grinding are presented in Figure 3. Figure 3a illustrates the tendency toward separation at the interface of substrate alloy and picture frame. This is probably caused by some flow of the cladding alloy between the substrate alloy and the picture frame and/or nonuniform deformation of the cladding alloy and substrate.



Neg. No. 38047
(a) Hot Rolled

Neg. No. 38048
(b) Sectioned and Surface Ground

Fig. 3 - Surface Appearance of Clad Composites After Hot Rolling and Surface Preparation.

2. Oxidation Tests

Clad composites were oxidation tested in static air at 2200°, 2500°, and 2700°F for 100 hr or to failure. Tensile tests were to be conducted after selected exposures, but this was precluded since the composites usually failed abruptly and catastrophically. In general, failure occurred due to fracture of the cladding between the picture frame and the substrate alloy. Only one failure could be attributed to the cladding performance; this failure occurred with a Hf-Ta-Cr-Si cladding on Cb-752 because of a blister on one face. The blister was probably due to inadequate bonding in a small area of one face of the composite.

Summaries of the weight change data for Hf-Ta-Cr-B-Al and Hf-Ta-Cr-Si clad composites are presented in Tables I and II, respectively. Oxidation data for the cladding alloys alone are included for comparison. In general, the weight changes for the composites compare with those of the cladding alloy up to the time of failure. Only 17 of the 24 composites were oxidation tested. The remaining 7 composites had visible surface defects and/or could not be surface ground to the desired dimensions. Unfortunately, a furnace failure occurred after 5 hr of exposure during the initial exposure at 2700°F causing a drop in temperature to 1400°F and the loss of four composites.

The mode of failure for each composite is presented in Table III. These results indicate that the majority of failures occurred at the interface between the picture frame and substrate alloy. Here cracks were formed, usually audibly, during cooling by differential expansion of the picture frame and substrate alloys aided by oxidation along the interface. Often, interfacial cracks were observed long before actual failure occurred. Exposures for an additional 25-50 hr were often obtained followed by abrupt failure during the next exposure cycle. For this reason, exposure times were modified slightly in some cases.

The Hf-Ta-Cr-B-Al cladding on Cb-752 also showed craze cracking of the cladding after exposure. This effect is shown in

TABLE I

OXIDATION BEHAVIOR OF Hf-Ta-Cr-B-Al CLAD COMPOSITES

Exposure Temp., °F	Substrate	Nominal Cladding Thickness, mils	Weight Gain in Given Time (hr), mg/cm^2						
			5	10	25	50	65	70	100
2500[(a)]	--	35	17.0	--	34.1	47.9	--	54.5	60.2
2500[(b)]	--	35	16.5	--	34.7	45.9	--	52.1	61.7
2200	Cb-752	10	11.5	--	22.5	30.0	--	34.9	41.0
2200	Ta-10W	10	11.7	--	22.9	29.9	--	34.2	39.1
2500	Cb-752	20	17.0	--	36.3	45.8	57.8		
2500	Ta-10W	20	16.9	22.5	44.6				
2700	Cb-752	20	31.9[(c)]						
2700	Ta-10W	20	32.7[(c)]						
2700	Cb-752	20	38.0	49.5	80.0				
2700	Ta-10W	20	35.0	42.7	88.5				

(a) Cladding alloy as-rolled.

(b) Cladding alloy surface ground.

(c) Furnace failure after 5 hr.

TABLE II

OXIDATION BEHAVIOR OF Hf-Ta-Cr-Si CLAD COMPOSITES

Exposure Temp., °F	Substrate	Nominal Cladding Thickness, mils	Weight Gain in Given Time (hr), Mg/cm^2							
			5	10	25	45	50	65	85	100
2500(a)	--	35	16.0	--	35.5	--	47.0	--	56.8	62.0
2500(b)	--	35	14.0	--	30.4	--	41.6	--	49.0	53.2
2200	Cb-752	10	15.5	--	25.2					
2200	Ta-10W	10	17.3	--	23.9					
2500	Cb-752	10	19.8	34.4	34.4	--	42.8			
2500	Cb-752	10	17.8	--	38.5	49.6				
2500	Ta-10W	10	21.7	--	40.5	--	49.2	57.7	65.5	
2500	Ta-10W	10	17.1	--	33.3	--	41.5	62.1		
2700	Cb-752	20	32.8(c)							
2700	Ta-10W	20	38.7(c)							
2700	Cb-752	20	30.0	41.2	67.0					

(a) Cladding alloy as rolled.

(b) Cladding alloy surface ground.

(c) Furnace failure after 5 hr.

TABLE III

SUMMARY OF FAILURE MODES OF CLAD COMPOSITES

Exposure Conditions				
Temp., °F	Time, hr	Sub-strate	Nominal Cladding Thickness, mils	Failure Mode
			Hf-Ta-Cr-B-Al Cladding	
2200	100	Cb-752	10	No failure in 100 hr; craze cracks after 25 hr.
2200	100	Ta-10W	10	No failure in 100 hr.
2500	65	Cb-752	20	Failure after 65 hr; craze cracks after 25 hr.
2500	25	Ta-10W	20	Sample cracked during cooling due to craze cracks.
2700	25	Cb-752	20	Edge crack after 25 hr; craze cracks after 5 hr.
2700	25	Ta-10W	20	Edge crack after 25 hr.
2700	5	Cb-752	20	Furnace failure after 5 hr.
2700	5	Ta-10W	20	Furnace failure after 5 hr.
			Hf-Ta-Cr-Si Cladding	
2200	25	Cb-752	10	Edge failure; failed on one face due to blister after 25 hr.
2200	25	Ta-10W	10	Sample fractured on cooling after 50 hr, due to edge defect observed after 25 hr.
2500	50	Cb-752	10	Furnace failure after 50 hr.
2500	65	Cb-752	10	Sample fractured on cooling due to edge crack observed after 40 hr.
2500	85	Ta-10W	10	Stopped after 85 hr due to edge crack observed after 25 hr.
2500	50	Ta-10W	10	Stopped after 85 hr due to edge crack observed after 25 hr.
2700	25	Cb-752	20	Edge crack after 25 hr.
2700	5	Cb-752	20	Furnace failure after 5 hr.
2700	5	Ta-10W	20	Furnace failure after 5 hr.

Figures 4 and 5. Although numerous cracks were readily visible, again they did not cause rapid failure of the cladding. Furthermore, the time for appearance of these cracks was temperature dependent varying from about 25 hr at 2200°F to 5 hr at 2700°F. Thus, it appears that the incubation time for cracking was related to the depth of oxidation of the cladding.

The surface appearance of selected composites after oxidation exposure are shown in Figure 5. Comparison of 5b and 5c indicates the different behavior of Hf-Ta-Cr-B-Al cladding on Cb-752 and Ta-10W. Figure 5a indicates the type of edge failure typical of Hf-Ta-Cr-Si alloys.

The oxidation lives obtained for the picture frame composites were disappointing, although 10-20 mil cladding did provide protection to 2700°F. Oxidation lives for 20 mil cladding of 900 hr at 2200°F, 400 hr at 2500°F, and 100 hr at 2700°F predicted by the oxidation behavior of the cladding alloys were not realized.(4) As previously stated, failure to approach these lives in this program was not the result of cladding failure. Only one of the failures could be attributed to inadequate bonding of the cladding alloy. The remainder of the failures were the result of stress-induced rupture of the cladding at the substrate picture frame interface. Thus, the majority of failures were directly related to the picture frame design rather than cladding performance.

Fractures at the cladding-substrate interface were caused by stresses induced by thermal cycling for weight change measurements at periodic intervals. Since the cladding layer was bonded to both the substrate and picture frame, stresses resulting from thermal exposure mismatch and/or thermal gradients were generated within the cladding. The picture frame substrate interface was the point of stress concentration in the composites. In a system where edge protection was achieved by other than a picture frame technique, this condition would not prevail;

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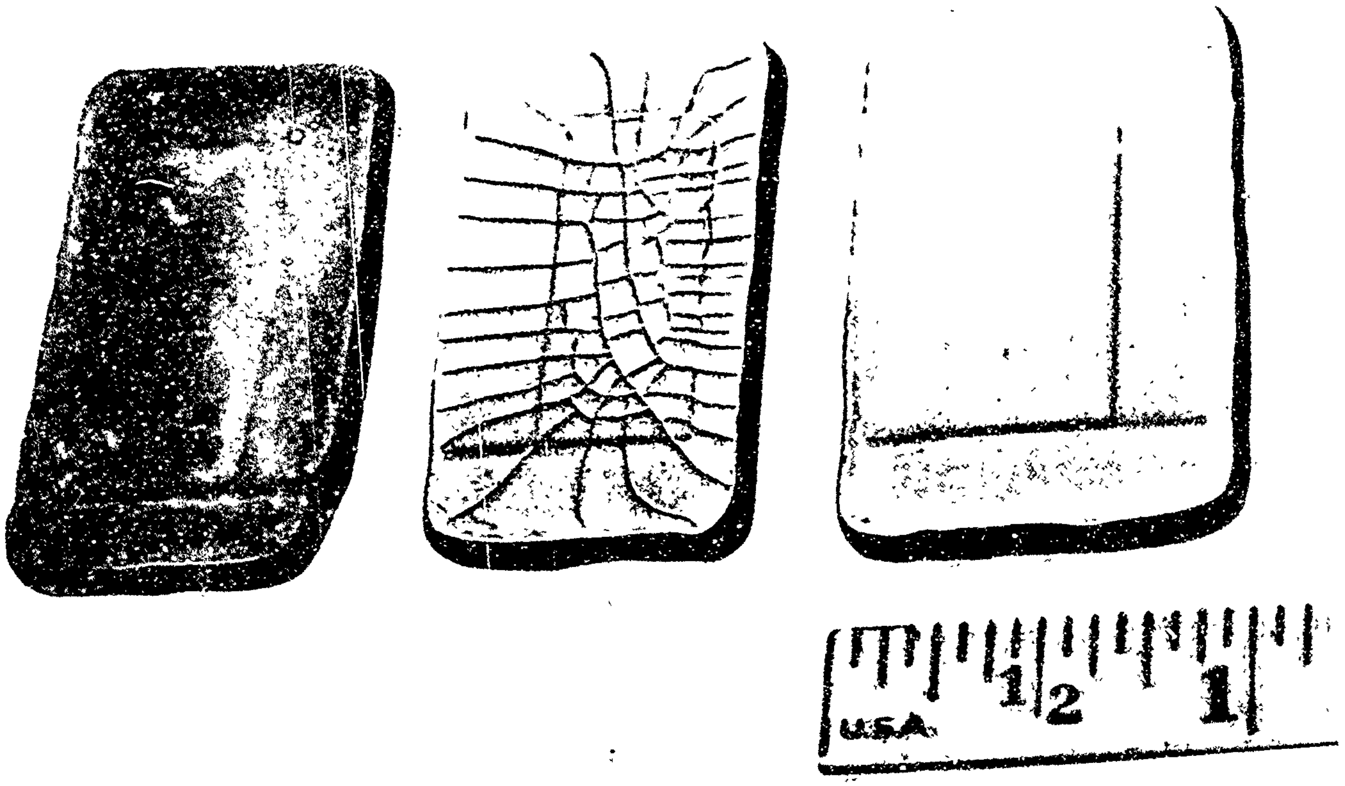
Fig. 4 - Surface of Hf-Ta-Cr-B-Al Cladding on Cb-752 Illustrating Cracking After Oxidation Exposure at 2500°F for 25 hr.



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(a)Hf-Ta-Cr-Si/Ta-10W
2500°F-85 hr

(b)Hf-Ta-Cr-B-Al/Cb-752
2200°F-100 hr

(c)Hf-Ta-Cr-B-Al/Ta-10W
2200°F-100 hr

Fig. 5 - Surface Appearance of Clad Composites After Oxidation Exposure.

oxidation lives approaching those predicted by the oxidation behavior of the cladding alloys would be obtained, at least for Ta-base substrates.

Edge cracking observed on the Hf-Ta-Cr-B-Al/Cb-752 composites would likely reduce the oxidation life of this composite system. Again, this was due to stresses resulting from a thermal expansion difference of the cladding alloy and Cb-752, which did not exist for the Ta-10W substrate. Since cracking occurred on cooling, the outer oxide on Hf-Ta-Cr-B-Al cladding apparently had a higher expansion coefficient than that of the underlying Cb-752/metallic cladding couple. It is apparent that the cracks were arrested at the subscale, since the composites did not fail immediately upon generation of the cracks. In general, the Hf-Ta-Cb-B-Al alloys appeared to be more tolerant to surface defects. On the other hand, the Hf-Ta-Cr-Si cladding was more resistant to thermal stress cracking. This could be associated with the lower oxidation rate of Cr-Si alloys.

B. Oxidation Screening Tests

Previous work on hafnium-base(1-4) alloys demonstrated that the best oxidation resistance was obtained in modified alloys containing about 25 w/o (25 a/o) tantalum. Similarly, Hf-Cb alloys with about 15 w/o columbium (~25 a/o) had the best oxidation resistance. Other work by Hill(5) and Marnoch(6) suggested that the relatively good oxidation resistance of Hf-Ta alloys was due to the development of a complex oxide of the type $6HfO_2 \cdot Ta_2O_5$ ($Hf_6Ta_2O_{17}$). The complex oxide was reported to be structurally similar to tetragonal HfO_2. Similar oxides have also been suggested for other combinations of Group IVB-VB oxides including the Zr-Ta, Hf-Cb, and Zr-Cb systems. Furthermore, the successful silicide coatings for tantalum and columbium also often contain a Group IVB component (Ti). All of this information, along with review of the literature, suggested that modified binary alloys of this type had the best potential for development of high-temperature oxidation resistance.

