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DEVELOPMENT OF PROTECTIVE COATINGS FOR TANTALUM-BASE ALLOYS

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FOREWORD

This report was prepared by Battelle Memorial Institute under USAF Contract No. AF 33(616)-7184. This contract was initiated under Project No. 7312, "Finishes and Materials Preservation", Task No. 73120, "Surface Treatments and Coatings". The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. N. M. Geyer acting as project engineer.

This report describes the results of research conducted during the period May 1, 1960, through August 31, 1961.

ABSTRACT

This program was started with a survey to determine potential coating materials for protecting tantalum alloys from oxidation and contamination at high temperatures. This survey and initial coating studies resulted in major emphasis being directed toward silicide-base coatings.

Straight silicide coatings and modifications with aluminum, boron, chromium, manganese, molybdenum, titanium, and vanadium were applied to tantalum, Ta-10W, Ta-10Hf-5W, and Ta-30Cb-5V by pack-cementation techniques. These coated materials were evaluated primarily by static, cyclic, and defect oxidation studies in the temperature range 1200 to 2700 F. Less extensive studies were conducted on tantalum coated with aluminum, chromium, hafnium, titanium, zinc, and Al_2O_3.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER

I. PERLMUTTER
Chief, Physical Metallurgy Branch
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INTRODUCTION

The need for structural materials capable of operation at temperatures in the vicinity of 3000 F has led to consideration of tantalum-base alloys. In spite of its moderately high density, tantalum is attractive because of its unique combination of high melting point, 5420 F, and excellent low-temperature ductility. Recent studies sponsored by the Air Force(1)* have shown that substantial improvements in the high-temperature strength of tantalum can be obtained by alloying. Two of the more attractive alloys under advanced evaluation, Ta-10Hf-5W and Ta-30Cb-7.5V, have tensile strengths of 17,800 and 10,200 psi, respectively, at 3000 F, compared with 3,600 psi for tantalum. These studies have also indicated that substantial improvements in the oxidation resistance of tantalum were possible by alloying. However, the oxidation rates of the most oxidation-resistant alloys are still too high for use in the unprotected condition in the anticipated service-temperature range.

Coatings provide an attractive method for protecting high-strength alloys from oxidation, provided that the many problems associated with coatings, such as compatibility with base, spalling tendencies, and self-healing properties, can be solved.

This report summarizes studies conducted on Air Force Contract AF 33(616)-7184, Task No. 73120, entitled "Development of Protective Coatings for Tantalum-Base Alloys", during the contract period May 1, 1960, to August 31, 1961. The report includes a literature survey, conducted at the initiation of the project, and results of subsequent experimental coating studies on tantalum and three tantalum alloys.

SUMMARY

Literature Survey

The current study was started with a literature survey to determine the possible coatings for tantalum of greatest potential interest. The survey included elements, refractory intermetallic compounds, and oxides. The metallurgical properties (alloying and diffusion behavior), physical properties (expansion coefficients, etc.), oxidation properties of elements, compounds, and alloys, and mechanical properties of 28 elements, 37 intermetallic compounds, and several oxides were reviewed and compared as possible protective coatings. On the basis of this study, which also included reviews of application techniques and properties of coatings on columbium and molybdenum, coatings in 17 systems were recommended for study on tantalum. These systems are as follows:

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*References listed at end of report.

Cr

Cr-Si

Ti-Si

Mo-Si

Hf-Si

ZrO_2 + glasses

Al_2O_3 + glasses

Al

Al-Cb

Al-Hf

Be

Be-Cb

Be-Hf

Be-Mo

Be-Ti

Be-W

Be-Zr

Coatings based on chromium, silicon, and oxides were evaluated in this program; coatings based on aluminum and beryllium were included in a similar concurrent study at Sylvania-Corning Nuclear Corporation under Contract AF 33(616)-7462.

Studies of Silicide-Coated Tantalum

Coatings of straight silicide and silicide modified with aluminum, boron, chromium, manganese, molybdenum, titanium, and vanadium were applied to tantalum by pack-deposition techniques. The straight silicide coating protected tantalum from oxidation and contamination for 5 to 10 hours at 2700 F. Codeposition of silicon with aluminum, boron, chromium, molybdenum, and titanium was studied, but the coatings appeared to contain appreciably less than the charged amounts of the addition elements and were no more protective than straight silicide coatings at 2500 and 2700 F. Alternate deposition of boron or manganese followed by silicon produced coatings which formed vitreous scales on exposure. The manganese-modified silicide coating was especially protective, showing no failure after 24 hours at 2700 F.

Accelerated "pest" oxidation was severe at 1800 F, reducing the protective life to 3 hours from 80 hours at 1200 F. None of the silicide coatings on tantalum were self-healing at 2500 or 2700 F.

Studies of Silicide-Coated Tantalum Alloys

The protectiveness of silicide coatings on Ta-10W, Ta-10Hf-5W, and Ta-30Cb-5V was, in general, moderately superior to that of similar coatings on tantalum. Markedly superior protection was afforded by the manganese-silicide coating on all three alloys and by straight silicide and aluminum and manganese-modified silicide coatings on the Ta-30Cb-5V alloy. Coatings on the latter alloy were resistant to low-temperature "pest" oxidation, showing no failures after 100 hours at 1800 F. All of the silicide-coated alloys showed some self-healing tendencies at 2500 F, and the manganese-silicide coating was self-healing on Ta-10W and Ta-30Cb-5V at 2700 F.

Studies of Other Coatings on Tantalum

Coatings of aluminum, chromium, hafnium, and titanium were applied to tantalum by the pack-cementation process. The aluminum coatings were only briefly studied, but were found to be protective for up to at least 6 hours at 2700 F. Chromium was difficult to deposit in thicknesses greater than about 0.5 mil and was nonprotective at 2500 F. Also, chromium hardens tantalum from about 100 KHN up to about 900 KHN during pack cementation. Titanium and hafnium also deposited slowly on tantalum and gave nonprotective coatings.

Flame-sprayed Al_2O_3 coatings were not protective. Glass impregnation of the coating did not improve its protectiveness.

Zinc apparently does not react with tantalum to form an intermetallic as it does with columbium. Mechanically adherent zinc coatings applied by hot dipping oxidized rapidly at 1700 F.

LITERATURE SURVEY

This program was started with a literature survey to determine the most promising potential coating combinations for tantalum and tantalum-base alloys. The basic properties of a large number of elements, intermetallic compounds, and oxides were briefly evaluated against several simple criteria. On this basis, 28 elements, 37 intermetallic compounds, and several oxides were selected for further review. Comparison of the pertinent properties of these materials led to the recommendation of 17 coating systems for experimental evaluation.

The complete survey comprised the First Quarterly Report on this project, dated August 15, 1960. The survey is briefly reviewed in the following sections.

Properties of Coating Materials

Consideration of the requirements for a suitable protective coating for tantalum allows the formulation of several criteria for selecting elements of interest as protective coatings. The coating element or its compound or alloy with tantalum should be solid at

2500 F (1370 C), it should have a relatively low vapor pressure, and its stable oxide should be refractory. These properties are given in Table 1 for most known elements, excluding the radioactive and rare-earth elements and most elements which are normally gaseous or liquid. The elements are rated as potentially attractive or unattractive as possible coatings for tantalum, based on the above criteria.

In addition to the elements listed above, a large number of refractory intermetallic compounds are known which are of interest. The number of potentially attractive compounds is considerably reduced as a result of the recent comprehensive studies by Paine, Stonehouse, and Beaver(10). Their studies indicated that the 37 systems listed in Table 2 contain intermetallics of interest.

These elements, intermetallics, and oxides were reviewed on the basis of their metallurgical properties (alloying behavior with tantalum, diffusion, and intermetallic growth rates), physical properties (primarily thermal expansion, thermal conductivity, melting point, and oxide thermodynamic stabilities), oxidation properties (behavior of pure elements, alloys, and intermetallics), and mechanical properties (hardness, strength, ductility, and elastic moduli).

Application of Coatings

A variety of techniques have been utilized for applying coatings on metals, most of which have their own peculiar advantages and disadvantages. The methods which have proven useful for applying coatings may be summarized as follows:

(1) Electroplating from aqueous solutions or from fused-salt baths

(2) Dip coating by immersion in a liquid metal or alloy

(3) Vapor or pack deposition

(4) Cladding

(5) Flame spraying

(6) Enamel and paint-and-sinter techniques.

Properties of Coated Refractory Metals

By way of summary, Table 3 lists the protective coating systems which currently are considered among the most effective for protecting molybdenum and columbium against oxidation. The preponderance of aluminum, nickel, and $MoSi_2$ coating systems, with modifications of boron, chromium, and silicon, is quite striking.

TABLE 1. ELEMENTS OF INTEREST FOR COATING TANTALUM[a]

Element	1 Melting Point[b], C	2 Boiling Point[b], C	3 Melting Point of Most Refractory Compound With Tantalum, C	4 Melting Point of Highest Stable Oxide[c], C	Rating[d]
C	(5000)	Subl 4500	3880 (Ta_2C)	Subl -78.5 (CO_2)	U - 4
W	3410	5680	Solid solution	1470 (WO_3)	A - 1, 3, 4
Re	3180	5530	>2500 (two compounds)	296 (Re_2O_7)	U - 4
Os	3000	4630	-- (two compounds)	42 (OsO_4)	U - 4
Ta	2996	6030	--	1890 (Ta_2O_5)	--
Mo	2610	4804	Solid solution	795 (MoO_3)	U - 4
Cb	2468	5130	Solid solution	1460 (Cb_2O_5)	A - 1, 3, 4
Ir	2442	4530	-- (Ta_3Ir)	d 990 (IrO_2)	A - 1
B	(2300)	(2550)	3000-3200 (TaB_2)	577 (B_2O_3)	U - 4
Ru	2250	4230	-- (two compounds)	Subl 1100 (RuO_x)	U - 4
Hf	1975	5230	Probably solid solution	2777 (HfO_2)	A - 1, 3, 4
Rh	1960	3880	-- (one compound)	d 1030 (Rh_2O)	A - 1
V	1900	3530	Immiscibility gap	660 (V_2O_5)	U - 4
Cr	1875	2220	2015 ($TaCr_2$)	2440 (Cr_2O_3)	A - 1, 4
Zr	1860	3580	No intermediate phases	2715 (ZrO_2)	A - 1, 3, 4
Pt	1769	3830	-- (two compounds)	-- (PtO_2)	A - 1
Th	1755	4230	No intermediate phases	2950 (ThO_2)	A - 1, 4
Ti	1660	3130	Solid solution	1860 (TiO_2)	A - 1, 3, 4
Pd	1552	3170	No intermediate phases	d 790 (PdO)	A - 1
Fe	1539	2735	1775 ($TaFe_2$)	1457 (Fe_3O_4)	A - 1, 4
Y	(1500)	3230	No information	2400 (Y_2O_3)	A - 1, 4
Co	1495	3100	1593 ($TaCo_2$)	1810 (CoO)	A - 1, 4
Ni	1455	2840	1545 ($TaNi_3$)	1960 (NiO)	A - 1, 4
Si	1410	2475	2500 (Ta_5Si_3)	1713 (SiO_2)	A - 1, 4
Be	1284	2510	1990 (Ta_2Be_{17})	2520 (BeO)	A - 4
Mn	1260	2100	-- (Ta_2Mn)	1790 (MnO)	A - 4
Sc	(1200)	2730	No information	-- (Sc_2O_3)	U - 3
U	1130	3550	No intermediate phases	2800 (UO_2)	A - 4
Cu	1083	2595	Probably immiscible	1230 (Cu_2O)	U - 1, 4
Au	1063	2966	No information	d	U - 1
Ag	980.6	2212	Immiscible with Ta	d 145 (Ag_2O)	U - 1, 4
Ge	959	2700	-- (three compounds)	1100 (GeO_2)	U - 1, 4
La	920	2730	No information	2320 (La_2O_3)	A - 4
Ca	850	1480	No information	2570 (CaO)	A - 4
As	(817)	Subl 616	-- (forms compounds?)	315 (As_2O_3)	U - 1, 2, 4
Ce	804	2530	No information	d 2300 (CeO_2)	A - 4
Sr	770	1384	No information	2450 (SrO)	A - 4
Ba	710	1638	No information	1920 (BaO)	A - 4
Al	660	2330	-- ($TaAl_3$)	2020 (Al_2O_3)	A - 4
Mg	650	1126	No information	2800 (MgO)	A - 4
Sb	630.5	1620	No information	655 (Sb_2O_3)	U - 1, 4
Zn	419.5	910	No information	d vol (ZnO)	A[e]
Pb	327.4	1740	No information	885 (PbO)	U - 1, 4
Cd	321	765	No information	d vol (CdO)	U - 1, 2, 4

TABLE 1. (Continued)

Element	1 Melting Point(b), C	2 Boiling Point(b), C	3 Melting Point of Most Refractory Compound With Tantalum, C	4 Melting Point of Highest Stable Oxide(c), C	Rating(d)
Tl	303	1460	No information	715 (Tl_2O_3)	U - 1, 4
Bi	271	1630	No information	817 (Bi_2O_3)	U - 1, 4
Sn	231.9	2730	1200-1550? (Ta_3Sn)	1040 ? (SnO)	A - 3
Se	220.5	685	No information	Subl 317 (SeO_2)	U - 1, 4
Li	180	1370	No information	Subl 1300 (Li_2O)	U - 1, 2, 4
In	156.4	2170	No information	>2000 (In_2O_3)	U - 1
S	112.8	444.5	-- (four compounds)	16.8 (SO_3)	U - 1, 2, 4
Na	97.8	914	No information	d 585 (Na_2O_2)	U - 1, 2, 4
K	63.6	779	No information	490 (K_2O_2)	U - 1, 2, 4
P	44.1	280	-- (two compounds)	Subl 250 (P_2O_5)	U - 1, 2, 4
Rb	38.8	679	No information	412 (RbO_2)	U - 1, 2, 4
Ga	29.8	2430	No information	1725 (Ga_2O_3)	U - 1
Cs	29.7	690	No information	502 (Cs_4O_6)	U - 1, 2, 4
Hg	-38.9	361	No information	d 430 (HgO)	U - 1, 2, 4
N	-210.0	-195.8	3090 (TaN)	30 (N_2O_5)	U

(a) Data are from References (2) through (9).