Currently, at least two oxidation-resistant alloys of the Group IVB-VB type are under investigation. These are the Cb-Ti-Al-Cr alloys being used as a composite matrix by Solar(7) and the Cb-Hf-W-Zr-Ti alloys (WC 3015) under development by Wah Chang.(8) In both cases, the concentration of Group IVB element or elements is in the range of 40-50 w/o. Thus, the oxidation behavior of alloys tends to verify the work on Hf-Ta alloys which demonstrated the necessity for a high concentration of IVB element. The significance of this information was that if complex oxides existed in several systems, oxidation-resistant alloys could be developed in other combinations of IV-VB alloys. Furthermore, the alloying additions and their combinations which were successful in improving oxidation of Hf-Ta alloys should be similarly effective in the other systems. It was recognized that the Ti-Cb system could deviate since complex oxides other than $6AO_2 \cdot B_2O_5$ have been reported in the TiO_2-Cb_2O_5 system.(9)

The oxidation behavior of binary Hf-Ta and Hf-Cb alloys was determined in previous work. As previously discussed, oxide adherence and oxidation rate at 2500°F was optimum at about 25 a/o of tantalum or columbium. Accordingly, binary alloys in only the Cb-Ti and Cb-Zr systems over the range of 0-80 a/o Group IVB element were arc-melted for oxidation testing. In addition, two Cb-rich binary alloys in the Cb-Hf system were prepared.

The results of the initial oxidation studies in static air at 2200° and 2500°F are presented in Table IV. Oxidation tests were conducted on cold-rolled material wherever possible. In general, the binary Cb-Ti and Cb-Zr alloys were cold workable in the arc-melted condition, whereas Cb-Hf alloys were not. Oxidation exposure was continued for 32 hr at 2200°F or 10 hr at 2500°F. Exposure of any sample was stopped until either the sample exhibited extensive spalling or excessive oxide growth

TABLE IV

OXIDATION BEHAVIOR OF BINARY COLUMBIUM ALLOYS IN STATIC AIR

Nominal Alloy Composition, w/o (a/o)	Weight Change in Indicated Time (hr), %								
	2200°F					2500°F			
	0.5	1	5	10	16	0.5	1	5	10
Cb-8.3Ti (15Ti)	-2.2[a]					-4.6[a]			
Cb-14Ti (24Ti)	-2.9[b]	-5.8[a]				-5.1[a]			
Cb-22Ti (35Ti)	-3.1[a]					-3.7[a]			
Cb-30Ti (45Ti)	-2.7[a]					-7.0[a]			
Cb-40Ti (56.4Ti)	-2.3[a]					-6.4[a]			
Cb-43.5Ti (60Ti)	2.6	5.0[b]				-7.5[a]			
Cb-55Ti (70Ti)	-	0.9[a]				-	2.3[b]	5.3[a]	
Cb-68Ti (80Ti)	-	2.4[a]				-	1.4[b]	3.5[a]	
Cb-14.7Zr (14.7Zr)	-2.9[a]					-5.2[a]			
Cb-29.6Zr (30Zr)	2.9[b]	4.0[b]				2.9[a]			
Cb-35Zr (35Zr)	3.9	5.8	18.1[c]			6.0[a]			
Cb-44.5Zr (45Zr)	2.5	3.4[b]				3.9			
Cb-50Zr (50.5Zr)	3.0	4.5	10.2	20.4[c]		5.1	7.5[b]		
Cb-55Zr (55.5Zr)	3.2	4.3	10.0			5.7[b]	8.0[b]		
Cb-60Zr (60.5Zr)	3.1	4.7	10.0	14.0	27.2[c]	5.8	8.3	18.0	26.7[c]
Cb-65Zr (65.5Zr)	3.0	4.4	9.4	13.5	29.2[c]	4.8	8.2	17.9	26.2[c]
Cb-70Zr (70.5Zr)	3.0	4.3	9.1	13.3	30.0[c]	6.1	8.8	18.5	27.7[c]
Cb-75Zr (75.5Zr)	3.2	4.3	9.4	20.6[c]		6.6	9.7	17.5	35.3[d]
Cb-80Zr (80.5Zr)	3.5	4.7	11.3[c]			7.5	10.6	21.0	52.0[d]
Cb-85Zr (85.5Zr)	4.0	5.7	18.8[c]			8.13	12.3	26.0[c]	
Cb-25.3Hf (15Hf)	-3.0[a]					-3.9[a]			
Cb-45.2Hf (30Hf)	1.1	3.6[a]				-1.3[a]			

[a] Heavy spalling.

[b] Light spalling.

[c] Cracking at edges.

[d] Extensive oxidation.

resulted in cracking. Excessive, essentially complete spalling occurred during cooling of the oxide layer formed during the exposure cycle. Spalling was typical of Cb-Ti alloys, whereas thick, adherent oxides were developed on Cb-Zr alloys.

Weight change data in this report are given in percent of the original sample weight. It is recognized that specific weight change provides a better comparison of oxidation rate of various systems. The use of percent change was dictated by the large number of arc-melted buttons evaluated and the inability to work a number of the alloys into sheet material with uniform dimensions. For this reason, oxidation data tables contain numerous notes on visual observation of spalling and/or oxide.

Data in Table IV indicate somewhat improved oxide adherence for Ti-Cb alloys at 60 to 80 a/o Ti. At 24 a/o Ti some improvement in oxide adherence was observed for short exposures. This may have been associated with formation of the $Ti_2Cb_{10}O_{29}$ complex oxide described by Wadsley.(11) The two Cb-Hf alloys also indicated improved oxide adherence with increasing hafnium concentration consistent with previous work.

On the other hand, the Cb-Zr alloys demonstrated a well-defined region of improved oxide adherence at both 2200° and 2500°F in alloys containing 60-70 a/o Zr. A similar behavior occurs in the Hf-Ta binary system at 70-80 a/o Hf; both systems also indicate a minimum in the oxidation rates in these composition ranges. If this minimum is the result of the formation of a complex oxide, the shift in optimum composition range for Cb-Zr alloys may be a diffusion-controlled effect.

The most effective alloying additions to Hf-Ta alloys for improving oxidation resistance were aluminum, boron, silicon, and chromium. Aluminum, boron, and chromium have valence 3 oxidation states, whereas silicon is valence 4. All of the most oxidation resistant Hf-Ta alloys contained chromium in combination with one of the other three elements. Thus a valence 3 addition seems necessary to obtain good oxidation resistance in Hf-Ta alloys.

Accordingly, a series of alloys in the Cb-Ti and Cb-Zr system modified with Cr, Al, B, Si, V, and Y were fabricated by arc-melting for oxidation testing at 2200° and 2500°F. A series of Cb-Cr-Al alloys were also prepared for comparison of alloys without a Group IV component. Since a clear range of oxide adherence was not established in the Cb-Ti system, alloys containing 16-42 w/o Ti were evaluated. Based on the data for the binary alloys, all of the modified Cb-Zr alloys contained 55-75 w/o zirconium. These alloys were oxidized in the arc-melted condition; both oxidation samples were sectioned from the same 10 g button.

A summary of oxidation behavior of modified Cb-Ti alloys at 2200° and 2500°F is presented in Table V. Weight change for selected alloys at 2200°F is plotted in Figure 6 and at 2500°F in Figure 7. The oxides on these alloys are generally not adherent; spalling normally occurred during cooling after exposures of 5-16 hr at 2200°F and 1-5 hr at 2500°F. The best oxidation resistance was obtained in Cb-40Ti-4Cr-4Al alloys, particularly those further modified with silicon. Boron and yttrium increased the spalling tendency of Cb-Ti alloys, whereas vanadium was mildly beneficial at 2200°F, but increased the spalling slightly at 2500°F.

A summary of the oxidation behavior of modified Cb-Zr alloys is presented in Table VI. Weight change for selected alloys at 2200°F is plotted in Figure 8. In contrast to Cb-Ti alloys, Cb-Zr alloys developed thick, adherent oxides that eventually cracked at edges. Thus, the Cb-Zr alloys were similar in oxidation behavior to slightly modified Hf-Ta alloys. The best oxidation resistance was obtained in the Cb-55Zr-2.5Cr-0.8Al alloy and in Cr-Si alloys at both 65 and 75 w/o zirconium. The Cb-65Zr-2.5Cr-1.0 Si alloy had a weight gain less than one-third that of the binary Cb-65Zr alloy after 16 hr at 2200°F, but only slightly less after 10 hr at 2500°F. It was also shown that small aluminum

TABLE V

OXIDATION BEHAVIOR OF MODIFIED Cb-Ti ALLOYS IN STATIC AIR

Alloy Composition, w/o	Weight Change in Indicated Time (hr), %									
	2200°F						2500°F			
	0.5	1	5	10	16	32	0.5	1	5	10
Cb-16Ti-4Cr-4Al	-0.5(a)						1.2	0.8(b)	6.5	14.4(c)
Cb-16Ti-4Cr-4Al-3Si	-	0.8	1.2(b)	0.5(b)			-	1.4	-0.8(b)	
Cb-16Ti-4Cr-4Al-0.7B	-	0.6	-5.2(a)				-	4.8	14.2(c)	
Cb-15Ti-10Ta-10W-7Hf-3Al	-	-0.8(b)	-3.9(a)				-	-2.2(a)		
Cb-18Ti-4Cr-4Al	0.02(b)						2.6	-3.4(c)		
Cb-18Ti-8Cr-10Al	-0.6	1.1	1.3(b)				-3.8	-18.7(a)	-16.2(a)	
Cb-18Ti-25Hf	-3.7(a)						-4.1(a)			
Cb-18Ti-24Hf-3V	-2.3(a)						-1.8(a)			
Cb-37Ti-4Cr-4Al	2.0	3.0(b)					5.3(c)			
Cb-40Ti-4Cr-4Al	0.4	0.7	1.9(b)				1.1	1.4	-1.5(b)	-5.7(a)
Cb-42Ti-4Cr-4Al	0.4	0.8	1.4	1.3(b)	0(b)	-6.3(a)	0.9	0.8	-3.5(a)	-7.1(a)
Cb-40Ti-4Cr-4Al-1V	0.6	1.0	1.5	1.5	0.6(b)	-4.9(a)	1.0	0.9	-2.9(a)	-8.4(a)
Cb-40Ti-4Cr-4Al-3V	0.5	0.8	1.3	1.6	1.2(b)	-2.9	1.0	0.6	-0.4(b)	-9.6(a)
Cb-40Ti-4Cr-4Al-0.3B	0.3	0.6	1.6	-1.6(b)	1.6(a)		0.8	0.6	-1.9	-4.8(a)
Cb-40Ti-4Cr-4Al-0.7B	0.4	0.7	1.6	-4.3(b)	4.7(a)		0.7	0.7	-1.9	-5.3(a)
Cb-39Ti-4Cr-4Al-1Si	0.5	0.7	1.5	-0.6(b)	-0.7(b)	-3.9(a)	0.5	0.4	-0.5	-8.5(a)
Cb-39Ti-4Cr-4Al-3Si	0.3	0.4	1.0	0.8(b)	1.4(b)	0.5(b)	0.4	0.2	0.3(b)	-4.1(a)
Cb-38Ti-4Cr-4Al-5Si	-	0.4	1.1	1.6	1.3(b)		-	1.1	-0.9(b)	-2.9(b)
Cb-38Ti-4Cr-4Al-7Si	-	0.5	1.0	1.5	1.9(b)		-	1.1	1.2(b)	-0.6(b)
Cb-40Ti-4Cr-4Al-1Y	-	0.8	1.1	-1.2	-3.3		-	0.5	-3.0(b)	-6.0(a)
Cb-40Ti-4Cr-4Al-2Y	-	1.0	0.5	-3.8	-3.2		-	0.9	-2.6(b)	-7.0(a)

(a) Heavy spalling.

(b) Light spalling.

(c) Edge growth, cracking.

(d) Extensive oxidation.

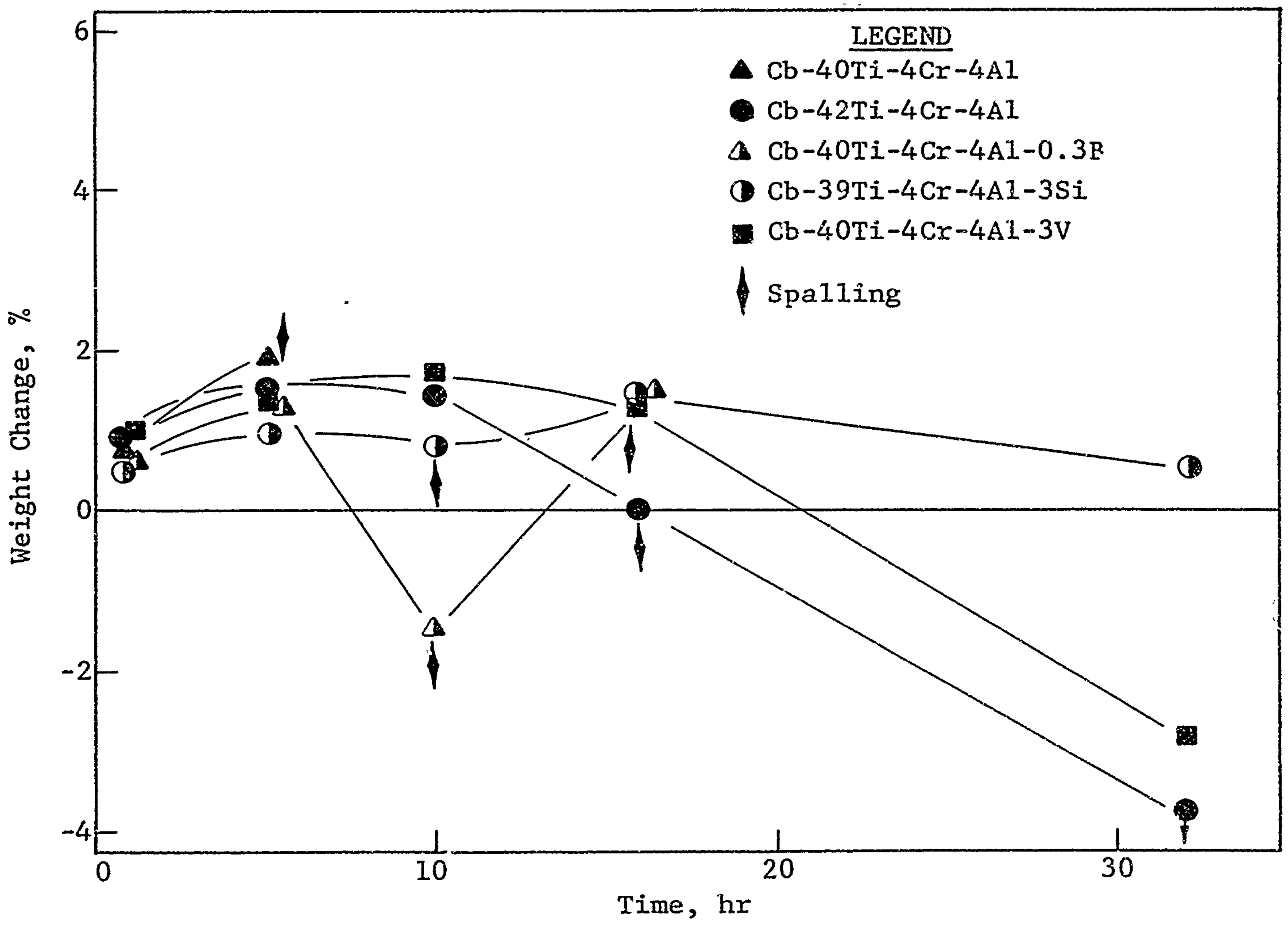

Fig. 6 - Oxidation Behavior of Modified Cb-Ti Alloys in Static Air at 2200°F.

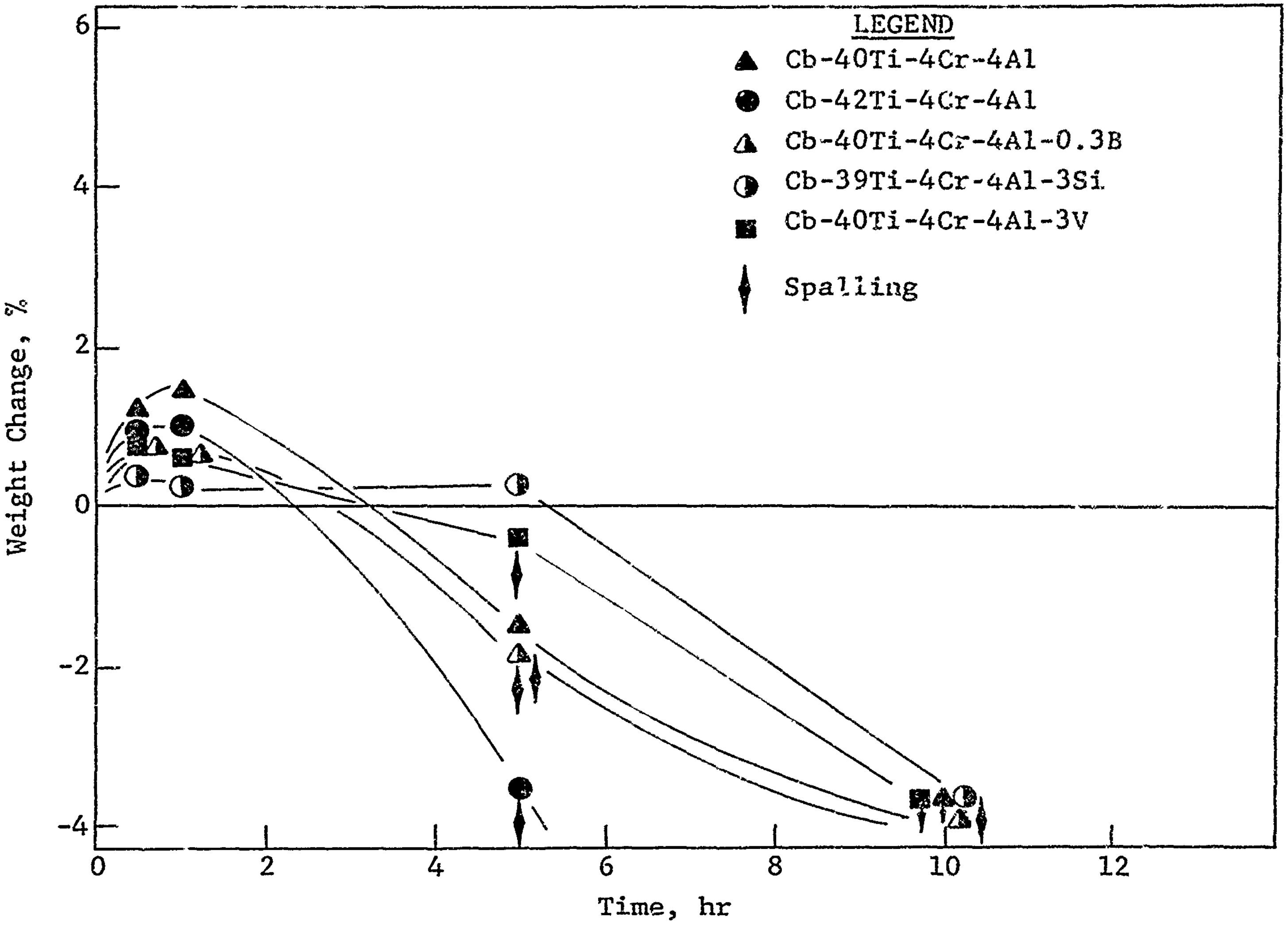

Fig. 7 - Oxidation Behavior of Modified Cb-Ti Alloys in Static Air at 2500°F.

TABLE VI

OXIDATION BEHAVIOR OF MODIFIED Cb-Zr ALLOYS IN STATIC AIR

Alloy Composition, w/o	Weight Change in Indicated Time (hr), %						
	2200°F				2500°F		
	1	5	10	16	1	5	10
Cb-55Zr-0.5Al	3.8	7.9	12.0	14.2(a)	6.3	13.6	19.4 .
Cb-55Zr-1.0Al	3.6	7.5	11.5	14.1(a)	6.4	14.3	18.4
Cb-55Zr-1.0Cr	4.0	8.2	12.6	14.2(a)	6.9	17.4	31.8(b)
Cb-54Zr-2.5Cr	2.8	8.0	8.9	10.3(a)	4.8	11.5	21.3(b)
Cb-65Zr-0.5Al	3.8	7.9	12.0	15.9(a)	7.5	15.7	27.2(b)
Cb-65Zr-1Cr	4.1	8.1	12.3	15.4	7.7	15.6	25.5(b)
Cb-65Zr-2.5Cr	3.0	6.4	11.0(a)		5.9	13.4	22.5(b)
Cb-68Zr-4Al	4.2	16.8(a)			6.5(b)		
Cb-68Zr-4Cr	3.3	7.4	13.6(a)		6.3	16.9(b)	
Cb-55Zr-2.5Cr-0.7B	2.6	5.3	8.3(a)		6.7(b)		
Cb-55Zr-2.5Cr-0.8Al	1.3	4.8	6.1(a)		4.4	10.5	11.1(a)
Cb-65Zr-2.5Cr-0.7B	3.5	7.7	14.0(a)		6.5	17.2	29.2(b)
Cb-65Zr-2.5Cr-0.8Al	3.8	8.3	13.7(a)		6.1	14.1	21.4
Cb-65Zr-2.5Cr-0.5Si	2.7	5.5	8.3	10.0(a)	5.6	12.8	
Cb-65Zr-2.5Cr-1.0Si	2.6	5.2	7.7	8.6(a)	4.4	8.8	20.4(b)
Cb-66Zr-4Al-4Cr	3.7				7.8(c)		
Cb-64.5Zr-4Cr-4Al-0.7B	4.5	7.9	11.5(a)		7.8(a,c)		
Cb-64Zr-4Al-4Cr-3V	2.4(d)				7.3(c,d)		
Cb-64.5Zr-4Al-4Cr-3Si	0.13	-7.3(d)			8.0(c)		
Cb-65Zr-2.5Cr-0.5Ti	4.1	8.7	11.7(a)		6.4	13.2	22.2(b)
Cb-65Zr-2.5Cr-1.0Ti	4.1	8.1	9.3(a)		6.5	13.2	22.3(b)
Cb-65Zr-1.0Cr-0.5Al-0.7B	2.5	5.6	11.8(a)		6.9	21.8	
Cb-71Zr-4Al-4Cr	1.3(a)				9.0(c)		
Cb-75Zr-3.4Cr-2.1Si	3.7	7.5	9.1	12.4	7.1	20.4(c)	
Cb-71Zr-0.23Cr-2.3Al-1.26B	3.9	7.1(a)			8.9	23.6(c)	

(a) Moderate spalling.

(b) Edge growth, cracks.

(c) Reaction with Al_2O_3 boat.

(d) Heavy spalling.

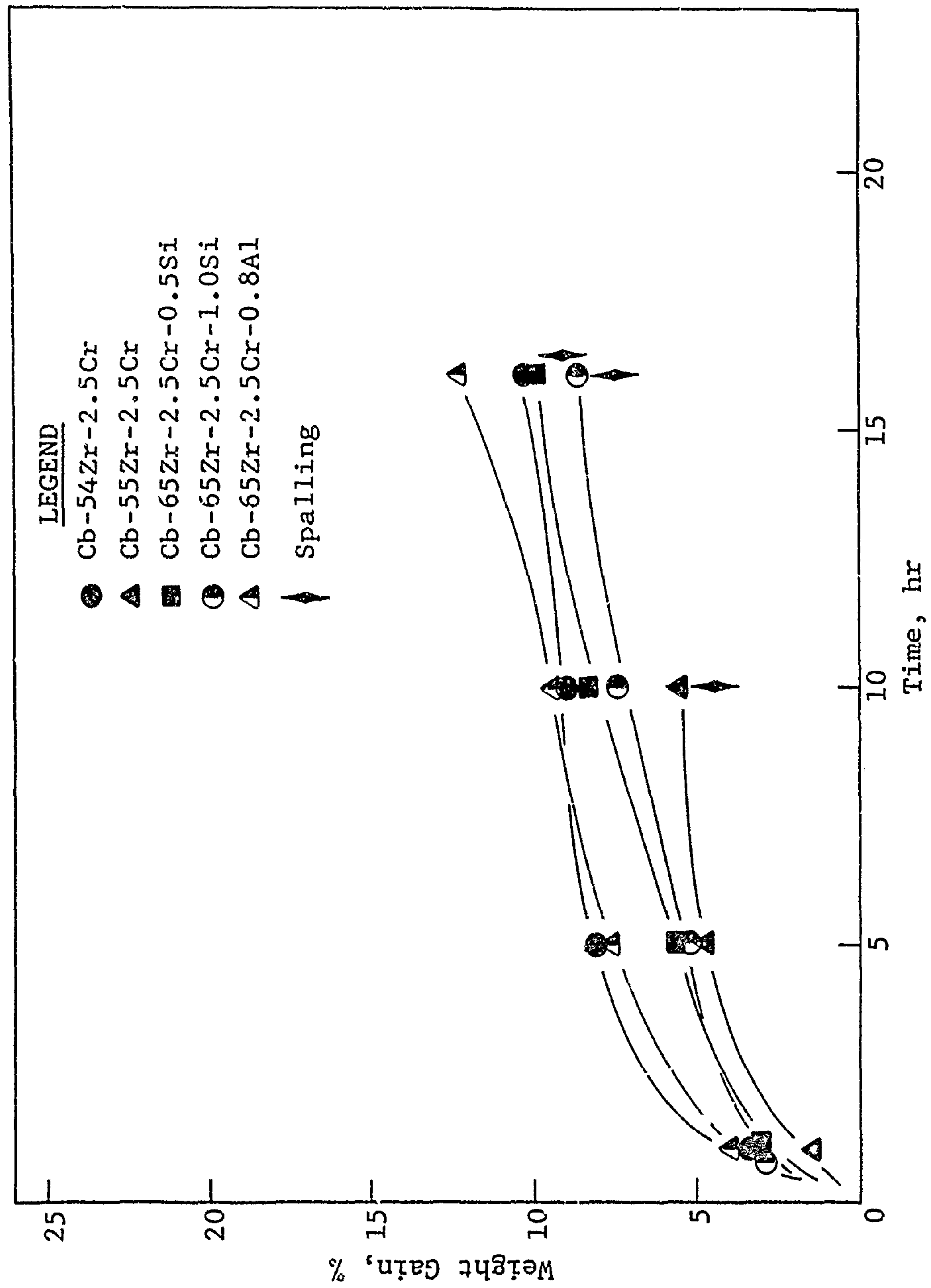

Fig. 8 - Oxidation Behavior of Modified Cb-Zr Alloys in Static Air at 2200°F.

and chromium additions were effective in reducing the weight gain of alloys containing 55-65 w/o Zr.