(b) Parentheses denote estimated melting or boiling point under pressure.

(c) Subl = sublimation point

d = dissociation temperature

d vol = dissociates into volatile products

(d) A = potentially attractive, or U = unattractive on the basis of information contained in Columns 1 through 4.

(e) Attractive on basis of effectiveness in coating columbium.

TABLE 2. BINARY METALLIC SYSTEMS KNOWN OR EXPECTED TO CONTAIN REFRACTORY, OXIDATION-RESISTANT INTERMETALLIC COMPOUNDS(10)

Known to Contain Refractory Compounds		Expected to Contain Refractory Compounds		
Al-Mo	-Zr	Al-Cb		
-Ni		-Ta		
-Ti				
Be-Cr	-V	Be-Cb	-Pt	-Ti
-Mo	-Zr	-Cd	-Re	-W
-Pd		-La	-Ta	
Si-Cb	-Mo			
-Ce	-Ta			
-Cr	-Ti			
Zr-Cr	-Sn			
-Mo				
-Ni				
Ge-Cb	-Zr			
-Mo				
-Ta				
Cr-Cb				
-Ta				
Fe-Cb				
-Ta				

TABLE 3. SUMMARY OF PROTECTIVE COATINGS WHICH ARE EFFECTIVE FOR COLUMBIUM AND MOLYBDENUM

Coating	Base Metal	Method of Application
$Al + Al_2O_3$	Cb	Flame spray
Al-Si	Cb	Flame spray or slurry dip and bake
Al-Cr-Si	Mo	Ditto
Al-10Cr-2Si	Cb	Dip
Al_2O_3 + glass	Cb	Flame spray
Cr	Cb, Mo	Aqueous electroplate
Cr-Ni	Mo	Ditto
Cr-34Si-20Al	Cb	Flame spray plus Al dip
Fe-25Cr-5Al	Cb	Ditto
$CrSi_2$-20Al	Cb	"
$TiSi_2$-25Al	Cb	"
Ni-32Al	Cb	"
Ni + (Si-Cr)(a)	Cb	Fused-salt electroplate plus Al dip
Ni + (Al_2O_3 + ThO_2 + SiO_2)(a)	Cb	Ditto
Ni + (Cr-B-Fe-Si)(a)	Cb	"
Ni-Cr-B	Mo	Flame spray
Ni-Si-B	Mo	Ditto
$MoSi_2$(b)	Cb, Mo	Vapor or pack deposition
LM-5(c)	Cb, Mo	Flame spray
Duplex LM-5(d)	Cb	Ditto
Si	Cb	Vapor deposit
ZrO_2 + glass	Mo	Enamel

(a) Materials in parentheses were occluded in the nickel plate.

(b) Includes modifications with additions of aluminum and perhaps boron as evolved in the proprietary Chromalloy W-2 and Durak coatings.

(c) Nominally 40 Mo, 40 Si, 8 Cr, 10 Al, 2 B.

(d) Overlay of LM-5 on 47 Cb, 30 Ti, 10 Cr, 10 Ni underlay.

Conclusions and Recommendations

The 17 recommended coatings systems are given in Table 4 which cites the specific intermetallic or oxide of interest in each system and includes recommended methods of application.

It should be emphasized that the 17 systems recommended for study in Table 4 are basic coating systems. Further improvements in the properties of each through auxiliary alloying may not only be desirable but necessary to achieve their optimum performance. Further boron additions, especially as borates, will undoubtedly prove to be of good advantage in promoting coating plasticity and self-healing characteristics.

The protective coatings systems recommended for study on tantalum and tantalum alloys can be conveniently divided into two groups, one consisting of the aluminides and beryllides (10 systems) and the other consisting of silicides, oxides, and chromium (7 systems). Studies on coatings in the first group, aluminides and beryllides, were initiated at Sylvania-Corning Nuclear Corporation in June, 1960, under Air Force sponsorship. Consequently, the initial Battelle studies have been limited to the silicide, oxide, and chromium systems outlined in Table 4.

EXPERIMENTAL PROCEDURES

Four materials were employed as coating substrates. These were unalloyed tantalum, the commercial Ta-10W alloy, and two advanced experimental alloys, Ta-30Cb-5V and Ta-10Hf-5W.

The unalloyed tantalum was obtained in the form of a 2-inch-diameter electron-beam-melted ingot having the analysis given in Table 5. The ingot was press forged cold to a 1-inch-thick slab and cold rolled to 0.040-inch-thick strip with one intermediate 1400 C (2550 F) vacuum anneal at a thickness of 0.10 inch. Initial coupons cut from this strip measured 0.75 by 1.0 inch; the coupon size was later reduced to 1/2 by 3/4 inch. A 1/8-inch-diameter hole was drilled near one end of the coupons to facilitate oxidation testing. All coupons were mechanically polished to 600 grit and the edges rounded. After etch polishing in a nitric-hydrofluoric-sulfuric acid pickle, the coupons were vacuum annealed for 1 hour at 1300 C (2370 F). The annealed tantalum coupons had an equiaxed microstructure and a hardness of 89 VHN.

The Ta-10W alloy was obtained as 0.25-inch-diameter rod. The rod was cold fabricated to 0.6-inch-wide by 0.04-inch-thick strip, cut into 1/2 by 3/4-inch coupons, and polished and annealed as described above.

The two experimental alloys, Ta-30Cb-5V and Ta-10Hf-5W, were obtained as annealed 0.04-inch sheet processed on Contract AF 33(616)-7452. The Ta-30Cb-5V alloy was intended to contain 7.5V; however, analyses revealed that the vanadium content

TABLE 4. RECOMMENDED COATINGS SYSTEMS FOR STUDY ON TANTALUM AND TANTALUM-BASE ALLOYS

Coating Systems	Specific Compounds of Interest	Recommended Methods of Application
Cr	$TaCr_2$	Vapor or pack deposition
Cr-Si	Cr_3Si	Ditto
Ti-Si	Ti_5Si_3, TiSi, $TiSi_3$	"
Mo-Si	$MoSi_2$	"
Hf-Si	Hf_xSi_y (?)	"
ZrO_2 + glasses	ZrO_2	Flame spray, enamel, or paint-and-sinter
Al_2O_3 + glasses	Al_2O_3	Ditto
Al	$TaAl_3$	Hot dip or vapor or pack deposition
Al-Cb	$CbAl_3$	Ditto
Al-Hf	$HfAl_3$ (?)	"
Be	$TaBe_2$, $TaBe_{12}$	Vapor or pack deposition
Be-Cb	Cb_2Be_{17}, $CbBe_{12}$	Ditto
Be-Hf	Hf_xBe_y (?)	"
Be-Mo	$MoBe_{12}$	"
Be-Ti	$TiBe_2$, $TiBe_{12}$	"
Be-W	"WBe_{12}"	"
Be-Zr	Zr_2Be_{17}, $ZrBe_{13}$	"

TABLE 5. ANALYSIS OF ELECTRON-BEAM REFINED TANTALUM

Element	Amount Present, wt.%	Element	Amount Present, wt.%
O	0.013	Mg	<0.002
C	0.006	Mn	<0.002
N	0.003	Mo	0.004
		Ni	<0.002
Al	<0.002	Pb	<0.002
Cb	<0.05	Si	<0.002
Co	<0.002	Sn	0.002
Cr	<0.002	Ti	<0.005
Cu	<0.004	V	<0.002
Fe	<0.005	W	<0.05

had been lowered during arc melting. Additional Ta-10Hf-5W material was prepared by arc melting as 150-gram ingots and warm rolling at 1800 F (in stainless packs) and 700 F to 0.04-inch strip with one intermediate vacuum anneal at 2550 F. Samples measuring 1/2 by 3/4 inch were cut from the strips, drilled, and polished as described above.

Three additional alloys, Ta-30Cb-10V, Ta-5V, and Ta-7.5V, were used in limited coatings studies. These alloys were obtained in sheet form from materials processed on Contract AF 33(616)-7688 and prepared for evaluation in a manner similar to that described above.

Coatings were applied by hot dipping (aluminum and zinc), vacuum distillation (zinc), paint and sinter (silicon), pack cementation (aluminum, chromium, silicon, titanium, and hafnium), vapor deposition (silicon), and flame spraying (Al_2O_3).

The hot-dipping studies were conducted by suspending the specimens on tungsten wire and dipping in molten zinc or aluminum. Various time-temperature combinations, fluxes, and postdipping heat treatments were employed, as described in the text.

Zinc coatings were also applied by vacuum distillation. For this work, the sample to be coated was sealed in an evacuated Vycor capsule with a measured amount of zinc and heated for various times at 1700 and 1900 F.

Limited paint-and-sinter studies were conducted with silicon coatings. Silicon powder, -200 mesh, was mixed with various carriers, as described in the text, painted onto tantalum, and sintered in vacuum at 2000 or 2200 F.

The pack-cementation process was used for applying most of the coatings evaluated in this study. The packs consisted of thin-wall mild-steel cans. Initially, cans 1.5 inches in diameter by 1 inch deep were used. Later, the pack size was increased to 2 inches in diameter by 1.25 inches deep. The standard pack mix consisted of 25 volume per cent coating powder, 75 volume per cent Al_2O_3 powder, and 2 or 4 weight per cent halide carrier. The Al_2O_3 powder was initially used "as received" and contained a considerable fraction of -325-mesh particles. In later work, the powder was sized to -100 +140 mesh (average particle diameter of 0.005 inch). Three samples were coated in each pack. The minor variations to this procedure which were evaluated are described in the text where applicable.

Heating of the packs to form the coatings was conducted in a horizontal tube furnace under a flowing argon atmosphere. Six or eight packs were heated in each run for periods up to 24 hours at temperatures from 1800 to 2400 F. The packs were removed from the furnace after cooling to about 600 F.

Vapor-deposition coatings were applied by flowing the desired gas mixture over samples suspended vertically in a Vycor tube. The samples were heated by an external resistance furnace or by induction.

Coatings of Al_2O_3 were applied by flame spraying as -200-mesh powder with an acetylene spraying torch. Several of the sprayed coatings were subsequently impregnated with glass by painting with a glass slurry and vacuum firing, as described later.

The coated samples were evaluated by means of static, continuous-weighing oxidation testing in air at 2200, 2500, and 2700 F, and by cyclic oxidation testing at 1200 to 2700 F. The criterion for failure during static testing was an upward inflection in the weight-gain curve. During cyclic testing, failure was judged to have occurred when the sample showed visible signs of accelerated oxidation at one or more points. Additional evaluations included metallographic examinations before and after air oxidation, Knoop hardness traverses on the coatings and substrates, spectrographic, X-ray diffraction, and electron-beam microprobe analyses of the coatings, bend and tensile tests of coated and exposed samples, and defect oxidation studies at 2500 and 2700 F. For the latter studies, coatings were defected by drilling a 0.04-inch-diameter hole through the coating, exposing the substrate. The coated samples were examined after each hour of exposure and were judged to have failed when accelerated oxidation was noted near the defect.

Compositions of the tantalum alloy substrates are given in weight per cent, while coating compositions are given in atom per cent, neglecting the tantalum content of the coating. For example, the coating referred to as 100Si is primarily $TaSi_2$, or Ta-67 at.% Si.

EXPERIMENTAL RESULTS

Silicide-Base Coatings on Tantalum

Silicide coatings were studied extensively on tantalum. These were deposited primarily by the pack-cementation method, with short studies of paint-and-sinter and vapor-deposition techniques. The coating compositions evaluated included straight silicide and modified silicides containing aluminum, boron, chromium, manganese, molybdenum, titanium, and vanadium. Variables in the coating process were also evaluated, including carrier composition, coating temperature, number of coating cycles, and Al_2O_3 filler particle size. The results of these studies are discussed in the following sections.

Straight Silicide Coatings

Data on the application of straight silicide coatings by pack cementation and the protective lives of the coatings at 2200 to 2700 F are summarized in Tables 6 and 7.

Pack-Cementation Process Variables. Various halides were studied as carriers during single-cycle deposition at 2000, 2200, and 2400 F. These included fluorides, chlorides, and iodides of sodium, potassium, calcium, barium, and ammonia. As seen in Table 6, the barium and calcium chlorides gave thin, nonprotective coatings. The best carrier, on the basis of coating thickness and protectiveness, was sodium fluoride. This carrier gives a 3-mil silicide coating in 16 hours at 2200 F which is protective for up to 210 minutes at 2700 F. Ammonium chloride was judged less satisfactory because of excessive volatilization during heating.

Other pack variables evaluated included number of samples per pack, sample and pack size, amounts of silicon and carrier in the packs, deposition temperature, number of deposition cycles, and filler particle size. As seen from the data in Table 6, reducing the number of samples per pack increased the static life at 2700 F by about twofold, although there was no significant change in the amount of coating deposited. This improvement is believed associated with better coating coverage at the edges and corners. Concurrently with this conclusion, the sample size was decreased from 0.75 by 1.0 inch to 1/2 by 3/4 inch, and the pack size increased from 1-1/2-inch diameter by 1 inch deep to 2-inch diameter by 1-1/4 inch deep.

Increasing the amount of silicon in the pack from the "standard" 25 volume per cent to 50 volume per cent increased the coating thickness slightly, while decreasing the amount of silicon to 10 volume per cent decreased the thickness slightly. The change in coating life at 2700 F was judged not significant in view of the scatter in lives observed. No significant effects resulted from changing the amount of halide carrier in the packs in the range 1 to 6 weight per cent, although it appears preferable to use only as much as necessary in order to reduce clogging and furnace-tube contamination.

A coating temperature of 2200 F was selected on the basis of coating rate and protective life. The coating rate was increased as the temperature was raised to 2400 F, but little improvement in protective life was noted.