A summary of the oxidation rates of modified Cb-15Cr-20Al alloys is presented in Table VII. Data for selected alloys are plotted in Figure 9. Additions of vanadium, boron, silicon, and yttrium were made to the Cb-15Cr-20Al base alloy. Again, silicon proved to be the most effective addition at both 2200° and 2500°F. In fact, the alloys with silicon modifications showed no increase in short-time oxidation rate at 2500°F compared to 2200°F. However, all of the Cb-Cr-Al alloys were very brittle, and work on these alloys was discontinued.

The results of the screening tests indicated that the oxidation resistance of Cb-40 a/o Ti alloys at 2200°-2500°F could be improved considerably by adding combinations of Cr-Al and Cr-Al-Si. These additions were less effective in Cb-(55-75)Zr alloys, particularly at 2500°F. Addition of Cr-Si appeared to be the most promising for Cb-Zr alloys. Combinations of Cr-B as minor alloying additions which are effective in Hf-Ta alloys were not studied in the initial work. Silicon appeared to be an effective additive for most systems, either as a third minor element or in combination with chromium.

The initial oxidation results also demonstrated that Cb-Zr alloys behaved similar to Hf-Ta alloys, whereas the Cb-Ti alloys did not. Thus, formation of a Cb-Zr oxide complex appeared possible based on the complex Hf-Ta oxide model. Deviation of Cb-Ti alloys from this model was not unexpected since the structure of TiO_2 (rutile) differs from that of zirconia and hafnia. The oxidation resistance obtained in Cb-Ti alloys could have resulted from the formation of a complex oxide other than $A_6B_2O_{17}$.

C. Extended Oxidation Testing

The results of screening tests suggested that zirconium- and hafnium-rich alloys containing columbium and/or tantalum would provide similar oxidation behavior. Titanium-rich systems were expected to differ somewhat from the other Group IVB alloys. In

TABLE VII

OXIDATION BEHAVIOR OF Cb-Cr-Al ALLOYS IN STATIC AIR

Alloy Composition, w/o	Weight Change in Indicated Time (hr), %								
	2200°F					2500°F			
	0.5	1	5	10	16	0.5	1	5	10
Cb-15Cr-20Al	0.3	0.6	1.8^{a}	5.5	11.0^{c}	0.6	1.4^{c}		
Cb-15Cr-20Al-1V	0.1	0.1	-1.5^{a}	1.3^{b}		0.9	1.5	1.5^{a}	5.0^{b}
Cb-15Cr-20Al-3V	0.7	1.4	-	1.3^{b}		0.8	1.6	5.6^{a}	3.2^{b}
Cb-15Cr-20Al-0.3B	0.6	1.1	3.0^{a}	3.9^{a}	6.9^{a}	0.8	1.3	3.5	8.6^{a}
Cb-15Cr-20Al-0.7B	0.6	1.0	1.3	8.3	3.6^{a}	0.9	1.3	3.4	6.3^{a}
Cb-15Cr-20Al-1Si	0.5	0.9	1.8	2.1^{c}		0.5	0.7	1.3	1.9
Cb-15Cr-20Al-3Si	0.4	0.5	1.7	2.0	2.6	0.3	0.5	1.0	1.2
Cb-15Cr-20Al-5Si	-	0.4	0.8	1.3	1.7^{c}	-	1.0	1.1	1.3
Cb-15Cr-20Al-7Si	-	0.8	1.8	3.0	4.2^{c}	-	1.0	1.8	2.3
Cb-15Cr-20Al-1Y	-	0.7	2.6	5.2^{c}		-	1.0	3.3	3.8^{c}
Cb-15Cr-20Al-2Y	-	0.6	2.4	5.8^{c}		-	0.8	2.7	6.6^{c}
Cb-7Cr-10Al-9Fe	0.5	0.7	2.2	1.7^{a}		1.0	1.5	3.9	7.6^{a}

[a] Light spalling.

[b] Heavy spalling.

[c] Edge growth cracking.

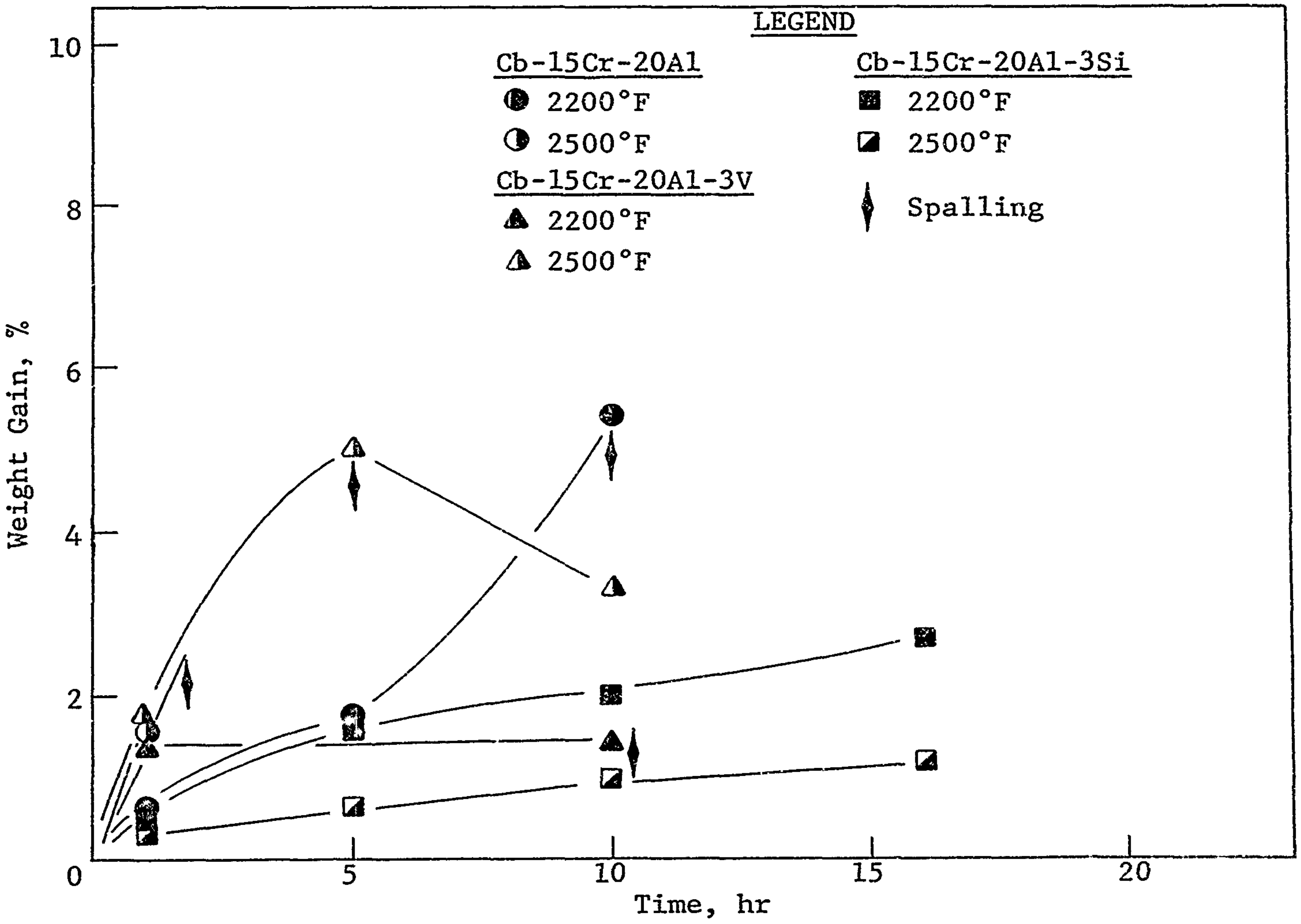

Fig. 9 - Oxidation Behavior of Modified Cb-Cr-Al in Static Air.

any case, a series of alloys was prepared based on the atomic concentration of the most oxidation-resistant Hf-Ta alloys. These alloys were analogs of Hf-23.5Ta-1.8Cr-1.1Si, Hf-24.5Ta-1.5Cr-0.7B, and Hf-24.5Ta-1.2Cr-0.7B-0.12Al. Also, Cr-B-Cr-Si and Cr-Al-Si additions were made to Cb-42Ti alloys.

Finally, two Hf-Ta alloys and one Cb-Zr alloy was prepared in which iron was substituted for chromium in the Hf-Ta-Cr-Si alloy. These alloys would then indicate whether equivalent oxidation behavior could be obtained with another valence 3 element with an atomic radius similar to chromium.

The alloys were prepared as 5 g buttons by arc-melting as previously and oxidized in the arc-melted condition. Three oxidation samples were sectioned from each button for exposure in static air at 2000°, 2200°, and 2500°F. The alloys were exposed for up to 60 hr at 2000°F and 40 hr at 2200° and 2500°F. As previously, exposures were terminated if excessive oxidation, edge cracking, or spalling occurred.

Weight change data in the following data tables are also given in percent of the original sample weight. Since all of the samples were approximately the same weight, the specific weight change in mg/cm^2 can be estimated from percent weight change. Weight change in mg/cm^2 for the Cb-Ti and Cb-Zr alloys is approximately the percent weight change multipled by 10. For the Ta-Si, Ta-Zr, Cb-Hf, and Ta-Hf alloys, the multiplication factor is 15. The higher factor for the heavier alloys is due to a lower surface area.

Oxidation data for modified Cb-Ti alloys at 2000°, 2200°, and 2500°F are presented in Table VIII. Weight change data for selected alloys are plotted in Figure 10. The most oxidation-resistant alloys were the Cb-42Ti-5.5Cr-4.0Al-3.5Si and Cb-55Ti-5.5Cr-3.5Si compositions. Both of these alloys survived 60 hr at 2200°F, but began spalling after 5-10 hr at 2500°F. The next most resistant composition was the Cb-42Ti-5.5Cr-3.5Si, which was more susceptible to spalling than the

TABLE VIII

OXIDATION BEHAVIOR OF COMPLEX Cb-Ti ALLOYS IN STATIC AIR

Alloy Composition, w/o	Exposure Temp., °F	Weight Gain in Given Time (hr), %						
		1	5	10	16	22	40	60
Cb-42Ti-4.7Cr-2.0B	2000	0.6	-0.7	-4.3(b)	-14.2(a)			
	2200	0.6	3.6(a)					
	2500	2.5(b)	21.7(c,d)					
Cb-52Ti-3.8Cr-2.0B-0.25Al	2000	0.6	0.6	-2.1(b)	-7.2(a)			
	2200	1.1	4.0	4.0(b)				
	2500	1.7	19.2(c)	32.6(d)				
Cb-42Ti-5.5Cr-4.0Al-3.5Si	2000	0.1	0.3	0.4	0.6	0.8	1.1(b)	
	2200	0.3	0.6	0.9	1.1	1.6	1.1(b)	0.02(b)
	2500	0.6	-0.2(b)	-2.4	-3.8	-8.0(a)	-11.4	
Cb-55Ti-5.5Cr-3.5Si	2000	0.3	0.9	1.3(b)	1.6	1.8	1.9	
	2200	0.4	1.1	1.0(b)	0.7	1.2	-2.6	-9.7(a)
	2500	1.0	0.2	-1.4(a)	-5.1	-8.0(a)	-7.7(c)	
Cb-42Ti-5.5Cr-3.5Si	2000	0.3	0.7	0.9	1.1	1.1	0.6(b)	
	2200	0.4	0.8	0.7(b)	-0.4	-0.02	-9.0(a)	
	2500	0.8	-2.7(b)	-7.5(a)	-13.0	-20.0	-33.0	
Cb-52Ti-4.7Cr-2.0B	2000	0.6	0.7	-1.5(b)	-7.7(a)			
	2200	0.8	2.4(b)					
	2500	1.5	10.8(c)	23.3(d)				

(a) Heavy spalling.
(b) Light spalling.
(c) Edge growth cracking.
(d) Extensive oxidation.