Deposition of straight silicide coatings in two cycles was evaluated, with results as given in Table 7. With sodium fluoride as the carrier, approximately equal coating weights were deposited in the first 4-hour cycle and in the subsequent 12-hour cycle. This parabolic behavior suggests that a diffusion process, possibly silicon diffusion through $TaSi_2$, is rate controlling. Linear coating behavior was observed on using sodium chloride as a carrier. This halide is a less effective carrier than sodium fluoride, and the coating rate may depend, for example, on gaseous transfer rates in the pack.

The static life at 2700 F was significantly improved for two-cycle silicide coatings as compared with that of coatings deposited in one cycle. As seen in Tables 6 and 7, the life was increased from about 130 to 150 minutes to 290 minutes. A further significant increase in protective life was obtained by employing sized 5-mil Al_2O_3 filler in the packs rather than the unsized Al_2O_3, which contained an appreciable fraction of minus 325-mesh particles. The average static life of two samples coated using sized Al_2O_3 was 580 minutes, Table 7. The reasons for the improved life of the two-cycle coatings are not clear at this time, but may well be associated with the slightly greater weight of coating and/or the better coverage of defects or thin spots achieved by repacking and recoating.

Cyclic and Defect Oxidation Studies. The results of cyclic and defect oxidation tests on silicide-coated tantalum at 1200 to 2700 F are included in Table 8. These data show that the oxidation resistance of the coating decreases with increasing temperature above 1200 F, reaching a minimum at about 1800 F. The average life at this temperature is estimated at 3 hours. At 2200 F, the life is improved to greater than 100 hours. This improvement is believed to result from a change in the reaction product from crystalline, nonadherent SiO_2 to partially amorphous, adherent, glassy SiO_2. Typical coated samples after exposures at the various temperatures are shown in Figure 1. At 2500 and 2700 F, the life decreased to 7.5 and 2.5 hours, respectively. The oxide film was glazed, especially at 2700 F, suggesting the presence of amorphous SiO_2.

TABLE 6. SINGLE-CYCLE DEPOSITION OF SILICIDE COATINGS ON TANTALUM

Charged Coating Composition, atom per cent	Deposition Conditions[a] Temp, F	Deposition Conditions[a] Carrier	Amount of Coating: Average Weight Gain, mg/cm^2	Amount of Coating: Average Thickness Increase, mil/side	Amount of Coating: Coating Thickness, mil/side[b]	Average Static Coating Life at Indicated Temperature, min[c]: 2200 F	2500 F	2700 F
				Straight Si Coatings				
100Si	2000	$BaCl_2$	0.98	0.07	0.4	--	<1(1)	--
		$CaCl_2$	2.0	0.02	0.4	--	<1(1)	--
		NaCl	3.7	0.27	0.8	25(1)	2(1)	--
		NH_4Cl	8.1	0.86	1.4	--	116(3)	58(3)
		NaCl+NaF	9.0	0.90	1.9	--	200(1)	85(1)
		NH_4F	10.9	0.90	2.1	270(1)	3(1)	--
		NH_4Cl+NaF	12.8	1.0	2.4	>360(1)	2(1)	--
		NH_4Cl+NH_4F	13.3	1.1	2.4	>360(1)	3(1)	--
	2200	NH_4Cl	12.1	1.4	2.3	--	110(2)	1(2)
		NaCl	12.5	1.2	2.6	--	>330(1)	8(1)
		NaCl+NaF	14.8	1.4	3.1	--	>390(1)	2(1)
		NaI	17.2	1.9	2.5	--	>450(1)	70(1)
		KF	17.7	2.2	3.6	--	55(1)	15(1)
		NaF	17.6	1.7	3.0	--	380(2)	105(6)
(1 spec/pack)		NaF	16.0	1.6	--	--	--	122(3)
(2 spec/pack)		NaF	17.0	1.6	3.1	--	--	190(3)
(10 vol % Si)		NaF	16.2	1.4	2.6	--	--	110(2)
(50 vol % Si)		NaF	19.5	1.6	3.4	--	--	150(1)
(1 wt % NaF)		NaF	16.0	1.2	2.7	--	--	130(1)
(6 wt % NaF)		NaF	14.5	1.2	2.2	--	--	102(2)
	2400	NaF	28.6	2.8	5.3	--	--	130(1)
		KF	30.3	2.7	6.1	--	--	210(1)
				Si-Al Coatings				
Si-25Al	2000	NH_4Cl+NaF	11.0	1.1	2.1	--	6(1)	2(1)
	2200	NaCl	1.9	0.8	0.8	--	<1(1)	--
		NaI	4.5	1.6	1.1	--	<1(1)	--
		NH_4Cl	6.7	1.0	2.0	--	160(1)	--
		NaI+KF	12.3	1.7	2.5	--	430(1)	3(1)
		KF	12.6	1.5	2.5	--	>390(1)	110(1)
		NaF+NaCl	15.2	1.9	2.5	--	70(1)	8(1)
		NaF	16.1	1.9	3.0	--	>360(1)	10(1)
	2400	NaI	0.9	0.1	0.2-0.4[d]	--	<1(1)	<1(1)
		KF	2.1	0.2	0.8-1.1[d]	--	<1(1)	<1(1)
Si-50Al	2000	NH_4Cl+NaF	6.8	0.9	0.8[e]	--	3(1)	<1(1)

TABLE 6. (Continued)

	Deposition Conditions(a)		Amount of Coating			Average Static Coating Life at Indicated Temperature, min(c)		
Charged Coating Composition, atom per cent	Temp, F	Carrier	Average Weight Gain, mg/cm^2	Average Thickness Increase, mil/side	Coating Thickness, mil/side(b)	2200 F	2500 F	2700 F
			Si-Al Coatings (Continued)					
Si-50Al	2200	NH_4Cl	3.5	0.6	0.4	--	2(1)	<1(1)
		NaCl	5.7	1.5	0.4-3.0(e)	--	1(1)	--
		NaI	6.3	1.25	1.5	--	20(1)	<1(1)
		KF	6.5	0.9	1.6	--	175(1)	60(1)
		NaI+KF	8.3	0.9	1.8	--	2(1)	55(1)
		NaF+NaCl	9.2	1.1	1.4	--	230(1)	70(1)
		NaF	13.0	1.7	2.3	--	260(4)	120(6)
(1 spec/pack)		NaF	11.4	1.6	--	--	--	90(2)
(2 spec/pack)		NaF	13.0	1.6	2.7	--	--	110(2)
	2400	NaI	1.3	0.1	0.4(d)	--	<1(1)	<1(1)
		KF	1.8	0.1	0.6(d)	--	<1(1)	<1(1)
Si-60Al	2200	NaCl	5.1	--	0.7-1.6(e)	--	--	5(1)
		KI	4.2	--	1.2(e)	--	--	<1(1)
Si-70Al	2200	NaCl	11.7	--	1.5-2.2(e)	--	--	<1(1)
		KI	5.5	--	1.3(e)	--	--	30(1)
Si-80Al	2200	NaCl	18.3	--	3.8(e)	--	--	95(1)
		KI	11.0	--	2.5(e)	--	--	60(1)
Si-90Al	2200	NaCl	20.2	--	4.1(e)	--	--	140(1)
		KI	13.6	--	2.6	--	--	70(1)
			Si-B Coatings					
Si-1B	2200	KF	17.7	2.6	3.3	--	220(1)	<1(1)
-5B	2200	KF	16.7	2.9	3.7(e)	--	2(1)	--
-10B	2200	KF	14.3	2.7	1.4-3.8(e)	--	5(1)	--
-20B	2200	KF	8.1	2.0	0.4-1.4(e)	--	<1(1)	--
			Si-Cr Coatings					
Si-25Cr	2200	NaCl+NaF	9.0	1.1	1.8	--	>150(1)	1(1)
Si-33Cr	2130(f)	NH_4Cl	6.6	0.5	0.9	--	300(1)	<1(1)
	2130(f)	NH_4Cl(g)	9.0	0.7	1.1	--	400(1)	1(1)
	2200	NaCl+NaF	4.7	0.8	0.3-1.3	--	2(1)	<1(1)
Si-50Cr	2200	NaCl+NaF	1.3	0.4	0-0.7	--	1(1)	--
Si-75Cr	2000(h)	NH_4Cl(i)	-22.9(e)	1.1	1.2	--	<1(1)	--
	2130(f)	NH_4Cl(g)	-20.7(e)	0.6	1.0	--	<1(1)	--
	2200	NaCl+NaF	1.5(e)	0.4	0.5	--	<1(1)	--

TABLE 6. (Continued)

Charged Coating Composition, atom per cent	Deposition Conditions(a) Temp, F	Carrier	Amount of Coating: Average Weight Gain, mg/cm^2	Average Thickness Increase, mil/side	Coating Thickness, mil/side(b)	Average Static Coating Life at Indicated Temperature, min(c)		
						2200 F	2500 F	2700 F
				Si-Mo Coatings				
Si-20Mo	2130(f)	NH$_4$Cl(g)	17.6	1.7	3.1	--	180(1)	23(1)
-33Mo	2130(f)	NH$_4$Cl(g)	-3.1	0.1	0.4	--	<1(1)	--
				Si-Ti Coatings				
Si-25Ti	2000(h)	NH$_4$Cl(g)	22.0	3.2	3.5(e)	--	20(1)	<1(1)
	2200	NaCl+NaF	9.2	1.0	2.0	--	5(1)	<1(1)
Si-33Ti	2200	NaCl+NaF	7.3	0.8	1.6	--	20(1)	--
Si-50Ti	2000(h)	NH$_4$Cl(g)	27.2	3.4	3.2(e)	--	25(1)	30(1)
	2200	NaCl+NaF	2.0	0.1	0.5-1.2	--	<1(1)	<1(1)
Si-63Ti	2000(h)	NH$_4$Cl(g)	8.8	1.8	2.2(e)	--	1(1)	--
Si-75Ti	2200	NaCl+NaF	0.9	-0.1	0.2(e)	--	<1(1)	--
				Si-V Coatings				
Si-2V	2200	NaF	16.3	1.8	2.8	--	--	15(1)
-5V	2200	NaF	16.6	2.1	3.0	--	--	115(1)
-10V	2200	NaF	16.4	1.9	2.6	--	--	115(1)
				Si-Al-Ti Coatings				
Si-5Al-5Ti	2200	NaCl	1.3	-0.2	0.2-0.6	--	--	<1(1)
-5Al-15Ti	2200	NaCl	0.9	0.4	0.2	--	--	<1(1)
-10Al-10Ti	2200	NaCl	0.9	0.4	0.3-0.6	--	--	<1(1)
-15Al-5Ti	2200	NaCl	1.1	0.4	0.3	--	--	<1(1)
-15Al-15Ti	2200	NaCl	1.1	0.3	0.2	--	--	<1(1)
-25Al-25Ti	2200	NaCl	0.9	0.3	0.2-0.4	--	--	<1(1)

(a) All coating runs were for 16 hours in argon at the indicated temperature.

(b) Coating thickness was measured metallographically.

(c) Numbers in parentheses indicate numbers of samples in averages.

(d) These coatings appeared metallographically to consist of the lower silicides rather than TaSi$_2$; hence, the low oxidation resistance.

(e) Coating was partly oxidized during deposition.

(f) Coating run was 12 hours.

(g) Sixty volume per cent coating elements.

(h) Coating run was 24 hours.

(i) Twenty volume per cent coating elements.

TABLE 7. TWO-CYCLE DEPOSITION OF

			4-Hour Cycle			
Calculated or Charged Coating Composition, at. %	Analyzed Coating Composition, at. %	Al_2O_3 Filler Particle Size	Charged Coating Composition, at. %	Carrier	Temp, F	Average Coating Weight Gain, mg/cm^2
						Straight Si
100Si	--	Unsized	100Si	NaCl	2200	2.1
	--	Unsized	100Si	NaI	2200	6.1
	--	Unsized	100Si	NaF	2200	11.5
	--	5 mil	100Si	NaF	2200	15.8
	100Si	5 mil	100Si	NaF	2200	13.9
						Si-Al
Si-50Al	--	Unsized	Si-50Al	NaCl	2200	2.3
	--	Unsized	Si-50Al	NaF	2200	7.1
	--	5 mil	Si-50Al	NaF	2200	9.3
	Si-5Al	5 mil	Si-50Al	NaF	2200	10.3
(100Al)(e)	--	Unsized	100Al	KI	2200	14.8
--(f)	--	5 mil	100Si	NaF	2200	16.4
						Si-B
Si-69B	--	Unsized	100B	NaCl	2200	5.5
Si-65B	--	5 mil	100B	NaF	1800	6.2
Si-79B	--	5 mil	100B	NaF	2200	18.8
						Si-Mn
Si-26Mn	--	5 mil	100Mn	NaF	2200	28.7
Si-11Mn	Si-3Mn	5 mil	100Mn	NaF	1800	11.7
						Si-Ti
Si-2Ti	--	Unsized	100Ti	NaF	2200	0.8
						Si-Al-Cr
Si-6Al-6Cr	--	Unsized	Al-50Cr	NaI	2200	3.9
						Si-Al-Ti
Si-3Al-3Ti	--	Unsized	Al-50Ti	NaF	2200	1.4

(a) Coating thickness is measured metallographically.
(b) Numbers in parentheses indicate numbers of samples in averages.
(c) Cyclic oxidation life; see Table 13 for results at lower temperatures.
(d) Coating was partly oxidized during deposition.
(e) Silicon oxidized during deposition.
(f) Silicon apparently oxidized during aluminum deposition, resulting in large weight losses. Composition of coating not estimated.