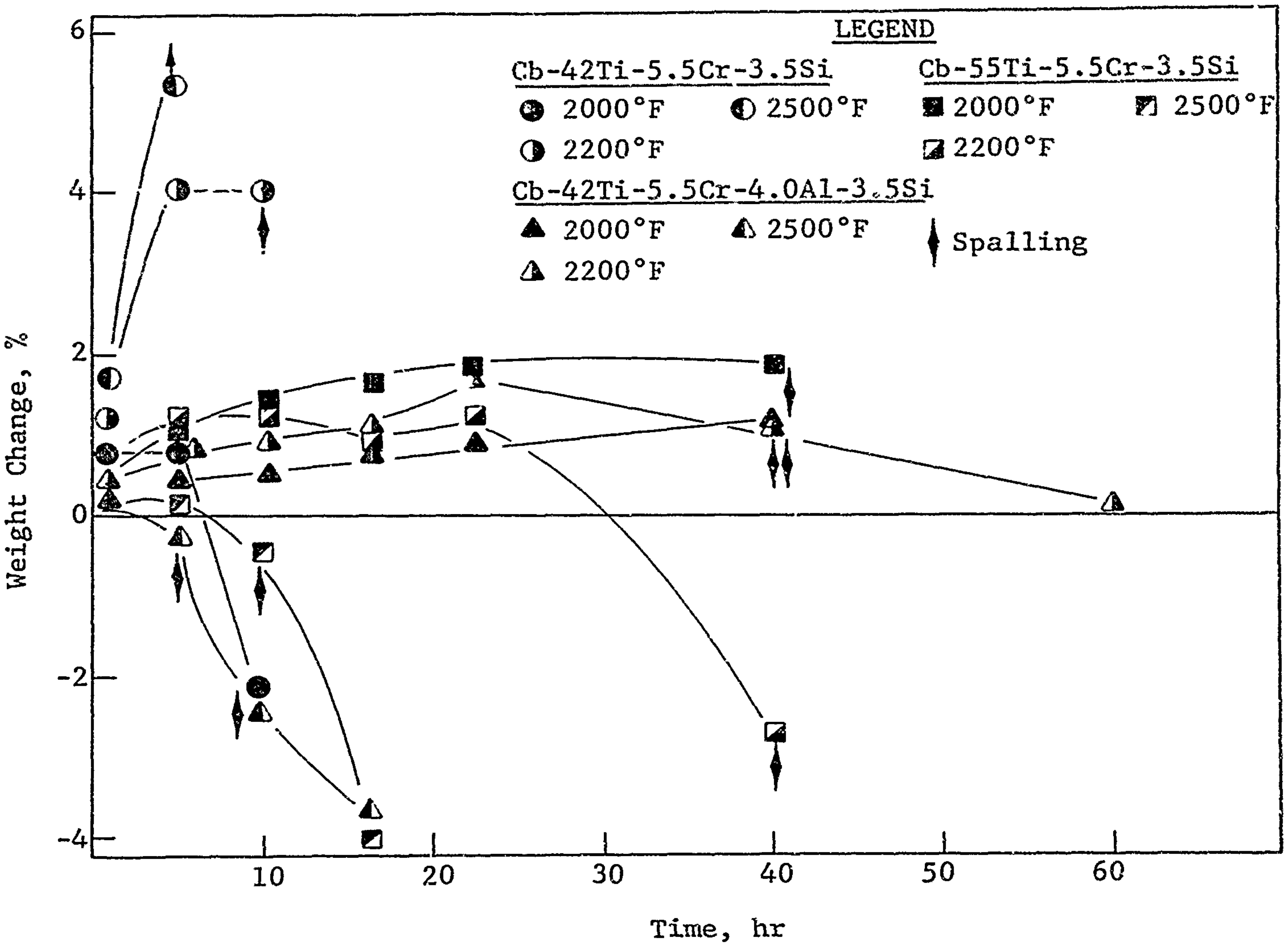

Fig. 10 - Oxidation Behavior of Modified Cb-Ti Alloys in Static Air.

comparable alloy with 52 a/o Ti. All of the Cr-B alloys had considerably poorer oxidation than the Cr-Si alloys.

Spalling of the oxides on Cb-Ti-Cr-Si alloys occurred primarily at edges of the samples, usually exposing the base metal. In spite of the observed spalling, these alloys exhibited good oxidation resistance even at 2500°F. For example, the weight loss of 11.4% after 40 hr at 2500°F for the Cb-Ti-Cr-Al alloy corresponds to average metal recession of about 0.007 in., assuming spalling of all of the oxide present on the sample. After 40 hr at 2000°F, the weight gain of 1.1% corresponds to a metal conversion of 0.0015-0.002 in. The latter calculation is less accurate because a minor amount of spalling can change the calculated metal recession. Weight gain resulting from oxygen uptake for these alloys is about one half the weight loss that would be measured if all of the oxide formed spalled from the surface.

The oxidation behavior of Cb-Zr analogs of oxidation-resistant Hf-Ta alloys is summarized in Table IX; data for selected alloys are plotted in Figure 11. As in the Cb-Ti alloys, Cr-Si additions were effective in improving the oxidation resistance considerably at 2000° and 2200°F, but were less effective at 2500°F. Again, the best overall oxidation resistance was obtained in the Cb-Zr-Cr-Si analogs. However, the Cr-B addition was more effective than in Cb-Ti alloys; 40 hr exposures were obtained at 3000°F in both Cb-Zr-Cr-B alloys. Substitution of iron for chromium in the Cb-67Zr base alloy resulted in approximately equivalent oxidation behavior to the Cb-Zr-Cr-Si alloys. Failure of all of the Cb-Zr alloys occurred by extensive oxidation and edge cracking after some period of exposure.

The oxidation behavior of Ta-Ti and Ta-Zr analogs is summarized in Table X; weight change data for selected alloys are plotted in Figure 12. As with Cb-Ti alloys, the most oxidation-resistant alloy was Ta-39Ti-4.0Cr-2.5Si. Addition of Cr-B resulted in considerably lower oxidation resistance. The

TABLE IX

OXIDATION BEHAVIOR OF Cb-Zr ALLOYS IN STATIC AIR

Alloy Composition, w/o	Exposure Temp., °F	Weight Gain in Given Time (hr), % 1	5	10	16	22	40
Cb-65Zr-2.5Cr-2.3Si	2000	1.2	1.8	2.0	2.4	2.6	3.1
	2200	2.1	4.6	6.1	10.2	1.9 (a)	6.1 (a)
	2500	3.7	8.6	15.0 (c,d)			
Cb-68Zr-3.7Cr-2.3Si	2000	1.3	1.8	2.1	2.4	2.7	3.2
	2200	2.2	4.7	4.4 (b)	4.6 (b)	-0.15 (b)	2.7 (a)
	2500	4.6	12.8 (c,d)				
Cb-67Zr-3.2Cr-0.7B	2000	1.4	1.9	2.1	2.3	2.6	3.0
	2200	2.5	5.3	8.4	13.3 (c)		
	2500	5.2	19.4 (d)				
Cb-67Zr-3.2Cr-1.3B	2000	1.4	2.2	2.8	4.2	6.0	-0.3 (b,c)
	2200	2.8	6.3	12.2 (d)			
	2500	5.5	14.0 (c)	20.8 (d)			
Cb-68Zr-2.6Cr-1.3B-0.17Al	2000	1.5	2.5	3.3	5.6	7.7	16.0 (b,c)
	2200	2.7	6.5	8.3 (d)			
	2500	5.7	14.6 (c)	20.3 (d)			
Cb-67Zr-2.5Fe-2.3Si	2000	1.5	2.5	2.3	2.6	2.9	3.9
	2200	2.4	-	7.4	10.3 (b,c)		
	2500	4.1	12.5 (c)	18.8 (d)			
Cb-67Zr-3.2Fe-0.7B	2000	1.4	2.4	3.4	4.9	7.5 (c)	
	2200	2.7	-	12.2 (c)	17.4 (d)		
	2500	5.0	14.4	19.9 (c)			

(a) Heavy spalling.
(b) Light spalling.
(c) Edge growth, cracking.
(d) Extensive oxidation.

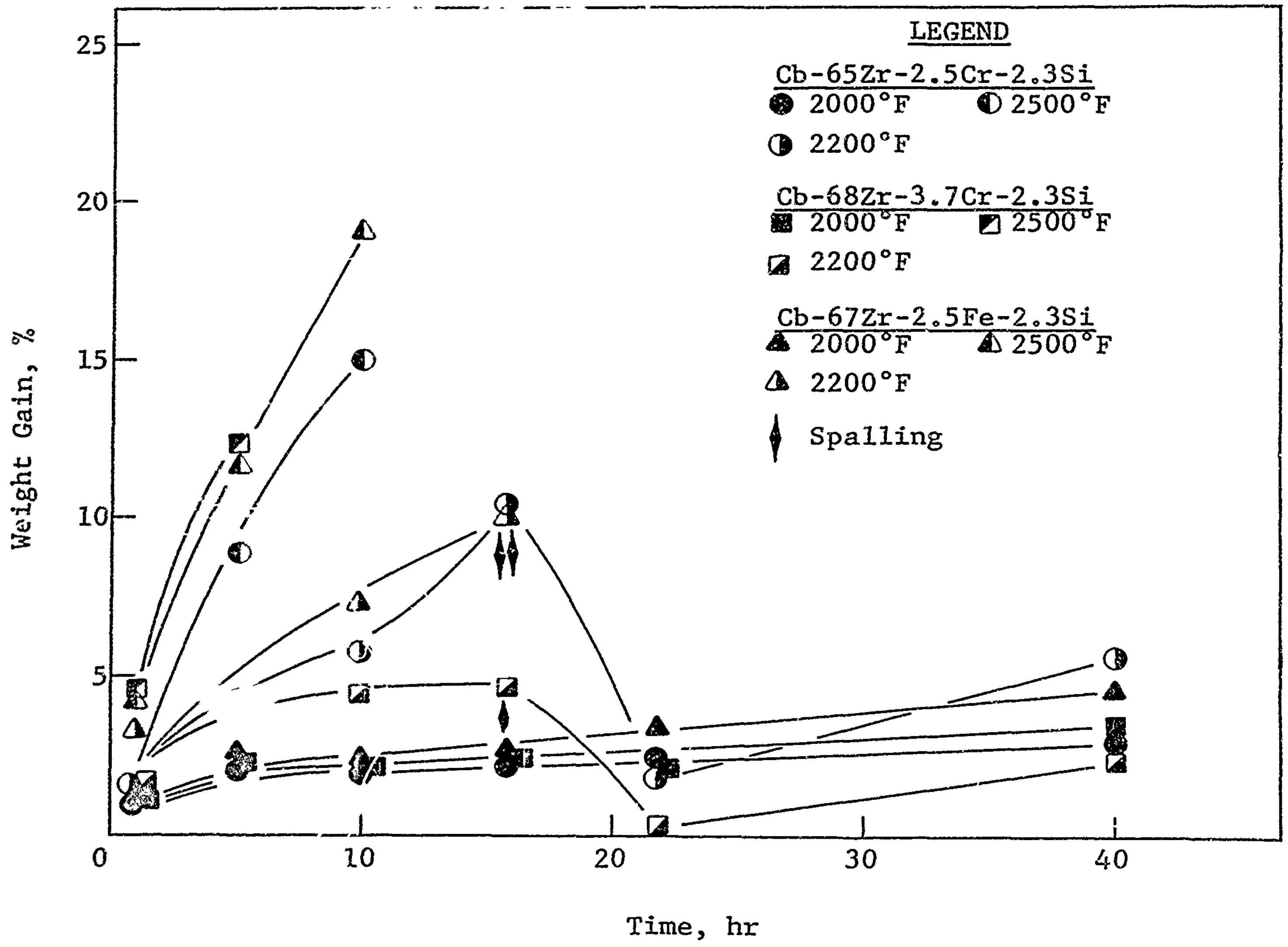

Fig. 11 - Oxidation Behavior of Modified Cb-Zr Alloys in Static Air.

TABLE X

OXIDATION BEHAVIOR OF Ta-Ti AND Zr-Ta ALLOYS

Alloy Composition, w/o	Exposure Temp., °F	Weight Gain in Given Time (hr), %						
		1	5	10	16	22	40	60
Ta-38.4Ti-3.4Cr-1.4B	2000	0.4	1.0	1.2	-0.2[(b)]	-6.4[(a)]	-11.6	
	2200	0.7	-0.9	0.14[(a)]				
	2500	0.6	4.2	9.9[(c)]	15.6[(c,b)]			
Ta-39Ti-4.0Cr-2.5Si	2000	0.1	0.3	0.4	0.5	0.7	1.0	
	2200	0.2	0.4	0.6	0.8	0.9	1.2	0.6[(b)]
	2500	0.4	1.0	0.3[(b)]	-1.5	-3.1	-11.5[(a)]	
Ta-55Zr-2.5Cr-1.1B	2000	0.6	2.4	(d)				
	2200	4.1	15.6[(d)]					
	2500	5.9	17.8[(c,d)]					
Ta-54Zr-3Cr-1.9Si	2000	3.1	12.3[(d)]					
	2200	2.0	4.2	7.0[(c)]				
	2500	3.4	8.0	15.4[(c,d)]				

(a) Heavy spalling.

(b) Light spalling.

(c) Edge growth cracking.

(d) Extensive oxidation.