SILICIDE COATINGS ON TANTALUM

12-Hour Cycle				Total Coating Weight Gain, mg/cm^2	Coating Thickness, mils/side(a)	Average Static Coating Life at Indicated Temperature, min(b)	
Charged Coating Composition, at. %	Carrier	Temp, F	Average Coating Weight Gain, mg/cm^2			2500 F	2700 F
Coatings							
100Si	NaCl	2200	6.2	8.3	--	120(3)	--
100Si	NaI	2200	9.1	15.2	--	>180(2)	--
100Si	NaF	2200	11.6	23.1	3.8	--	290(4)(c)
100Si	NaF	2200	14.7	30.5	--	--	580(2)
100Si	NaF	2200	8.2	22.1	--	450(4)(c)	150(4)(c)
Coatings							
Si-50Al	NaCl	2200	4.4	6.7	--(d)	--	<1(1)
Si-50Al	NaF	2200	8.5	15.6	2.6	--	150(4)(c)
Si-50Al	NaF	2200	8.7	18.0	--	--	270(2)
Si-50Al	NaF	2200	7.8	18.1	--	390(4)(c)	120(4)(c)
100Si	NaF	2200	9.3	24.1	4.7	--	305(2)
100Al	KI	2200	-41.4	-25.0	--	--	<1(1)
Coatings							
100Si	NaCl	2200	6.4	11.9	--	--	40(2)
100Si	NaF	2200	8.8	15.0	--	5(1)	20(1)
100Si	NaF	2200	13.1	31.9	7.8	--	80(2)
Coatings							
100Si	NaF	2200	42.8	71.5	9.3	--	>1440(2)
100Si	NaF	2200	48.3	60.0	--	660(4)(c)	290(4)(c)
Coatings							
100Si	NaF	2200	19.1	19.9	3.2	--	200(2)
Coatings							
100Si	NaF	2200	20.5	24.4	3.9	--	175(2)
Coatings							
100Si	NaF	2200	19.6	21.0	3.4	--	215(2)

TABLE 8. CYCLIC AND DEFECT OXIDATION DATA FOR SILICIDE-COATED TANTALUM AND TANTALUM ALLOYS

Coating Composition, atom per cent[(a)]	Amount of Coating[(b)]		Average Cyclic Coating Life at Indicated Temperature, hr[(d)]						Average Cyclic Life of Defect Coatings at Indicated Temperature, hr[(d, e)]	
	mg/cm^2	mil/side[(c)]	1200 F	1500 F	1800 F	2200 F	2500 F	2700 F	2500 F	2700 F
					Tantalum					
100 Si	22.1	3.4	60(2)	35(2)	3(2)	>100(2)	7.5(4)	2.5(4)	<1(2)	<1(2)
Si-5Al	18.1	2.9	100(2)	85(2)	20(2)	95(2)	6.5(4)	2(4)	<1(2)	<1(2)
Si-3Mn	60.0	9.7	>100(2)	25(2)	3(2)	100(2)	11(4)	4(4)	<1(2)	<1(2)
					Ta-10W					
100 Si	36.0	5.8	100(2)	15(2)	3(2)	50(2)	10(2)	4.5(2)	4.5(2)	<1(2)
Si-5Al	22.0	3.5	>100(2)	25(2)	10(2)	15(2)	3.7(3)	4.2(3)	4.5(2)	<1(2)
Si-8Mn	44.9	7.3	40(1)	15(1)	3(1)	70(2)	>20(2)	10(2)[(f)]	4.5(1)	10(2)[(f)]
					Ta-10Hf-5W					
100 Si	19.6	3.2	85(1)	15(1)	35(1)	55(1)	8(2)	2(2)	9.5(1)	<1(1)
Si-6Al	17.5	2.8	100(1)	>100(1)	>100(1)	55(1)	9.5(2)	4(2)	4.5(1)	<1(1)
Si-5Mn	52.5	8.4	>100(1)	10(1)	1(1)	95(1)	14.5(2)	7.5(2)	4.5(1)	<1(1)
					Ta-30Cb-5V					
100 Si	26.2	4.2	>100(1)	>100(1)	>100(1)	>100(1)	>20(4)	9(4)	2(2)	<1(2)
Si-9Al	20.7	3.3	>100(1)	>100(1)	>100(1)	95(1)	>20(4)	3.3(4)	2(2)	<1(2)
Si-8Mn	57.1	8.9	>100(1)	>100(1)	>100(1)	30(1)	>20(3)	4.8(3)	10(2)[(f)]	10(2)[(f)]

(a) Analyzed compositions, see Table 17.

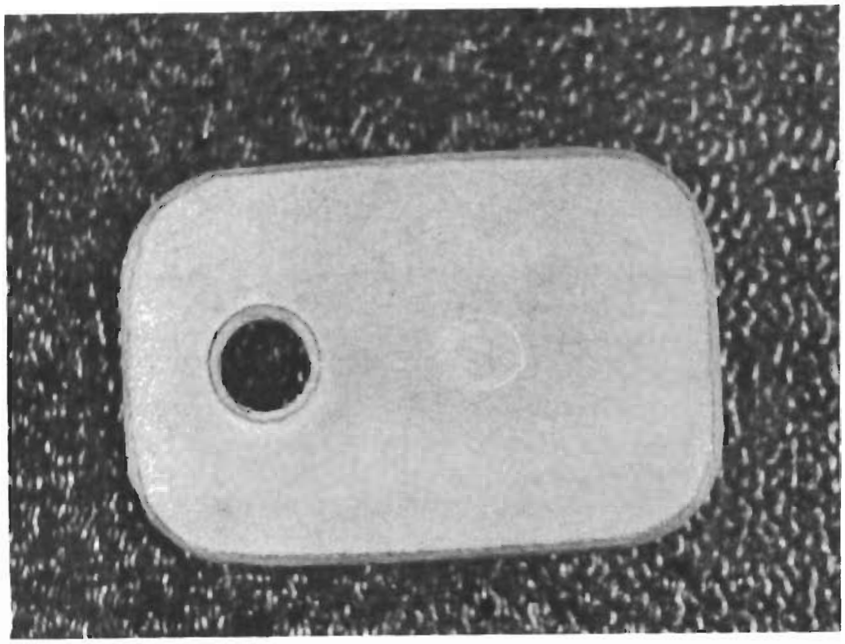
(b) The silicon and silicon-aluminum coatings were applied in two cycles, 4 hours and 12 hours, at 2200 F. The silicon-manganese coatings were applied by depositing manganese for 4 hours at 1800 F, followed by siliconizing for 12 hours at 2200 F. Sized, 5-mil Al_2O_3 was used as filler in depositing all coatings.

(c) Coating thickness is estimated on the basis of coating weight gain.

(d) Samples were exposed at 1200 F to 2200 F for up to 100 hours with cooling and examination twice each day. Samples at 2500 F and 2700 F, including defect samples, were exposed for up to 20 hours and 10 hours, respectively, with cooling and examination after each hour of exposure. Numbers in parentheses indicate numbers of samples exposed.

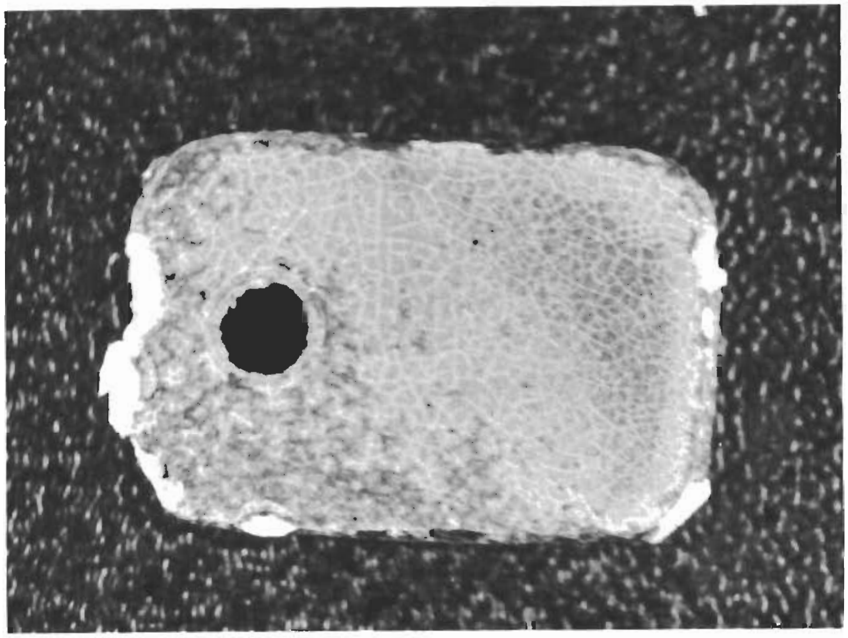
(e) Defects consisted of a 40-mil-diameter hole drilled halfway through each sample.

(f) One sample did not fail in 10 hours: the second sample failed after 9 or 10 hours of exposure.



3X N394

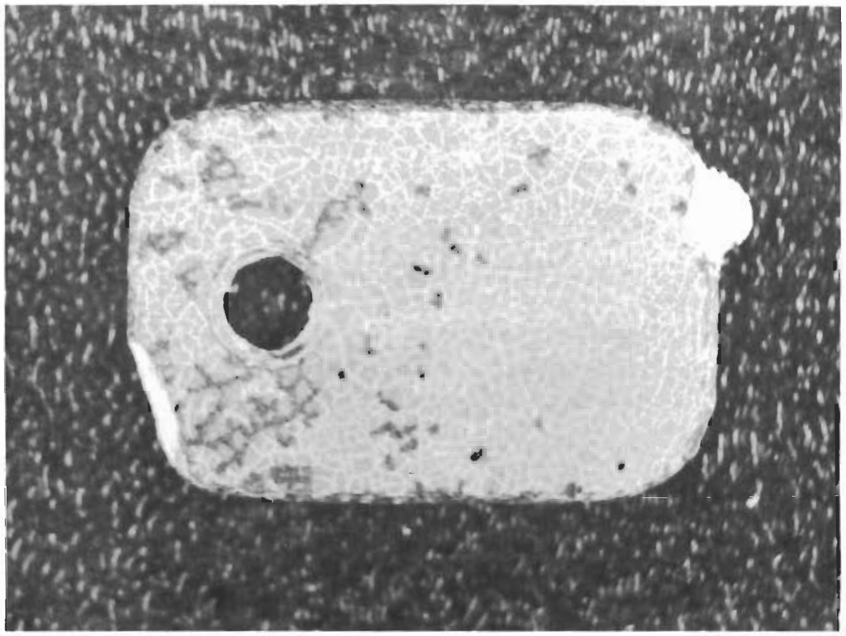
a. Exposed at 1200 F, Average Cyclic Life 60 Hours



3X N395

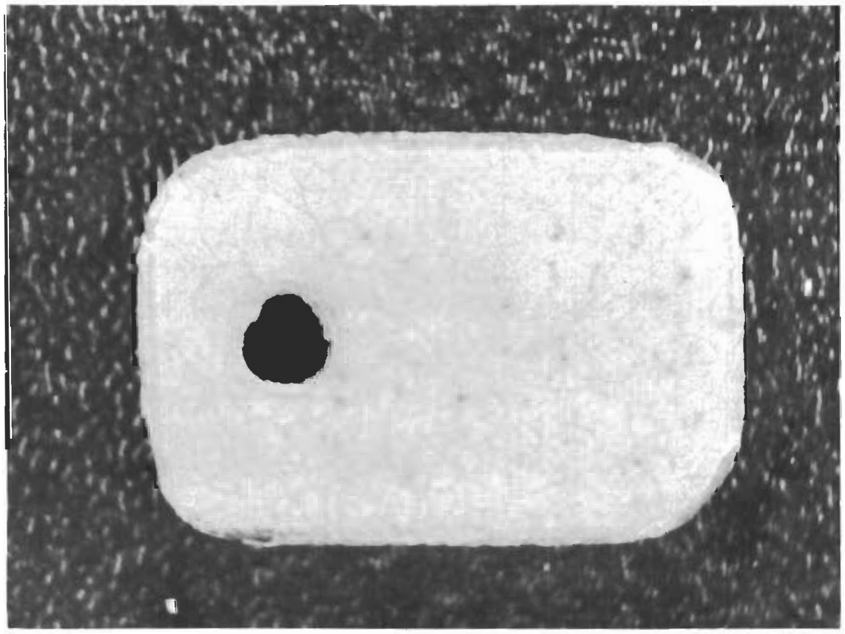
b. Exposed at 1500 F, Average Cyclic Life 35 Hours

FIGURE 1. SILICIDE-COATED TANTALUM AFTER EXPOSURES AT 1200 TO 2700 F



3X N396

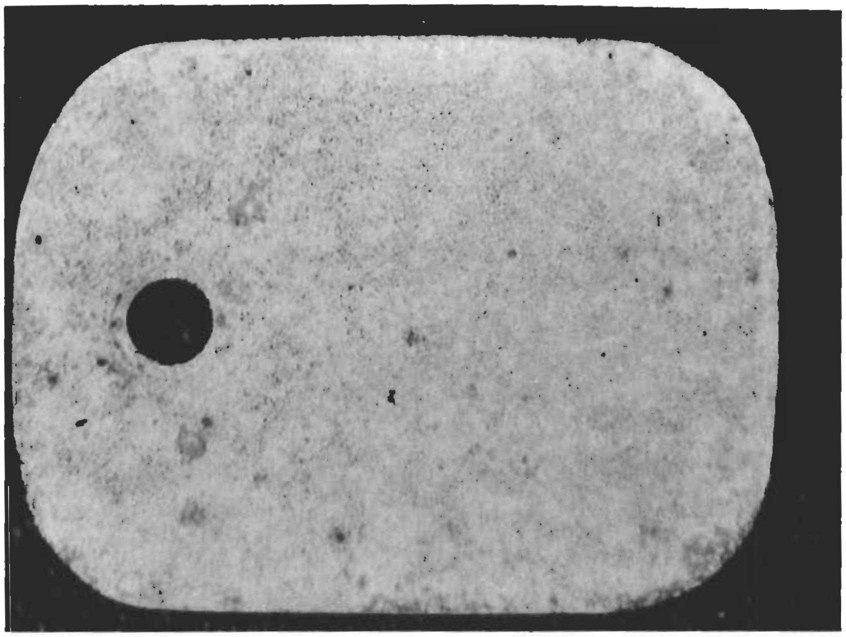
c. Exposed at 1800 F, Average Cyclic Life 3 Hours