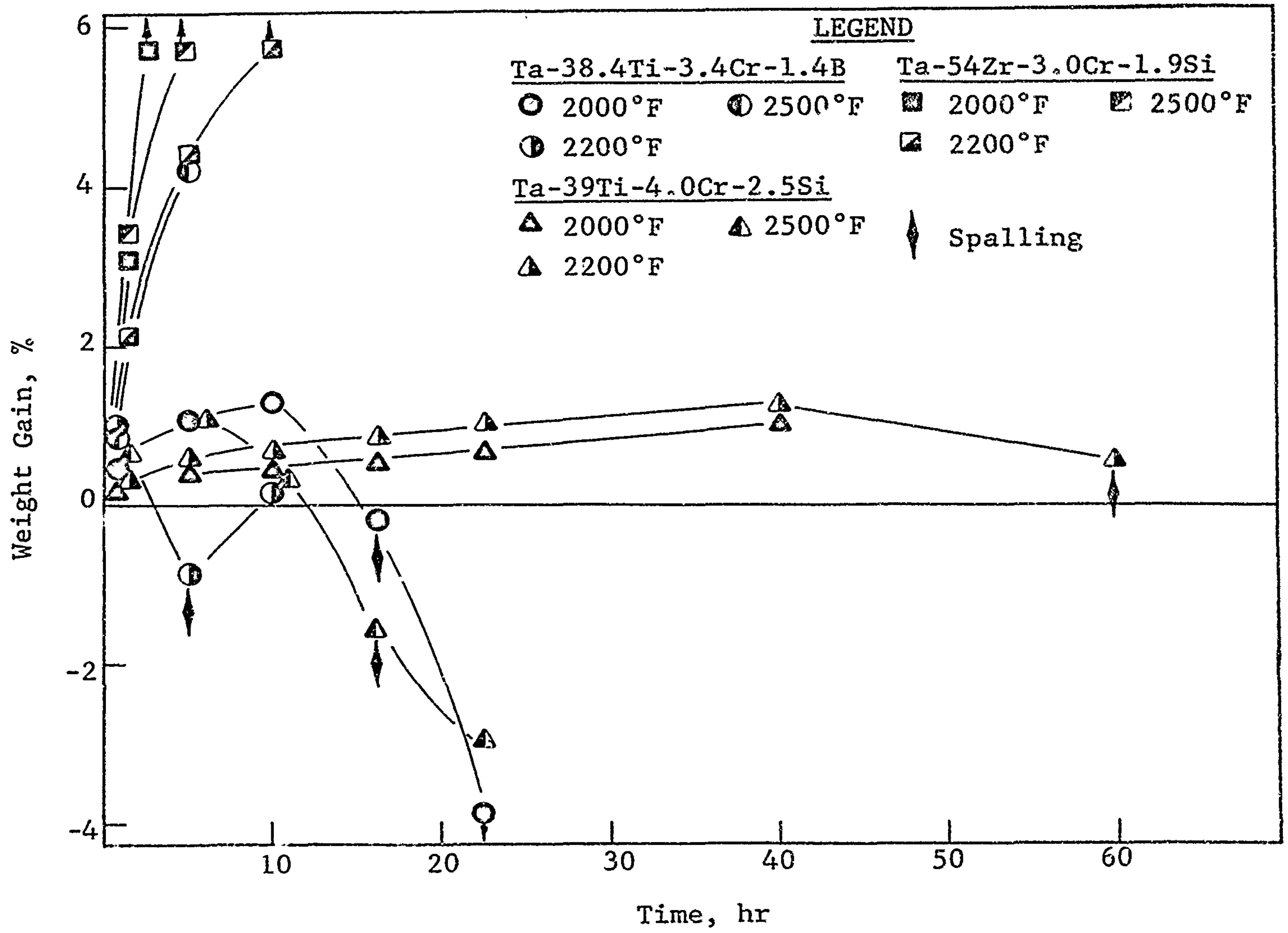

Fig. 12 - Oxidation Behavior of Modified Ta-Ti and Ta-Zr Alloys in Static Air.

Ta-Ti-Cr-Si alloy had slightly better oxidation resistance than the comparable Cb-Ti analog.

In Ta-Zr alloys, both the Cr-B and Cr-Si additions failed to provide significant oxidation resistance; the maximum exposure obtained was 10 hr at any exposure temperature. These alloys also failed by extensive oxidation and edge cracking, as observed for comparable Cb-Zr alloys.

The oxidation rates of modified Cb-Hf and Ta-Hf alloys at 2000°, 2200°, and 2500°F are summarized in Table XI. Weight change data are plotted in Figures 13 and 14. Alloys in the Cb-Hf system were also analogs of the oxidation-resistant Hf-Ta alloys. The Ta-Hf alloys were two modifications of the oxidation-resistant Hf-Ta-Cr-Si alloy in which iron was substituted for chromium. Weight change data for the Cb-Hf alloys again demonstrate the overall better performance of the Cr-Si additions. The Cr-B modification was equally resistant at 2200°F, but somewhat less resistant at 2000° and 2500°F. The Cr-B-Al modification was generally less oxidation-resistant than the two other modifications at all temperatures, except for the 2500°F data for the Cr-B alloy. However, the Cb-Hf alloys were generally less oxidation-resistant than their Ta-Hf analogs over the whole temperature range (Tables I and II), particularly at 2500°F. For example, the specific weight change of the Cb-80Hf-2.2Cr-1.1Si after 22 hr at 2500°F was about 100 mg/cm^2 (~0.015 in. metal conversion) compared to about 35 mg/cm^2 (~0.006 in.) for the Ta-Hf-Cr-Si alloy.

The Ta-Hf-Fe-Si alloys (Table XI) do provide weight gains approximating those of the Ta-Hf-Cr-Si alloy. After 40 hr at 2500°F, the Fe-Si modified alloy had a weight gain of about 65 mg/cm^2 compared to 45 mg/cm^2 for the Cr-Si modification. The higher gain for the Fe-Si alloy is expected since the oxidation results for the Cr-Si modified alloy were obtained on hot rolled material and those for the Fe-Si on the arc-melted alloy. All of the oxidation-resistant Hf-Ta alloys exhibit better oxidation

TABLE XI

OXIDATION BEHAVIOR OF Cb-Hf AND Ta-Hf ALLOYS IN STATIC AIR

Alloy Composition, w/o	Exposure Temp., °F	Weight Gain in Given Time (hr), %					
		1	5	10	16	22	40
Cb-80.5Hf-1.9Cr-0.8B	2000	0.5	1.0	1.4	2.3	3.4	8.0
	2200	0.6	1.2	1.6	2.0	2.5(c)	3.8(d)
	2500	1.2	3.4	5.4	8.6	10.5(c)	
Cb-80Hf-2.2Cr-1.4Si	2000	0.4	0.7	0.8	1.0	1.1	1.4
	2200	0.5	1.0	1.3	1.8	2.3(c)	3.5(d)
	2500	0.9	2.7	4.2	4.6	7.0(c)	
Cb-80.5Hf-1.5Cr-0.8B-0.1Al	2000	0.5	1.4	2.7	4.2	11.3(b)	9.9(a,c)
	2200	0.6	1.4	2.3	3.3	4.1(c)	5.7(d)
	2500	1.3	3.6	5.5	7.5	9.9(c)	
Ta-73.4Hf-1.5Fe-0.6Si	2000	0.3	0.6	0.7	0.9	1.1	1.4
	2200	0.5	-	1.4	1.7	-	3.7
	2500	0.8	1.9	2.6	3.2	3.9	5.1(c)
Ta-73.5Hf-1.8Fe-1.1Si	2000	0.4	0.7	0.9	1.1	1.4	2.2
	2200	0.5	-	1.3	1.6	-	2.9
	2500	0.8	1.6	2.2	2.9	3.9	4.5(c)

(a) Heavy spalling.

(b) Light spalling.

(c) Edge growth, cracking.

(d) Furnace failure, temperature dropped to 1400°F.

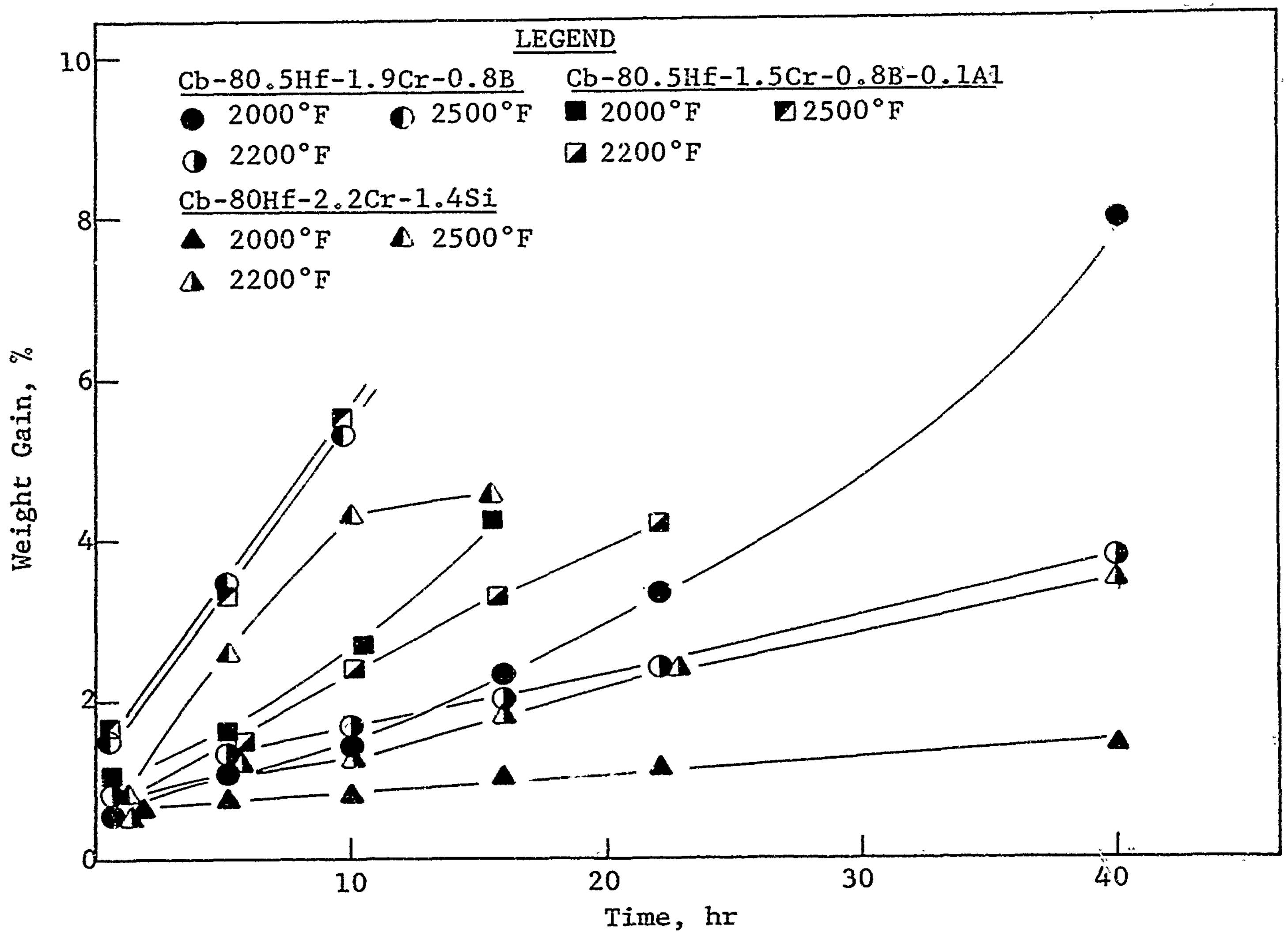

Fig. 13 - Oxidation Behavior of Modified Cb-Hf Alloys in Static Air.

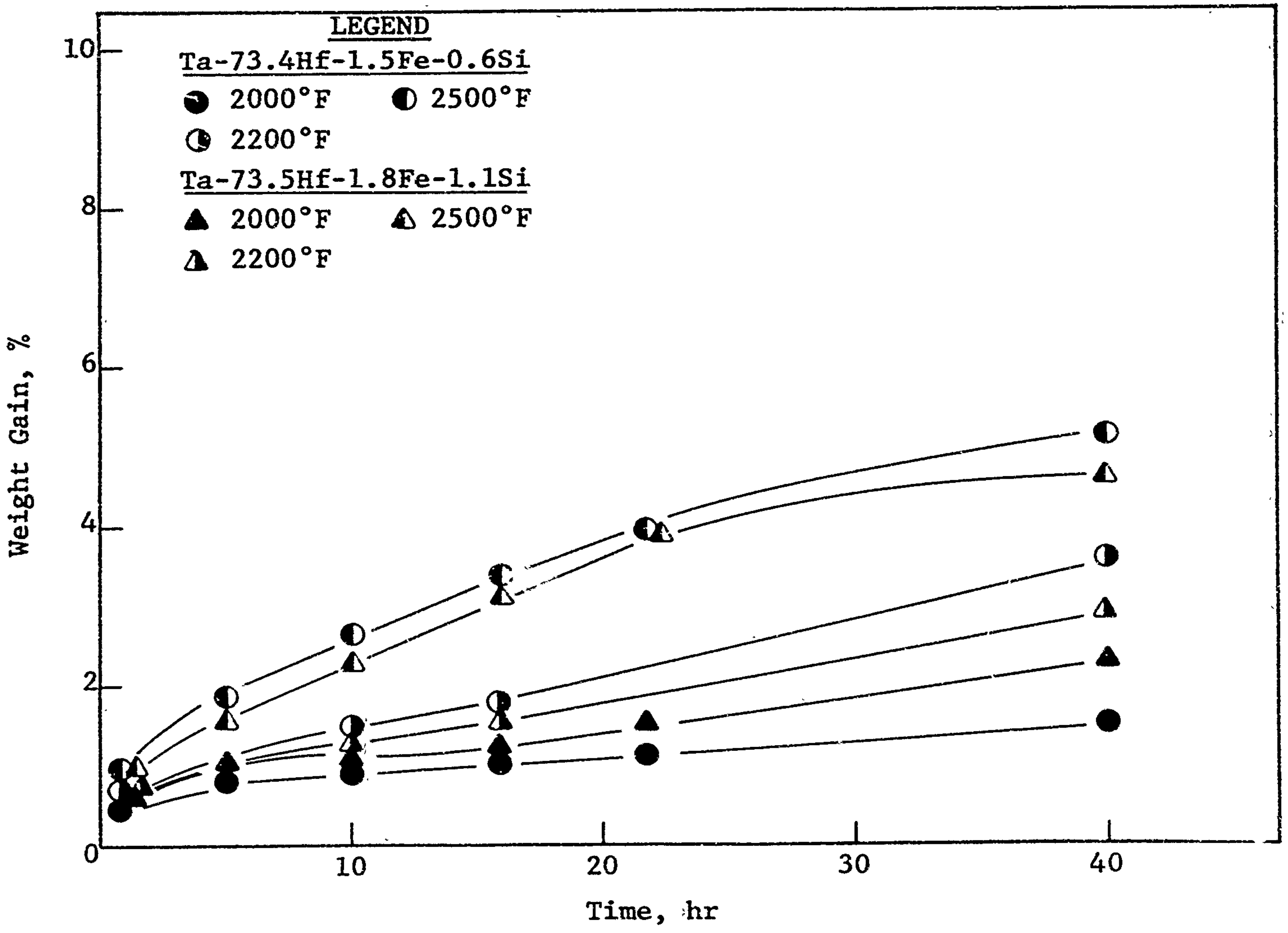

Fig. 14 - Oxidation Behavior of Modified Ta-Hf Alloys in Static Air.

resistance after hot working, apparently because of improved homogenization.