3X N397

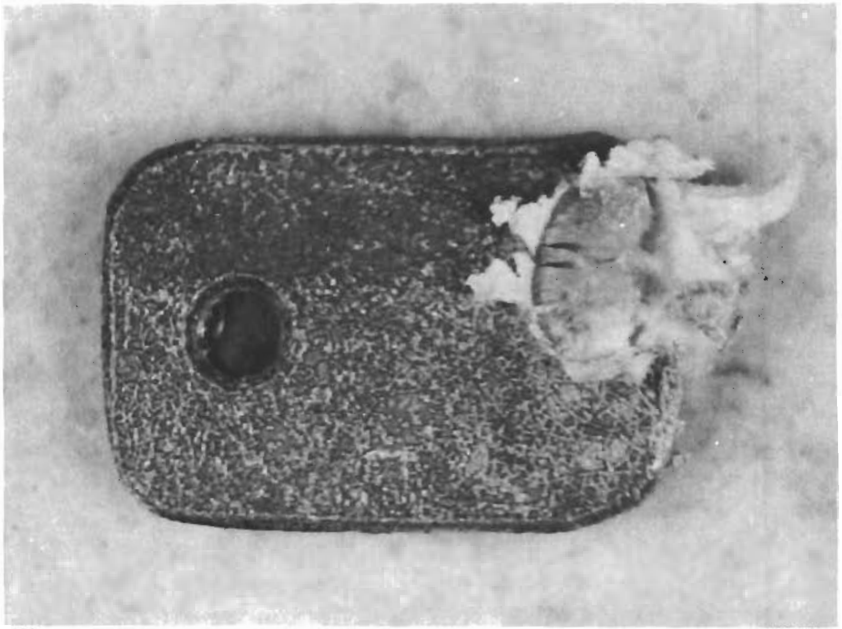
d. Exposed at 2200 F, Average Cyclic Life Greater Than 100 Hours

FIGURE 1. (CONTINUED)



3X N197

e. Exposed at 2500 F, No Failure After 7.5 Hours Static Oxidation



3X N319

f. Exposed at 2700 F, Failed After 4.7 Hours Static Oxidation

FIGURE 1. (CONTINUED)

Although the average cyclic lives at 2500 and 2700 F for silicide-coated tantalum were shorter than lives previously observed in static oxidation tests, no spalling or cracking was detected when the samples were cooled during the cyclic tests. The presence of microcracks would, however, be expected to shorten the protective life, since the defect tests indicated that this coating is not self-healing. It should also be noted that the coating weight on the cyclic samples, 22.1 mg/cm^2 (Table 8), was less than that on the samples which lasted almost 10 hours in static oxidation, 30.5 mg/cm^2 (Table 7).

Metallographic Studies. Silicide-coated tantalum in the as-deposited condition and after various oxidation exposures is shown in Figure 2. The as-deposited coating (Figures 2a and 2b) was shown by X-ray diffraction studies to consist primarily of $TaSi_2$. Two thin layers are also observed between the $TaSi_2$ and the tantalum substrate. Although unidentified, these layers are presumed to consist of lower silicides, such as Ta_5Si_3, Ta_2Si, and $Ta_{4.5}Si$. No difference was detected metallographically between coatings deposited in one or two cycles.

The progress of oxidation is illustrated in Figures 2c through 2e. Figure 2c shows patches of oxide forming on the surface of the disilicide after 15 minutes at 2700 F. The oxide was identified by X-ray diffraction as β Ta_2O_5 (low-temperature form). A weak, unidentifiable phase was also observed; this may be SiO_2 or a tantalum silicate. Apparently, the silicate which forms is unable to prevent oxidation of the tantalum in the $TaSi_2$ layer into porous, nonprotective Ta_2O_5. The pentoxide grows until the entire surface of the coating is covered as illustrated in Figure 2d. Here, the oxide penetrates the disilicide nonuniformly and shows a tendency to follow cracks in the coating. The final stage before failure is shown in Figure 2e. Most of the disilicide has been consumed by oxidation, and the subsilicides, which have been increasing in thickness, are exposed to the advancing oxide. The subsilicides are less oxidation resistant than $TaSi_2$, as indicated by undercutting of the disilicide. Failure subsequently occurs by oxidation of the tantalum substrate after penetration of the subsilicide. Oxidation curves* for samples oxidized at 2500 and 2700 F were approximately linear, further suggesting that the oxidation product is only partially protective.

The disilicide is also depleted by conversion into the lower silicides during exposure at elevated temperatures. The rates of growth of the composite subsilicide layer were determined as 2.9×10^{-2} mil^2/hr and 1.1×10^{-1} mil^2/hr at 2500 and 2700 F, respectively. The parabolic nature of the growth curves, shown in Figure 3, indicates that the growth is a diffusion-controlled reaction. The data at 2700 F further indicate that a 3-mil coating would be substantially converted into lower silicides after about 50 hours' exposure, neglecting consumption by oxidation.

Hardening of the tantalum substrate by silicon or by oxygen diffusing through the silicide coating was studied by Knoop hardness traverses and by room-temperature bend tests on both as-coated and exposed samples. The results of the hardness traverses, presented graphically in Figure 4, indicate very slight hardening at about 0.07 mm beneath the coating-substrate interface, but no other significant hardening effects resulting from either coating or subsequent exposure.

Bend tests showed that the substrate retained its original excellent ductility. Thus, after coating and after exposures at 2500 and 2700 F, the substrate showed 0 T bend ductility although the coating itself was brittle and flaked off. The disilicide coating had a Knoop hardness of about 1300 KHN.

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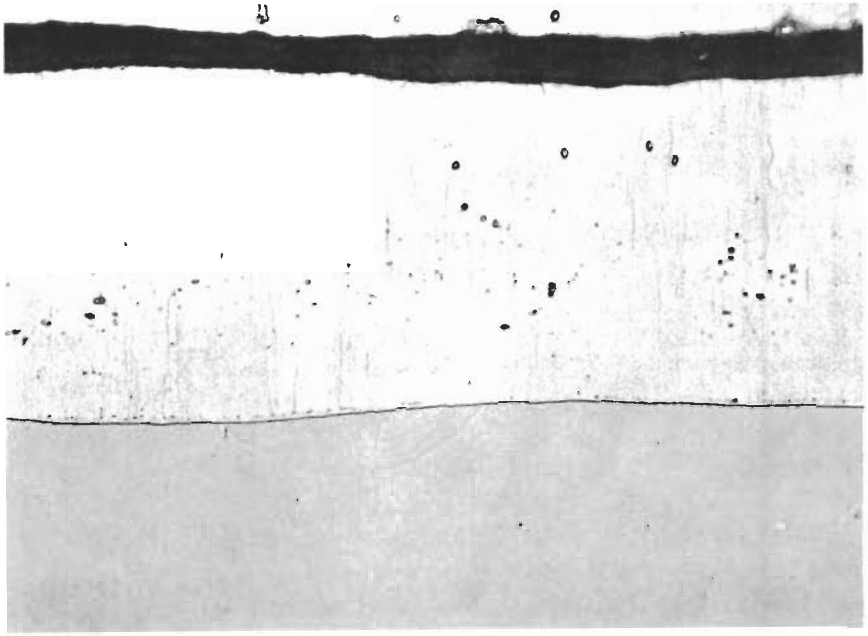
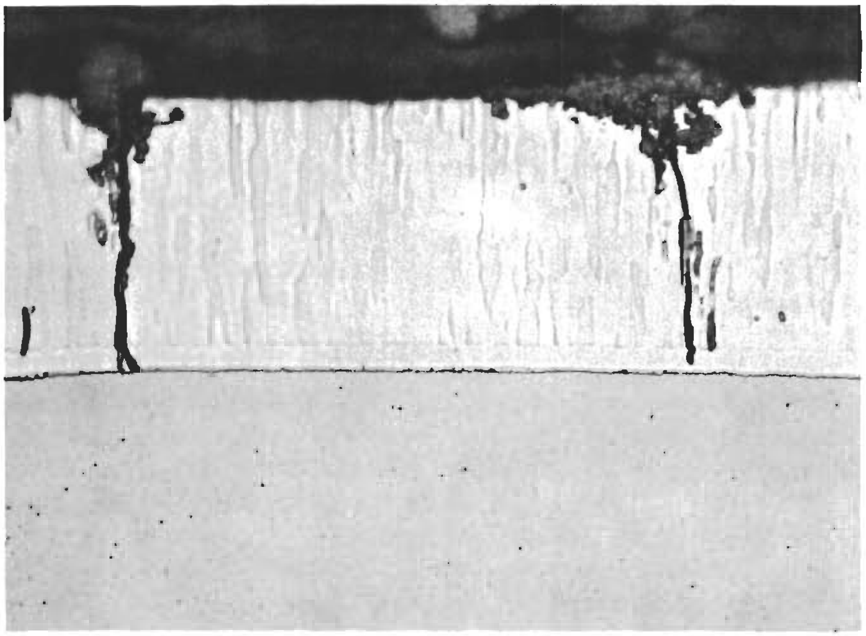
*See Figure 16.



a. As Coated in One 16-Hour Cycle, 3.4 Mil

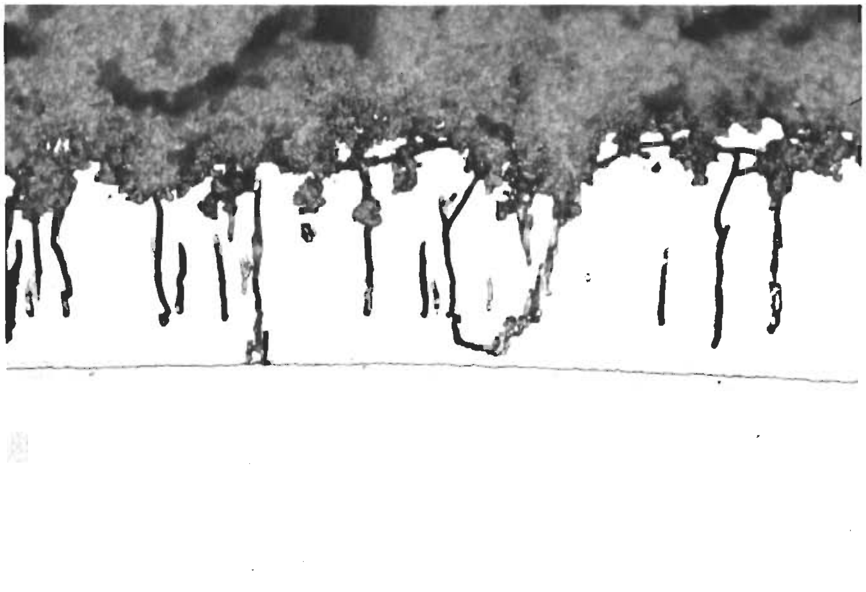
b. As Coated in Two Cycles, 4 Hours and 12 Hours, 3.7 Mil

FIGURE 2. SILICIDE-COATED TANTALUM AS COATED AT 2200 F AND AFTER EXPOSURES AT 2500 F AND 2700 F



500X N77608

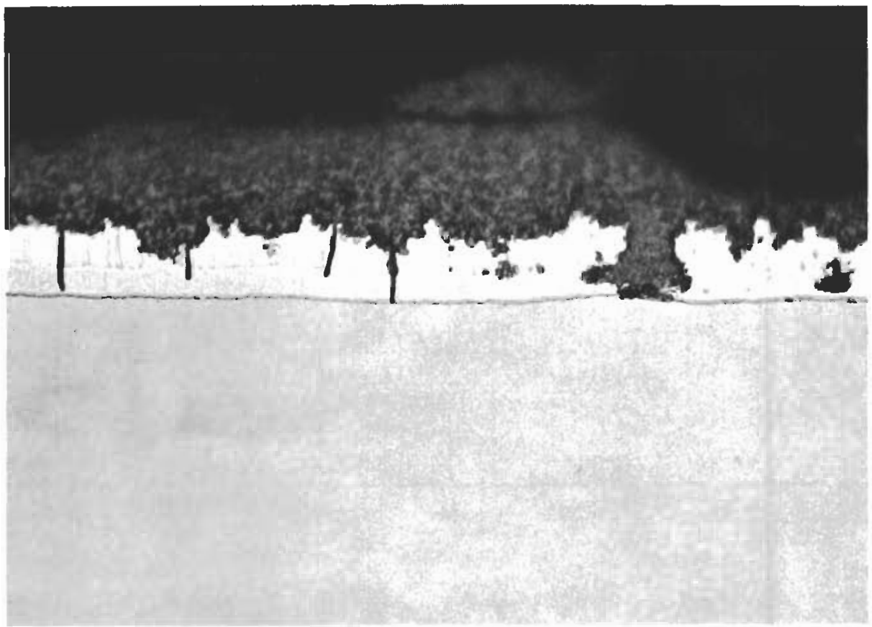
c. 15 Minutes' Exposure at 2700 F



500X N77614

d. 150 Minutes' Exposure at 2700 F

FIGURE 2. (CONTINUED)



500X N77611

e. 175 Minutes' Exposure at 2500 F (Nominal Si-50Al Coating)

FIGURE 2. (CONTINUED)

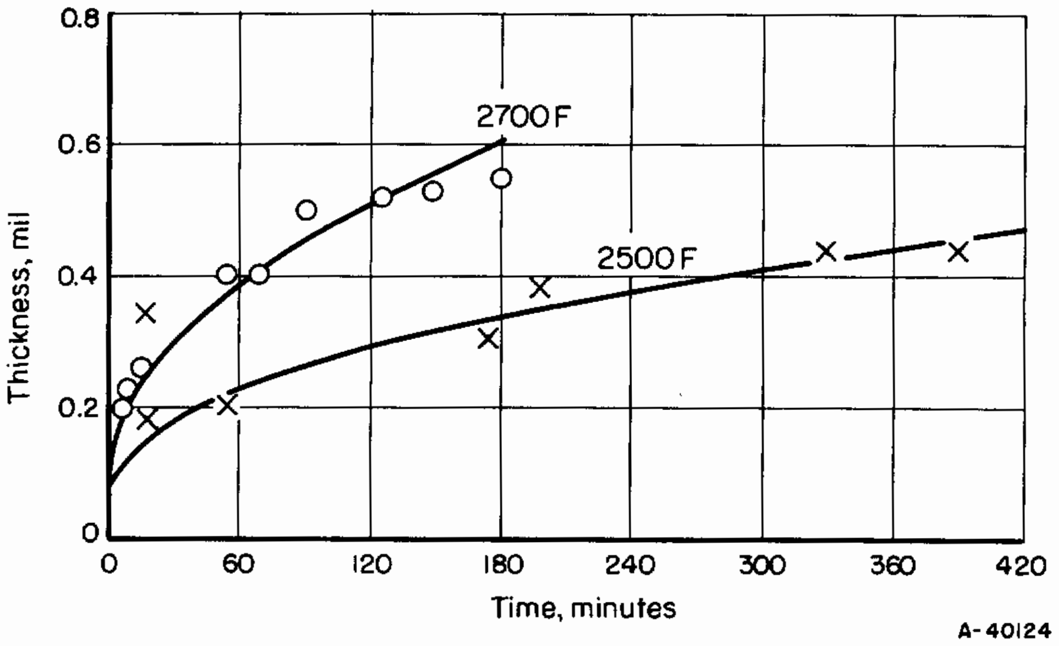


FIGURE 3. GROWTH OF SUBSILICIDE LAYER DURING EXPOSURE OF SILICIDE-COATED TANTALUM AT 2500 AND 2700 F

Initial thickness of subsilicide is 0.08 mil.

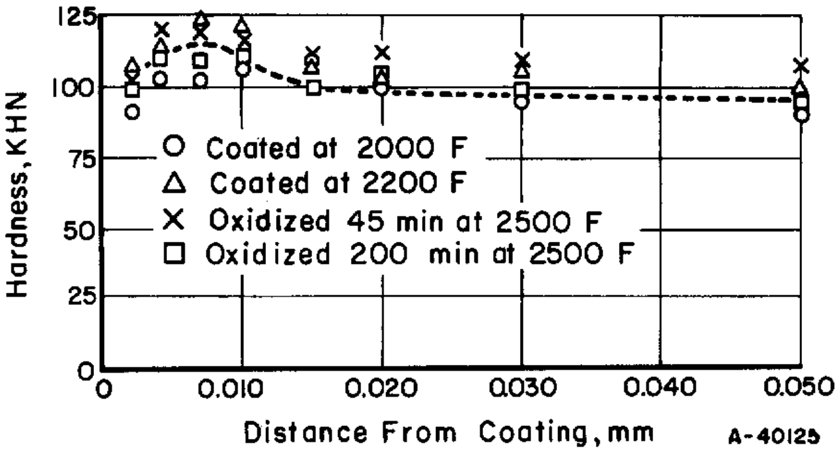


FIGURE 4. HARDNESS TRAVERSES ON SILICIDE-COATED TANTALUM AS COATED AND AFTER EXPOSURES AT 2500 F

Vapor-Deposition and Paint-and-Sinter Studies. Straight silicide coatings were also applied by vapor deposition and by the paint-and-sinter method.

Two groups of samples were silicon coated by hydrogen reduction of $SiCl_4$ for 4 hours at 2370 F (1300 C). One group was coated by flowing a mixture of $2H_2 + SiCl_4$ in an argon carrier over externally heated samples to give a silicide layer about 0.2 mil thick. The silicide layer was relatively adherent but could be chipped off. A second group of samples was coated under similar conditions except that the argon carrier was omitted and the $H_2/SiCl_4$ ratio was increased from 2 to 2.7. The silicide layer on these samples was about 1 mil thick but had poor adherence, as evidenced by flaking during handling.

Both silicide coatings applied by the hydrogen-reduction process had poor oxidation resistance. No protection was achieved with either the 0.2-mil coating at 2500 or 2200 F or the 1-mil coating at 2500 F.

Initial studies on paint-and-sinter silicide coatings have shown some promise with an alcohol-glyptal mixture as a bonding agent. Slurries of silicon powder in water, alcohol, and glycerine were painted on tantalum but produced only powdery cakes of silicon which would not adhere during handling. A slurry of silicon powder with alcohol-glyptal, however, produced an adherent coating on drying.

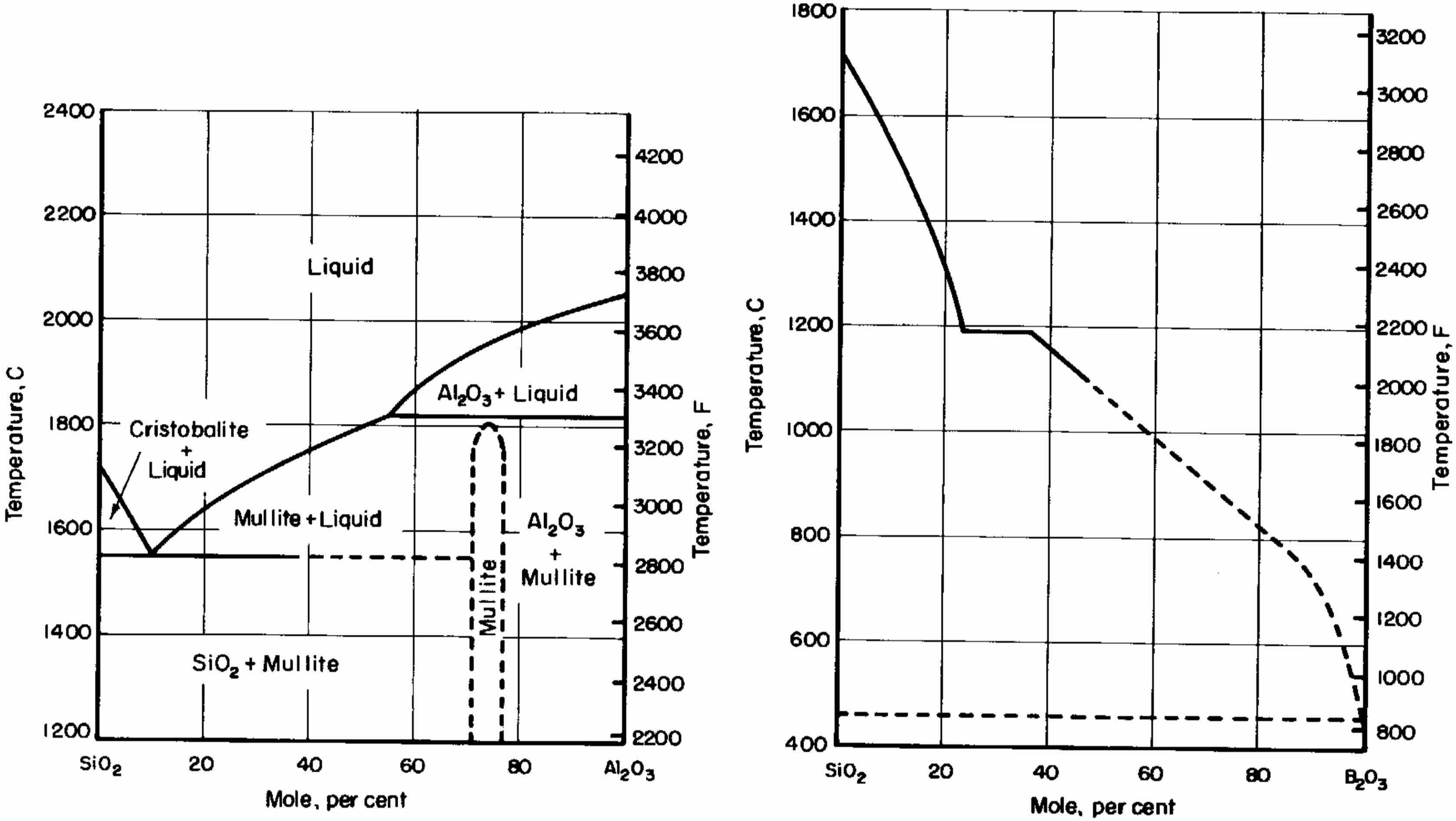
Sintering of the glyptal-bonded coating for 16 hours at 2000 F in vacuum densified the silicon coat but did not promote interdiffusion with the tantalum substrate. A subsequent coating, applied with an alcohol-glyptal-NaF bonding mixture, interdiffused with tantalum at 2200 F to give a silicide coating approximately 0.2 mil thick. This coating, however, was not oxidation resistant at 2700 F.

Modified Silicide Coatings

Modified silicide coatings containing aluminum, boron, chromium, manganese, molybdenum, titanium, and vanadium were applied to tantalum using pack-deposition techniques.

Aluminum-Silicide Coatings. Aluminum-modified silicide coatings are of interest because of the known refractory and protective properties of Al_2O_3 and also from the phase relationships between SiO_2 and Al_2O_3. The phase diagram for this system, shown in Figure 5a, shows a eutectic at 10 mole per cent Al_2O_3 at about 1550 C (2820 F). This decrease in melting point from that of straight SiO_2 should also lower the temperature at which the amorphous, protective glass forms when the coated samples are exposed.

Aluminum-modified silicide coatings were applied by both codeposition and by alternate deposition of aluminum and silicon, as seen in Tables 6 and 7. Pack compositions evaluated in codeposition ranged from Si-25Al to Si-90Al. Several process variables were studied, primarily on the Si-25Al and Si-50Al packs. These variables included temperature, time, carrier, number of samples per pack, number of deposition cycles, and particle size of Al_2O_3 filler. The optimum coating conditions were found to be similar to those found best for application of straight silicide coatings, namely, two-cycle

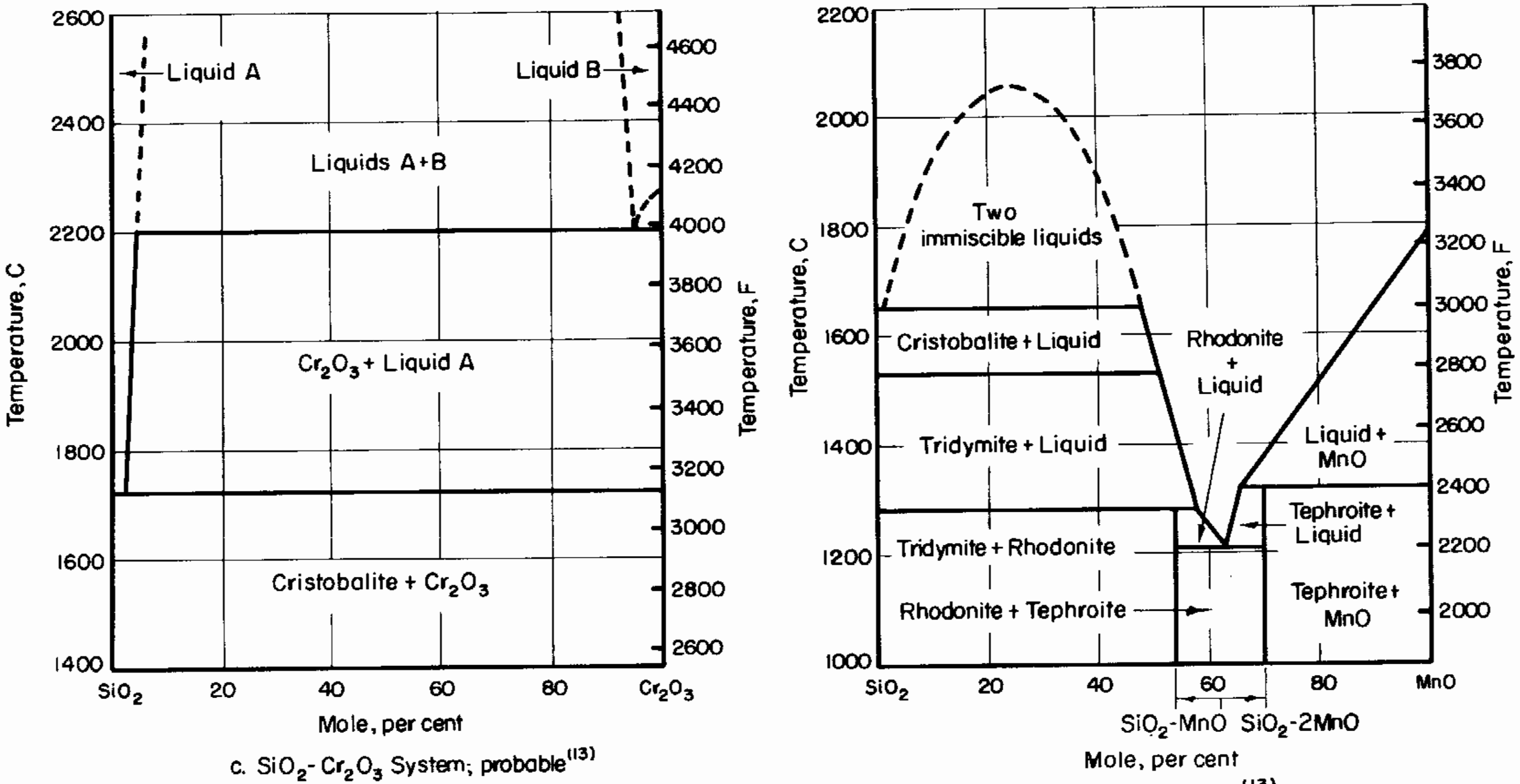


a. SiO_2-Al_2O_3 System(1)

b. SiO_2-B_2O_3 Liquidus(12)

A-40126

FIGURE 5. PHASE DIAGRAMS FOR SELECTED SiO_2 – OXIDE SYSTEMS



c. SiO_2-Cr_2O_3 System; probable(13)

d. SiO_2-MnO System(13)

A-40127

FIGURE 5. (CONTINUED)

deposition at 2200 F with sized 5-mil Al_2O_3 filler and NaF carrier. Likewise, the static, cyclic, and defect oxidation behavior of the coating deposited from the Si-50Al packs was similar to that of straight silicide-coated tantalum, Tables 6, 7, and 8. Some improvement was noted in the low-temperature oxidation resistance, but there was no significant evidence suggesting that the oxide formed at high temperatures was more vitreous than that from silicide-coated tantalum.