The tests on analogs of the oxidation-resistant Hf-Ta alloys demonstrate that reasonable oxidation resistance at 2000° to 2500°F can be developed in several IVB-VB alloy systems. Only the Ta-Zr system failed to provide lives of at least 40 hr at 2000°-2200°F. The Cr-Si modified alloys were the best of the various modifications studied in this phase. However, the oxidation screening studies demonstrated that Cr-Al and Cr-Al-Si additions are also beneficial, at least in Cb-Ti alloys. Oxidation-resistant Hf-Ta-Cr-Al alloys were developed previously.(3) Consequently, similar results might be obtainable with other combinations of Cr-Al and IVB-VB alloy systems.

The results of extended oxidation tests point to the following conclusions:

1. Modified Hf-Ta alloys provide the best overall oxidation resistance, particularly above 2200°F. The next best were modified Cb-Ti and Ta-Ti alloys.
2. The mechanisms of oxidation of hafnium- and zirconium-rich alloys are probably similar.
3. Titanium-rich alloys differ in oxidation mechanism from the heavier IVB-rich alloys.
4. Other elements (for example, iron) can be substituted for chromium to obtain oxidation resistance in hafnium- and zirconium-rich alloys. The necessity of a valence 3 oxidation state for the substitution element has not been established.

The mechanism of oxidation in Hf-Ta alloys is discussed in the following section.

D. Supplemental Studies

1. X-Ray Diffraction

The oxide structures developed on oxidation-resistant hafnium-base alloys were not examined previously. The major reason for this was the lack of standard X-ray patterns for the complex oxide structures probably occurring. Without standard patterns, identification of the oxide structures would be difficult. A limited amount of work had been conducted on mixed oxides of hafnium and tantalum on Contract AF33(615)-3071.(5) The results of oxidation studies described in the previous section suggested that the oxides developed on modified hafnium-base alloys might be similar. Accordingly, samples of the Hf-Ta-Cr-B, Hf-Ta-Cr-B-Al, and Hf-Ta-Cr-Si alloys were oxidized for X-ray diffraction examination.

Hafnia exists in at least two allotropic forms: monoclinic below about 3300°F and tetragonal above this temperature. A cubic structure may also exist at very high temperatures. Similar structures are also present in zirconium, with a transformation temperature of about 1900°F. Thus, it is probable that much of the data on the crystal structures of zirconia applies also to hafnia. The monoclinic to tetragonal transformation in zirconium is accompanied by a large decrease in volume of about 9%. This results in cracking of the ceramic during thermal cycling. For this reason, zirconium is usually stabilized in the cubic form by addition of at least 6 w/o CaO, or about 8-15 w/o of Y_2O_3. Originally, the monoclinic form of zirconia was thought to be simply a distorted fluorite structure; however, work by Teufer(11) suggests that it is closer to that of red HgI.

The cubic MO_2 fluorite structure ideally consists of four metal atoms located in the 0,0,0 and 1/2, 1/2, 0 positions and eight oxygen atoms in the 1/4, 1/4, 1/4 and 1/4, 3/4, 3/4 positions. Each metal atom is located equidistant from eight metal atoms, and each oxygen atom is located at the center of a regular tetrahedron of metal atoms. The unit cell is therefore face-centered in metal atoms with oxygen atoms located in the tetrahedral holes. This is a relatively open structure and should therefore have a relatively high oxygen mobility.

Work by Marnoch(6) and Hill and Rausch(5) on Hf-Ta alloys suggested that the good oxidation resistance of these alloys at high temperatures was due to the oxide structures developed on these alloys. A mechanism based on the formation of a $Hf_6Ta_2O_{17}$ complex oxide formed on alloys containing 20-25 w/o tantalum was proposed. An X-ray pattern for the complex oxide was not available. Consequently, the X-ray patterns of a series of mixed oxides in the HfO_2-Ta_2O_5 system were obtained on Contract AF33(615)-3071.(6) It was found that the oxide $75HfO_2$-$25Ta_2O_5$ (in w/o) exhibited a diffraction pattern similar to that of tetragonal zirconia. The X-ray patterns of this oxide in comparison to those of monoclinic and tetragonal HfO_2 are presented in Table XII.

The $75HfO_2$-$25Ta_2O_5$ oxide, according to the table, does compare reasonably well with that of tetragonal zirconia. Some extra lines are present, fortunately at low angles, which may be due to incomplete homogenization of the mixed oxide sample. However, the high intensity $11\bar{1}$ and 111 lines of monoclinic zirconia are absent. Thus, it appears that a complex oxide does exist in the HfO_2-Ta_2O_5 system which is structurally similar to tetragonal zirconia and can be obtained by sintering of the mixed oxides at high temperature.

It appears that the complex oxide is obtained by substitution of up to one-fourth of the hafnium atoms by tantalum atoms. Assuming a fluorite-like structure, the actual stoichiometry is probably $Hf_6Ta_2O_{16}$, since the only available site for the remaining oxygen atoms is the 1/2, 1/2, 1/2 position. This position is approximately equidistant from six hafnium atoms, although in the tetragonal structure, two of those atoms are located at a slightly greater distance. The four closest metal atoms are in a planar array rather than tetrahedrally arranged. This site, therefore, differs from that of the other oxygen positions, suggesting that the reported $Hf_6Ta_2O_{17}$ may simply be an oxygen-excess $Hf_6Ta_2O_{16}$ structure.

TABLE XII

X-RAY DIFFRACTION PATTERNS OF OXIDES OF HAFNIUM AND TANTALUM

Monoclinic HfO_2 ASTM 6-0318			Tetragonal HfO_2 ASTM 8-342			$75HfO_2$-$25Ta_2O_5$	
hkl	I/I_1	S	hkl	I/I_1	S	I/I_1	S
100	20	5.07					
011	40	3.68					
110	30	3.61				7	3.59
$11\bar{1}$	100^+	3.15					
			111	100	2.97	100	2.94
111	100	2.82					
002,020	60	2.59	002	40	2.62	20	2.62
200	50	2.52	200	50	2.55	24	2.55
$10\bar{2}$	20	2.48				13	2.46
012,021, 120	50	2.32	102	40	2.356	9	2.34
$21\bar{1}$	60	2.196					
$102,12\bar{1}$	30	2.171					
112	30	2.006				6	2.08
211,202	40	1.981					
$21\bar{2},022$	60	1.838	202	80	1.837	17	1.83
220	60	1.807	220	80	1.811	22	1.80
$12\bar{2}$	20	1.794				25	1.77
$22\bar{1}$	30	1.768				12	1.70
300,202	50	1.684	103	5	1.675	9	1.69
221	60	1.653				9	1.65
$013,031,11\bar{3}$	40	1.634				6	1.65
311,310, 212	40	1.600	113	60	1.578	15	1.57
$13\bar{1}$	30	1.580					
$131,30\bar{2}$	50	1.533	311	70	1.548	21	1.54
	0	1.501				17	1.50
	50	1.467	222	60	1.497	14	1.47

I = Intensity

S = Spacing

A comparison of the X-ray patterns developed on Hf-Ta-Cr-Si, Hf-Ta-Cr-B, and Hf-Ta-Cr-B-Al alloys by exposure at 2500°F for 2 hr is given in Table XIII. The X-ray patterns were obtained on 0.5 x 0.5 in. specimens at 50 kv and 19 ma using copper radiation, a 1° divergent slit, and a nickel filter. The ASTM standard pattern for monoclinic HfO_2 and the pattern proposed for the complex oxide are included. The oxides developed on the alloys appear to be mixture of the monoclinic form and the complex oxide. Based on the intensity of the 3.15 line, the Hf-Ta-Cr-Si and Hf-Ta-Cr-B alloys have only a small concentration of monoclinic oxide, but a greater percentage of the monoclinic form exists in the Hf-Ta-Cr-B-Al oxide.

A similar comparison of the X-ray patterns after oxidation at 2500°F for 20 hr is given in Table XIV. The Hf-Ta-Cr-B and Hf-Ta-Cr-B-Al alloys do not appear to be changed significantly by further oxidation. The Hf-Ta-Cr-Si alloy, however, appears to have increased in amount of the monoclinic phase. The line with the 3.32 spacing which is present in all patterns of the oxidized alloys is unexplained. This line may be that of a separate oxide, but cannot alone be attributed to any simple oxide of the constituents hafnium, tantalum, and chromium which were present in all alloys.

The results of X-ray diffraction indicate that the good oxidation resistance of modified Hf-Ta alloys is the result of development of complex oxide similar to tetragonal hafnia. Improved adherence of this oxide occurs because of a lower volume ratio of oxide to metal and by the formation of a subscale oxide which buffers the expansion mismatch that still exists. It is further proposed that the improved oxidation resistance afforded by combining the alloying additions Cr, Al, B, and Si results because these elements occupy the 1/2, 1/2, 1/2 position in the tetragonal structure. Occupancy of this octahedral site results in a much lower oxygen permeability through the oxide. Chromium is a necessary base addition in all oxidation-resistant alloys

TABLE XIII

X-RAY DIFFRACTION PATTERNS OF SURFACE OXIDES ON Hf-Ta ALLOYS OXIDIZED IN AIR AT 2500°F FOR 2 HOURS

Monoclinic HfO_2		Complex Oxide $75HfO_2$-$25Ta_2O_5$		Oxidized Hf-Ta Base Alloys Cr-Si		Cr-B		Cr-B-Al	
I/I_1	S	I/I_1	S	I/I_1	S	I/I_1	S	I/I_1	S
20	5.07								
40	3.68								
30	3.61	7	3.59	3	3.61	4	3.61	8	3.64
				8	3.32	8	3.32	18	3.31
				5	3.29				
100	3.15			6	3.14	4	3.14	21	3.14
		100	2.94	100	2.95	100	2.94	100	2.95
100	2.82							44	2.80
		20	2.63	84	2.63	36	2.63	36	2.64
60	2.59			18	2.58	12	2.58	36	2.57
50	2.52	24	2.55	34	2.55	15	2.55		
				4	2.52				
20	2.48	13	2.46	7	2.48	8	2.48	59	2.46
50	2.32	9	2.34	17	2.342	13	2.34	16	2.34
60	2.20							10	2.19
30	2.17								
		6	2.08	6	2.084	6	2.080	10	2.091
								8	1.976
60	1.838	17	1.83	21	1.832	20	1.830	23	1.832
60	1.807	22	1.80	11	1.803	12	1.802	18	1.801
30	1.768	25	1.77	15	1.776	19	1.774	16	1.775
50	1.684	12	1.70	10	1.732	10	1.732	32	1.733
60	1.653	9	1.69	6	1.700	6	1.699	11	1.700
40	1.634	9	1.65	16	1.653	15	1.654	23	1.653
		6	1.45						
40	1.600	15	1.57	24	1.573	19	1.572	30	1.573
30	1.580	21	1.54	27	1.537	10	1.537	26	1.539
50	1.533			10	1.505	10	1.515	14	1.501
40	1.501	17	1.50	4	1.483	10	1.485	12	1.483
50	1.47	14	1.47	9	1.471	10	1.471	19	1.473

I = Intensity

S = Spacing

TABLE XIV

X-RAY DIFFRACTION PATTERNS OF SURFACE OXIDES ON Hf-Ta ALLOYS OXIDIZED IN AIR AT 2500°F FOR 20 HOURS

Monoclinic HfO_2		Complex Oxide $75HfO_2$-$25Ta_2O_5$		Oxidized Hf-Ta Base Alloys					
				Cr-Si		Cr-B		Cr-B-Al	
I/I_1	S	I/I_1	S	I/I_1	S	I/I_1	S	I/I_1	S
20	5.07								
			3.95						
40	3.68	7	3.59	3	3.66	4	3.62	13	3.64
				3	3.61	2	3.52		
30	3.61								
				12	3.32	11	3.32	7	3.31
100	3.15			28	3.14	4	3.14	11	3.14
		100	2.94	100	2.95	100	2.95	100	2.97
100	2.82			5	2.83			38	2.80
		20	2.63	41	2.64	42	2.64	14	2.64
60	2.59			31	2.58	16	2.58		
50	2.52	24	2.55	24	2.55	16	2.55	21	2.56
								12	2.49
20	2.48	13	2.46	24	2.49	10	2.49	43	2.46
50	2.32	9	2.34	16	2.34	15	2.34	9	2.34
60	2.196			7	2.19			6	2.19
30	2.170								
		6	2.08	6	2.08	5	2.08		
								9	2.09
						2	2.203	7	1.979
						2	1.978	10	1.888
60	1.838	17	1.83	25	1.832	19	1.831	10	1.851
60	1.807	22	1.80	11	1.803	12	1.802		
30	1.768	25	1.77	20	1.777	15	1.776	8	1.803
								8	1.778
						11	1.734		
50	1.684	12	1.70	15	1.732	7	1.699	9	1.718
60	1.653	9	1.69	15	1.653			4	1.698
40	1.634	9	1.653	1	1.597	13	1.654	26	1.653
		6	1.648	4	1.573				
40	1.600								
30	1.580	15	1.57	18	1.573	19	1.573	10	1.574
50	1.533	21	1.54	20	1.537	14	1.536	14	1.539
				9	1.502	10	1.504	5	1.505
40	1.501	17	1.50						
								8	1.486
				15	1.484	6	1.485	7	1.481
50	1.470	14	1.471	11	1.471	10	1.471	8	1.475

I = Intensity

S = Spacing

because of greater diffusional stability than that of the smaller atoms. This model also appears to explain the surprising effectiveness of small additions of platinum and iridium (2-5 a/o) in increasing the oxidation resistance of binary Hf-Ta alloys.$^{(3)}$ Thus, the effectiveness of the alloying addition may be more dependent on diffusional stability than the valence of the oxidation state.