Metallographic studies and analyses indicated that these coatings were primarily silicide and contained very little aluminum. Micrographs of the as-deposited coatings, Figures 6a and 6b, showed the structures to be quite similar to those of straight silicide coatings, aside from a tendency for the coatings to oxidize during deposition. Spectrographic analyses, Table 9, showed that the aluminum contents of the thicker coatings deposited using NaF were only 2 to 5 atom per cent.

Higher-aluminum-content coatings were investigated also by codeposition and by alternate deposition. The results of codeposition studies on Si-60Al to Si-90Al coatings are given in Table 6. These coatings apparently contained more aluminum than the nominal Si-50Al coating but oxidized more during deposition and were generally unsatisfactory. The protectiveness of the Si-60Al and Si-70Al coatings was low, although the protectiveness increased with increasing aluminum content. A micrograph of the as-deposited Si-80Al coating is shown in Figure 6c.

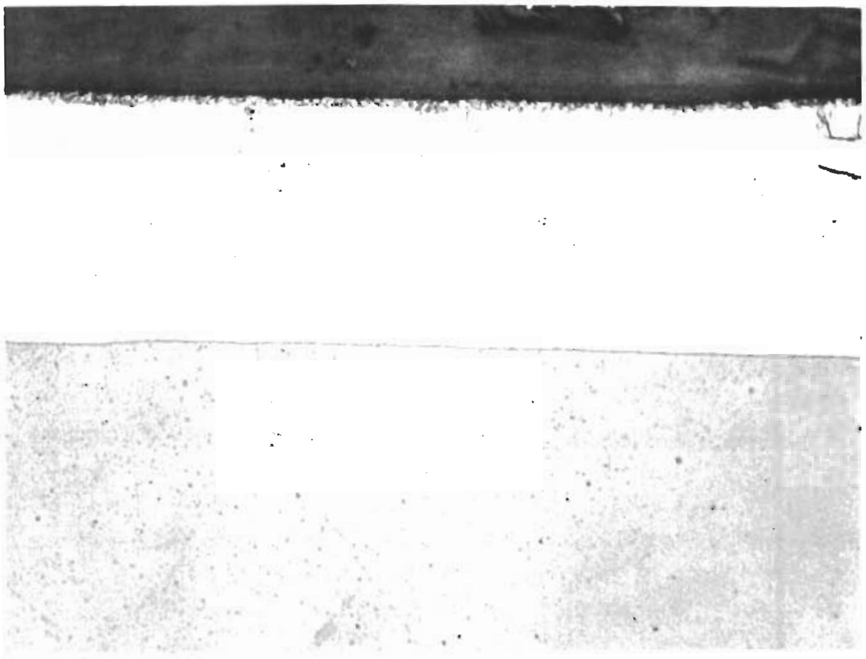
Alternate deposition of aluminum and silicon and of silicon and aluminum was studied, with results as given in Table 7. In each case, the silicon layer was badly oxidized. When aluminum was deposited before siliconizing, the resultant coating was protective but is believed to have consisted primarily of $TaAl_3$ rather than an aluminum-silicon-containing intermetallic.

It was concluded from these studies that aluminum-modified silicide coatings containing more than small amounts of aluminum are difficult to apply as protective coatings with the techniques employed.

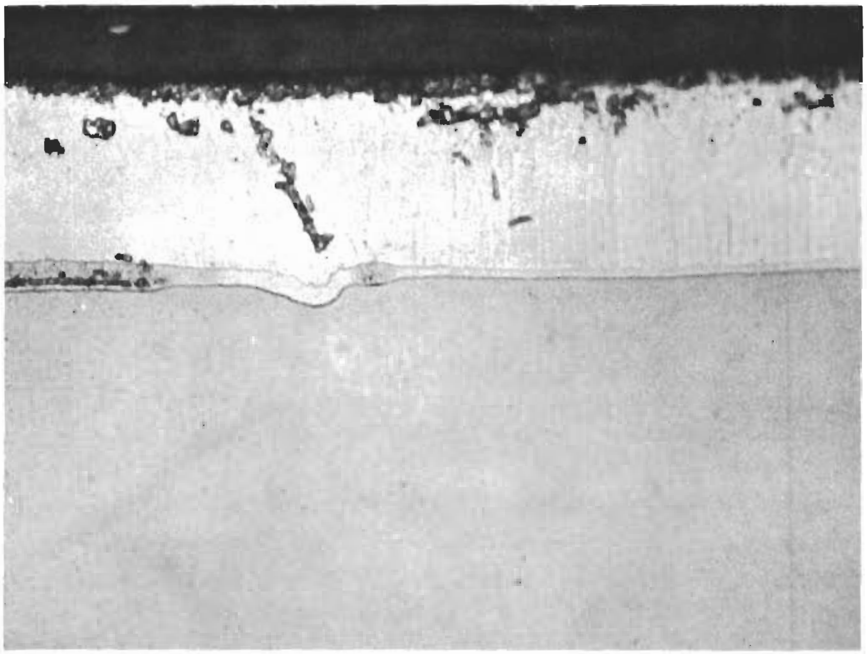
Boron-Silicide Coatings. Boron-modified silicide coatings are of interest because of the known ability of B_2O_3 to lower the vitrification temperature of SiO_2. The liquidus line in the SiO_2-B_2O_3 system has recently been determined(12) and is shown in Figure 5b.

Boron-silicide coatings were applied to tantalum both by codeposition and alternate deposition. Data on these coatings are given in Tables 6 and 7. Codeposition of boron with silicon was generally unsuccessful, as the coatings oxidized during deposition. A typical coating, Si-10B (nominal composition), is shown in Figure 7a. The protectiveness of these coatings decreased with increasing boron content.

Deposition of boron in one cycle followed by a second siliconizing cycle produced adherent, nonoxidized coatings. The boron content was high, however, ranging from 69 to 79 atom per cent boron. Application of the boron at 1800 F reduced the boron content slightly to 65 atom per cent. These coatings formed glassy scales on exposures, as seen in Figure 7d, but had relatively short lives, on the order of 1 hour at 2700 F. The short lives are attributed to the high boron content, which lowers the melting point of the resultant oxide. The Si-79B coating as deposited and after air exposure is shown in Figures 7b and 7c. It is of interest to note that the glassy scale prevented visible consumption of the coating by oxidation.

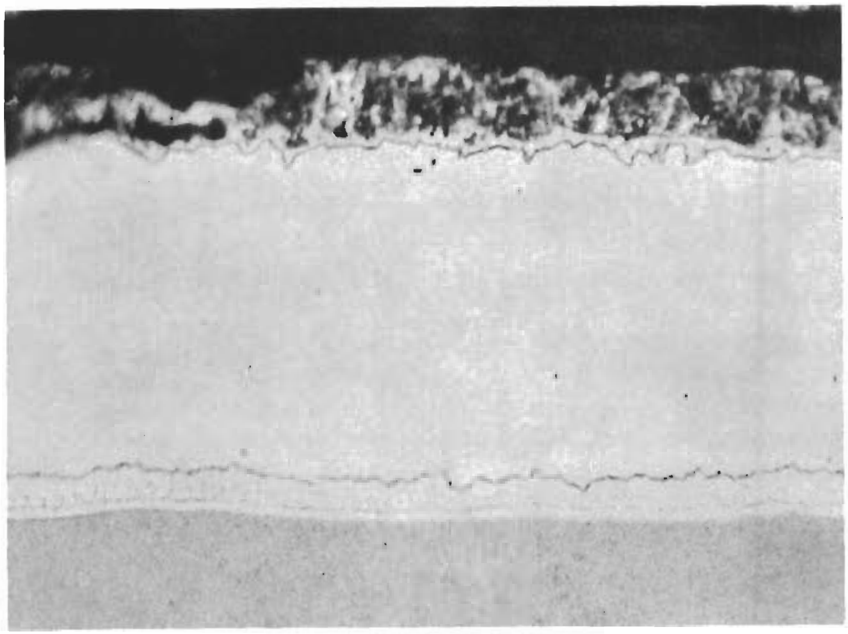


a. Coating Deposited From Si-25Al Pack With NaI + KF Carrier, 2.6 Mil



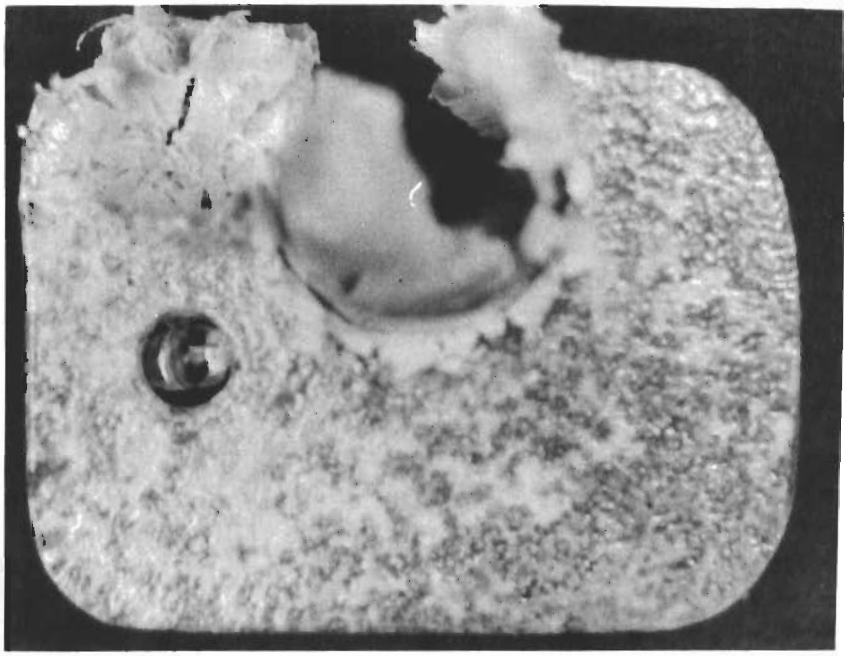
b. Coating Deposited From Si-50Al Pack With NaF Carrier, 2.0 Mil

FIGURE 6. Si-Al COATED TANTALUM AS COATED AND AFTER EXPOSURE AT 2700 F



500X P18

c. Coating Deposited From Si-80Al Pack With NaCl Carrier, 4.8 Mil



3X A173

d. Nominal Si-50Al Coated Tantalum, Failed in 100 Minutes' Static Exposure at 2700 F (2.2 Mil Coating)

FIGURE 6. (CONTINUED)

TABLE 9. SPECTROGRAPHIC ANALYSES OF COATINGS ON TANTALUM

Charged Coating Composition, atom per cent	Deposited Coating Composition, atom per cent	Carrier	Weight of Coating, mg/cm^2	Analysis of Coating, weight per cent(a)							
				Ta	Si	Al	B	Mn	Cr	Fe	Ti
100Si	100Si	NaF	18.0	50-80	30	--	--	--	--	0.2	--
		NaF	17.9	50-80	40	--	--	--	--	0.2	--
		NaF	21.2(b)	40-70	30-50	0.08	--	--	--	--	--
Si-25Al	Si-22Al	NaI	4.5	50-80	18	5	--	--	--	0.3	--
	Si-2Al	NaF	16.1	50-80	30	0.5	--	--	--	1	--
Si-50Al	Si-16Al	NaI	6.3	50-80	28	5	--	--	--	<0.2	--
	Si-2Al	NaF	13.3	50-80	30	0.5	--	--	--	1	--
	Si-5Al	NaF	18.2(c)	40-70	30-50	2	--	--	--	--	--
Si-10B	Si-22B	KF	14.3	50-80	14	2	1.5	--	--	<0.2	--
Si-33Cr	Si-29Cr	NH_4Cl	6.6	50-80	27	--	--	--	20	0.5	0.5
Si-33Ti	Si-4Ti	NH_4Cl+NaF	7.3	50-80	30	--	--	--	--	0.3	0.3
Si-11Mn	Si-3Mn	NaF	60.2(d)	63	35	--	--	2	--	--	--
Al-50Cr	Al-16Cr	NaI	14.4	40-60	--	40	--	--	15	<0.2(e)	--

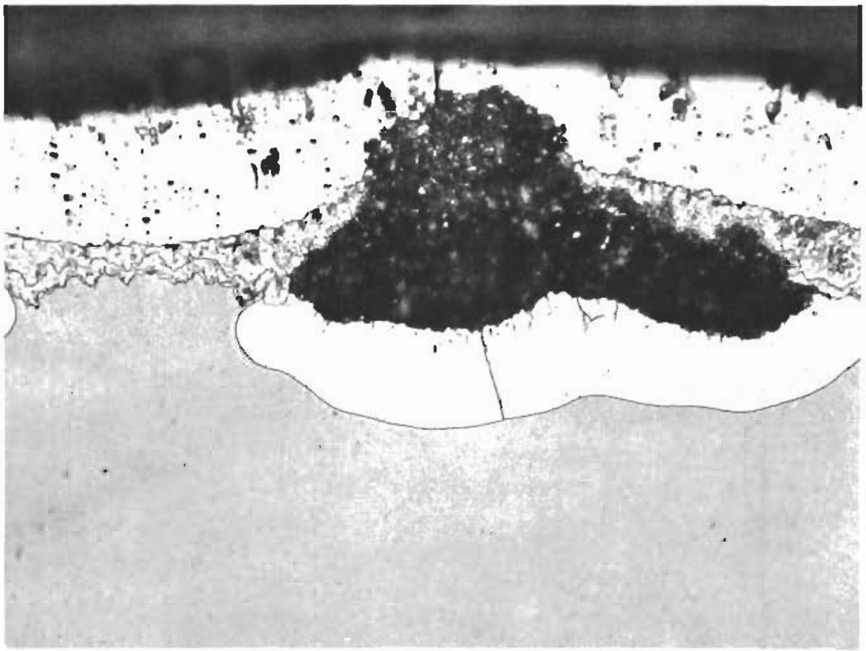
(a) Analyses are considered accurate ±25 relative per cent.

(b) Silicide coating applied in two cycles at 2200 F.

(c) Si-Al coating codeposited from Si-50Al mix in two cycles at 2200 F.