Assuming the proposed oxide model is correct, the concentration of chromium in a Hf-Ta-Cr alloy necessary without diffusion to occupy all of 1/2, 1/2, 1/2 complex oxide positions is 20 a/o (6.8 w/o), i.e., the same atomic concentration as tantalum. The oxide formed would essentially be Hf_3TaCrO_8, with one formula weight per unit cell. This concentration probably exceeds the solubility limit of chromium in the Hf-Ta solid solution, even at high temperature. Consequently, chromium concentrations of 20 a/o will result in precipitation of Hf-Cr compounds in a matrix of the Hf-Ta-Cr solid solution. Chromium in these compounds, particularly if the precipitates are coarse, cannot be as effective in decreasing oxidation as chromium in solid solution. Decomposition of the compounds and distribution of chromium by diffusion throughout the oxide is required. The time required for diffusion limits the effectiveness of precipitated chromium in decreasing diffusion of oxygen through the complex oxide structure. Thus, the major decrease in oxidation rate of Hf-25Ta alloys through additions of chromium should occur within the solid solubility range.

Data obtained by Van Thyne for ternary Hf-Ta-Cr alloys verify the above discussion.$^{(1)}$ The minimum weight gain in 10 hr at 2500°F was obtained at 20 a/o chromium, although the improvement was small above 5 a/o (1.5 w/o). Similar results were obtained with boron (10 a/o), aluminum (10 a/o), and silicon (5 a/o).$^{(2)}$ It is not surprising, then, that the combined concentration of minor alloying elements in the most oxidation resistant Hf-Ta alloys is in the range of 13-20 a/o. The combined minor alloying additions for the five most oxidation resistant modified Hf-Ta alloys developed are: Cr-Al (9 a/o), Cr-Si (13 a/o), Cr-B-Al (14.5 a/o), Cr-B (15 a/o), and Ir-Al-Si (20 a/o). The oxidation rates of these alloys at 2500°F generally decrease with increasing atomic concentration of minor elements in the order shown above. The only deviation from this order is that Cr-Si alloys are slightly more oxidation resistant than the Cr-B and Cr-B-Al systems. Modified Hf-Ta-Cr-Si alloys are probably more oxidation resistant than Cr-B types because of the formation of a glassy oxide on these alloys. In general, the oxidation data obtained empirically appear to support the proposed complex oxide model.

As previously stated, hot working improves the oxidation resistance of some of the modified Hf-Ta alloys. All of these alloys are multiphase; the concentration of one or more of the minor alloying elements exceeds the solid solubility limit in all cases. Hot working breaks up the relatively massive precipitates in the cast structure and distributes them more uniformly. In effect, working tends to distribute the precipitated minor alloying element toward the homogeneous atomic distribution existing in the solid solution. If, for example, the precipitates were as fine as the ThO_2 particles in TD nickel, the minor alloying element in the precipitate could be as effective as that in solid solution in modifying the oxide structures. Hot working obviously cannot provide an ultrafine distribution of precipitated phase, but it can decrease the diffusion distances considerably and minimize anomalous oxidation behavior resulting from the location of a massive precipitate at or near the surface. The hot working in this program and in previous work(2-4) was primarily effective in minimizing anomalous oxidation. Hot-worked alloys, however, also generally demonstrated lower weight gains than as-cast alloys.

2. Siliconizing

The results of oxidation tests on Hf-Ta alloys indicated that Cr-Si alloys provided the best high-temperature oxidation resistance. A limited study was conducted to determine the influence of high silicon concentrations at the surface on the oxidation resistance of these alloys. Siliconizing studies were conducted on both the Hf-Ta-Cr-B-Al and Hf-Ta-Cr-Si alloys. However, difficulties could be expected with siliconized Cr-B-Al alloys. Previous work had shown that silicon added to Hf-Ta-Cr-B alloys as a bulk addition caused cracking and spalling of the oxides during oxidation exposure. Thus, this work was concerned primarily with the Cr-Si modified alloys.

Initially, siliconizing was attempted by packing Hf-Ta-Cr-Si samples in high-purity silicon powder and heating in vacuum at 2100°-2300°F. Weight gains were obtained by these treatments, but examination of the specimen indicated that the silicon particles reacted with the alloy producing localized areas of high silicon concentration. These results suggested that siliconizing could be accomplished by application of a silicon slurry followed by heating above 2100°F.

Accordingly, siliconized Hf-Ta-Cr-B and Hf-Ta-Cr-Si samples were prepared by heat treatment of a slurry of -400 mesh solar cell grade silicon. Siliconizing samples were fabricated from hot rolled and surface ground 0.017 in. thick sheet material. Heat treatment consisted of 0.5 hr at 2300°F, followed by 1 hr at 2500°F in high purity argon. The air-dried slurries weighed 5-6 mg/cm^2, of which 4 mg/cm^2 was retained after heat treatment on the Cr-Si samples. Hf-Ta-Cr-B-Al alloy samples retained only about 2 mg/cm^2 after heat treatment; the remaining silicon powder was readily removed from the surface with a brush. Thus, it appears that the boron and/or aluminum in the Cr-B-Al alloy resisted silicon diffusion. Weight gains of 2 and 4 mg/cm^2 compare approximately to an increase in silicon concentration to 20 w/o Si for depths of 0.25 and 0.5 mil, respectively.

A summary of the oxidation rate of siliconized samples at 2200° and 2500°F is presented in Table XV. Data for hot-rolled material(4) is included for comparison. Oxidation exposure was stopped after 40 hr at 2200°F and 22 hr at 2500°F because of minor edge growth and cracking on the siliconized samples. The weight gains of the siliconized samples are somewhat less than those of the base alloy for all exposure conditions. Weight gain after 22 hr at 2500°F was about 15% less for both alloys. Thus, some improvement was obtained by the initial siliconizing treatment, suggesting that a further decrease in oxidation rates may be possible by further siliconizing studies.

IV. SUMMARY AND CONCLUSIONS

Clad composites consisting of Cb-752 and Ta-10W clad with Hf-24.5Ta-1.8Cr-1.1Si and Hf-24.5Ta-1.2Cr-0.7B-0.12Al were fabricated for oxidation testing at 2200°-2700°F. The picture-frame composites were fabricated by edge welding followed by roll cladding at 2100°F in 410 stainless steel cans. A roll cladding reduction of 5% was sufficient to produce bonding of the cladding.

Seventeen clad composites with 0.010 and 0.020 in. thick cladding exposed in static air at 2200°, 2500°, and 2700°F. The lives of these composites varied from 65-100 hr at 2200°F to 25 hr at 2700°F. Failure of the composites usually occurred at the interface of the picture frame and the substrate. Failure of the cladding-substrate interface occurred on only one Hf-Ta-Cr-Si composite. Hf-Ta-Cr-B-Al cladding on Cb-752 exhibited craze cracks after exposure at all three temperatures, but did not cause rapid failure of the composites.

TABLE XV

OXIDATION OF SILICONIZED Hf-Ta-Cr-Si AND Hf-Ta-Cr-B-Al ALLOYS IN STATIC AIR

Alloy Composition, w/o	Exposure Temp., °F	Weight Gain in Given Time (hr), mg/cm^2					
		1	5	10	16	22	40
Hf-25Ta-1.5Cr-0.66B-0.12Al	2200	5.6	8.0	13.3	--	16.7	25.0(b)
	2200(a)	5.7	10.2	14.0	--	19.1	24.3
	2500	6.7	15.7	20.4	25.7	29.5(b)	
	2500(a)	9.8	19.8	25.9	29.7	34.9	
Hf-24.5Ta-1.5Cr-1.1Si	2200	3.4	5.9	11.2	--	13.2	20.2(b)
	2200(a)	5.6	10.3	13.6	--	18.4	22.7
	2500	6.1	12.7	20.3	23.2	28.1(b)	
	2500(a)	9.3	18.7	24.5	29.3	33.1	

(a) Data from reference 4, for hot-rolled material.

(b) Testing stopped due to edge growth cracking.

Oxidation screening studies were conducted on binary Cb-Ti and Cb-Zr alloys containing 0-80 a/o Ti or Zr at 2200° and 2500°F. Cb-Ti alloys exhibited spalling after 1-5 hr at both temperatures. In contrast, Cb-Zr alloys developed thick, adherent oxides similar to Hf-Ta alloys. Modification of Cb-(16-42) w/o Ti alloys with Cr-Al or Cr-Al-Si resulted in a significant increase in oxidation resistance at both temperatures. Silicon also increased the oxidation resistance of Cb-Cr-Al alloys significantly. Modification of Cb-(55-65) w/o Zr alloys by small additions of Cr, Al, Cr-Al, and Cr-Si resulted in only moderate improvement in oxidation resistance at 2200° and 2500°F.

Analogs of the oxidation-resistant Hf-Ta-Cr-B, Hf-Ta-Cr-B-Al, and Hf-Ta-Cr-Si alloys were prepared in the Cb-Ti, Cb-Hf, Cb-Cr, Ta-Ti, and Ta-Zr systems. A limited number of alloys were also fabricated in the Cb-Zr and Ta-Hf systems in which iron was substituted for chromium. These alloys were exposed in static air at 2000°, 2200°, and 2500°F for periods of up to 60 hr. Good oxidation resistance was obtained with Cr-Si addition in all systems, except Ta-Zr. The alloys containing iron provided nearly comparable oxidation behavior to their chromium-containing counterparts. The results of these oxidation tests indicated that the mechanism of oxidation is probably similar to that of hafnium-rich alloys for zirconium-rich alloys but differs for titanium-rich alloys.

X-ray diffraction patterns were obtained of the oxides developed on Hf-24Ta-1.5Cr-0.7B, Hf-24Ta-1.8Cr-1.1Si and Hf-23.1Ta-1.2Cr-0.7B-0.12Al in 2 and 20 hr at 2500°F. The patterns were similar both to that of a complex oxide obtained by sintering $75HfO_2$-$25Ta_2O_5$ and to tetragonal HfO_2. It was proposed that the good oxidation resistance obtained in modified Hf-Ta alloys is the result of the stabilization of the tetragonal HfO_2 phase by tantalum. Addition of chromium and other elements decreases the mobility of oxygen by occupying the octahedral holes in a fluorite-like tetragonal structure.

The oxidation-resistant Hf-Ta-Cr-B and Hf-Ta-Cr-Si alloys were siliconized by applying a silicon slurry and heating in argon at 2300°-2500°F. Silicon uptake obtained by this treatment was 2-4 mg/cm^2. Oxidation tests at 2200° and 2500°F of siliconized samples resulted in about a 15% decrease in weight gain after 22 hr at 2500°F.

V. RECOMMENDATIONS

Further work should be conducted on the oxidation resistant Hf-Ta alloys, and their Group IV-VB analogs, investigated in this program. This work should include:

1. X-ray diffraction studies of oxides developed on selected alloys to verify the proposed oxide studies.
2. Further modification of the alloys to optimize the alloy compositions for diffusion effects.
3. Establish the difference in oxide structure developed on titanium-base alloys from that of the hafnium- and zirconium-base systems.

This work could provide a basis for the development of improved oxidation resistance in structural alloys. In addition, the results would contribute in developing new coatings for high-temperature alloys based on more refractory oxides than silica and alumina.

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13. ABSTRACT

The objective of this program was to investigate oxidation-resistant hafnium-base alloys as cladding for columbium- and tantalum-base alloys. Oxidation behavior of other combinations of Group IVB-VB alloys was also studied.

Clad composites consisting of Cb-752 and Ta-10W clad with Hf-Ta-Cr-B-Al and Hf-Ta-Cr-Si alloys were exposed at 2200°, 2500°, and 2700°F. Oxidation life varied from about 100 hr at 2200°F to 25 hr at 2700°F. Failure of the composites generally occurred at edges between the picture frame and substrate. The Hf-Ta-Cr-B-Al alloy indicated greater tolerance to surface defects than the Hf-Ta-Cr-Si alloy.

Oxidation studies of modified Group IVB-VB alloys at 2000°-2500°F showed that oxidation resistance could be developed in several systems. The minor alloying additions employed were chromium, boron, columbium, silicon, yttrium, vanadium, and combinations of these elements. Chromium-silicon additions were the most effective in improving oxidation resistance in nearly all systems, although Cr-Al-Si combinations were also effective in Cb-Ti alloys.

X-ray diffraction examination of oxides developed in oxidation-resistant hafnium-base alloys suggested that the oxide structures, probably a complex Hf-Ta oxide, were similar for all alloys. A model for the oxidation resistance obtained in Hf-Ta alloys is proposed.

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