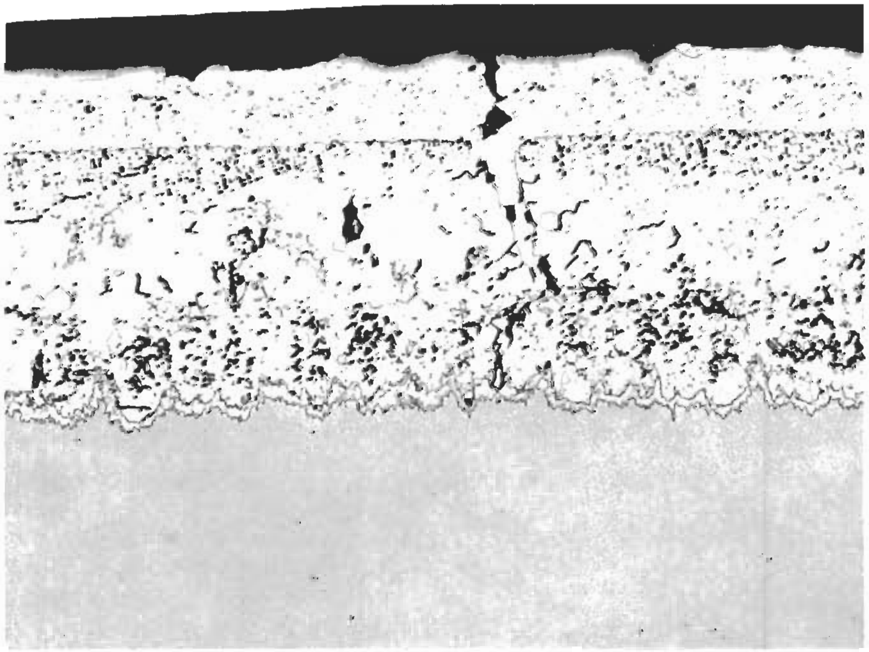
(d) Coating applied by pack cementation with manganese for 4 hours at 1800 F, followed by siliconizing for 12 hours at 2200 F.

(e) Coating was applied in a graphite can; other coatings were applied in mild-steel cans.



500X N75732

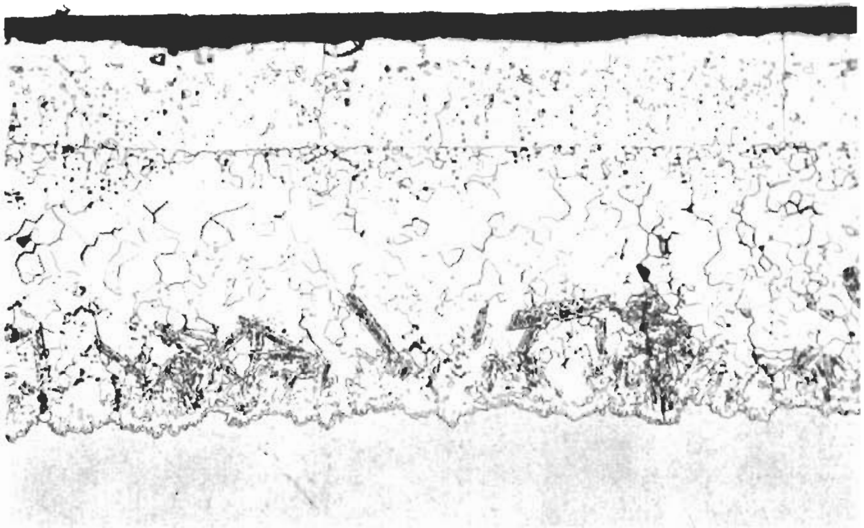
a. Nominal Si-10B Coating Applied to Tantalum by Codeposition for 16 Hours at 2200 F, 1.8 to 3.8 Mil



250X N80521

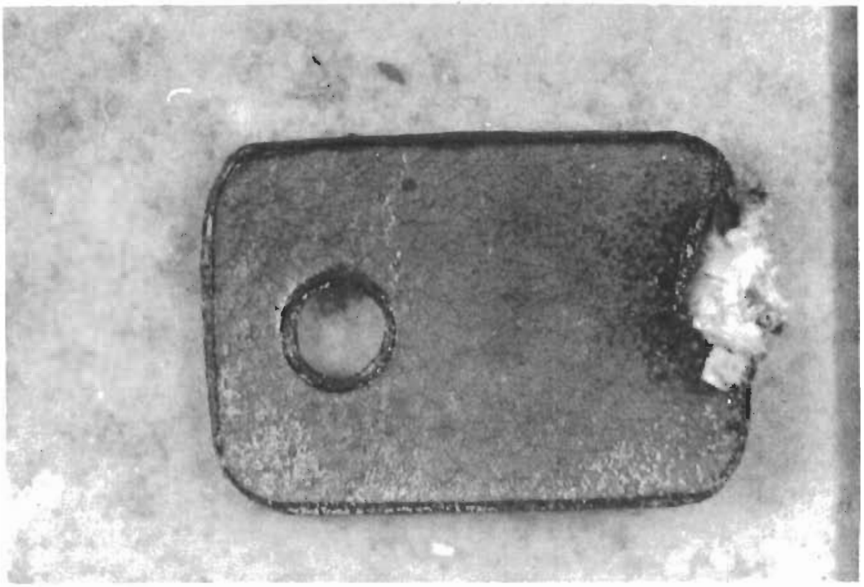
b. Calculated Si-79B Coating Applied to Tantalum by Boronizing for 4 Hours and Siliconizing for 12 Hours at 2200 F, 7.2 Mil

FIGURE 7. Si-B COATED TANTALUM AS COATED AND AFTER EXPOSURE AT 2700 F



250X N82373

c. Calculated Si-79B Coated Tantalum After 70 Minutes' Static Exposure at 2700 F



3X N379

d. Si-79B Coated Tantalum, Failed After 70 Minutes' Static Exposure at 2700 F

FIGURE 7. (CONTINUED)

Chromium-Silicide Coatings. Chromium is of interest as an addition to silicide coatings because of the refractory, protective nature of its major oxide Cr_2O_3. The ceramic phase diagram, shown in Figure 5c, however, indicates that SiO_2 and Cr_2O_3 are immiscible even in the molten state. Furthermore, studies on straight chromium coatings, discussed later, revealed that chromium hardens the tantalum substrate detrimentally.

Chromium-modified silicide coatings were deposited on tantalum by codeposition at 2000 to 2200 F, as seen in Table 6. The coatings, however, were relatively thin and, at high chromium levels, were oxidized during deposition. Analyses of the coatings, shown in Table 9, indicated that chromium transfers to the coatings in approximately the charged ratio with NH_4Cl carrier. Based on the microstructures of the coatings, the transfer is believed less with other carriers which gave thicker, more protective coatings. The protectiveness of the chromium-modified silicide coatings is seen from Table 6 to decrease with increasing chromium content of the pack.

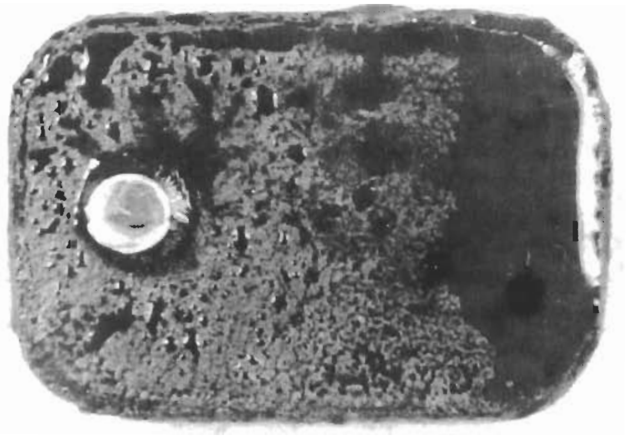
Manganese-Silicide Coatings. Manganese-modified silicide coatings were applied to tantalum by alternate deposition and are the most protective developed in the current study. The attractiveness of manganese lies in its ability to promote a glassy scale with SiO_2 at temperatures of 2500 F and above. The SiO_2-MnO phase diagram, Figure 5d, shows a eutectic at 2200 F and 63 mole per cent MnO. Compositions richer in SiO_2 than the eutectic composition are partially liquid above 2340 F.

The initial manganese-modified silicide coating was applied by pack cementation with elemental manganese for 4 hours at 2200 F, followed by siliconizing for 12 hours at 2200 F. Manganese was found to deposit rapidly at 2200 F, about twice as fast as silicon, as seen in Table 7. Furthermore, the manganese coating increased the subsequent siliconizing rate, giving a coating calculated as Si-26Mn which was 9.3 mils thick compared with about 4 mils for a similarly applied straight silicide coating. Two coated samples had excellent oxidation resistance at 2700 F, both lasting for over 24 hours. A photograph of an exposed sample, Figure 8a, shows that a glassy scale formed which was quite protective. The micrographs before and after exposure further show that the coating itself was relatively unattacked during the exposure.

Electron-probe analyses were made on these coated samples to determine the relative distribution of silicon and manganese. The various phases indicated in Figures 8b and 8c had the following compositions:

	As Deposited, atom per cent			After 24 Hours at 2700 F, atom per cent		
	Ta	Si	Mn	Ta	Si	Mn
Phase 1	51.2	43.7	5.1	48.1	46.5	5.4
Phase 2	26.0(a)	53.6(a)	20.4(a)	28.9	50.2	20.9
Phase 3	26.7	72.7	0.6	24.8	74.8	0.4
Phase 4	11.2	47.3	41.5		Not present	

(a) Analysis is tentative because of small size of precipitate phase.



a. Si-26Mn Coated Tantalum After 24 Hours' Exposure at 2700 F, No Failure

b. Si-26Mn Coated Tantalum as Coated at 2200 F

FIGURE 8. Si-Mn COATED TANTALUM AS COATED AND AFTER EXPOSURE AT 2700 F

Coating was applied in 2 cycles at 2200 F and calculated as Si-26Mn

250X N80525

c. Si-26Mn Coated Tantalum After 24 Hours' Exposure at 2700 F

FIGURE 8. (CONTINUED)

Phase 1 is a complex tantalum-rich intermetallic, while Phase 2 corresponds roughly to to $TaMnSi_2$. Phase 3 appears to be based on $TaSi_2$ which is saturated with manganese. The fourth phase, which was not present after the high-temperature exposure, is most likely tantalum-saturated MnSi.

Bend tests performed on one silicon-manganese-coated sample exposed for 24 hours at 2700 F gave 0 T ductility for the substrate, indicating that this coating, like the straight silicide coating, prevents contamination hardening of the substrate.

A similar silicon-manganese coating was applied to a group of samples by pack cementation with manganese at 1800 F, followed by siliconizing at 2200 F. Although the calculated composition was Si-11Mn, analysis of the coating, given in Table 9, showed Si-3Mn, indicating that manganese is lost during the siliconizing cycle. The Si-3Mn coating provided better protection than the straight silicide and aluminum-modified silicide coatings during cyclic exposures at 2500 and 2700 F, as seen in Table 8, but was also subject to "pest" oxidation at 1800 F. The exposed samples are shown in Figure 9. Although the glassy oxide was formed as during static oxidation of the Si-26Mn coating, the Si-3Mn coating exhibited no self-healing qualities during defect testing.

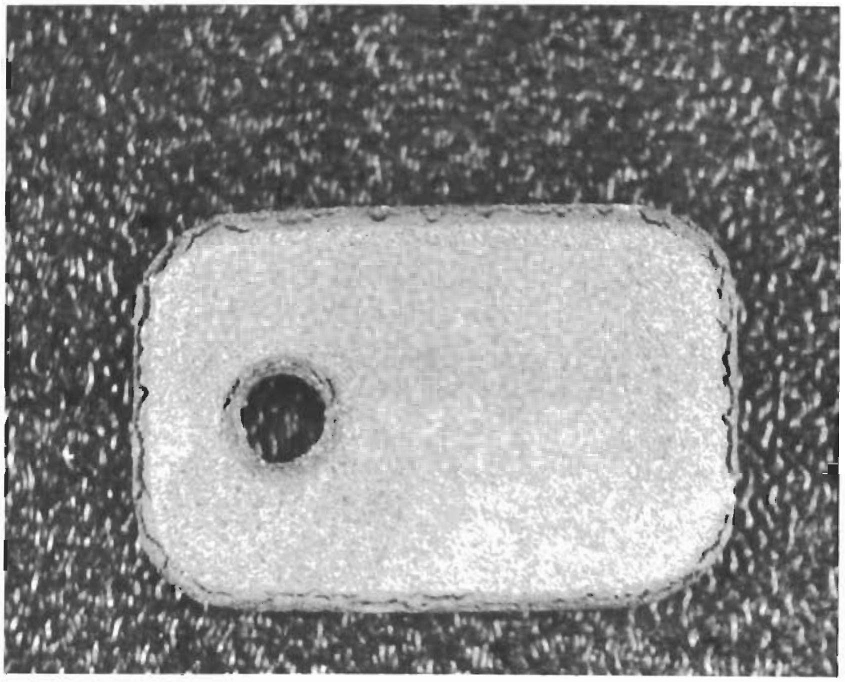
Molybdenum, Titanium, and Vanadium-Silicide Coatings. Modified-silicide coatings were also applied from packs containing nominally up to 33 atom per cent molybdenum, 75 atom per cent titanium, and 10 atom per cent vanadium. Data on these coatings, which were less protective than the straight silicide coatings, are included in Table 6. On the basis of the appearances of the coatings and the relative stabilities of the halides of molybdenum, titanium, and vanadium, it is estimated that the coating contained little of these three metals. This is substantiated by an analysis, given in Table 14, which indicates that the nominal Si-33Ti coating actually consisted of Si-4Ti.

Ternary Silicide Coatings. Similarly, codeposition of ternary coatings of silicon-aluminum-titanium was attempted, with results as shown in Table 6. None of these coatings were oxidation resistant at 2700 F.

Silicide coatings containing 2 to 6 atom per cent of titanium, aluminum-chromium, and aluminum-titanium were applied by two-cycle deposition as indicated in Table 7. These coatings provided protection for 3 to 3-1/2 hours at 2700 F, but showed no significant difference in behavior as compared with straight silicide coatings.

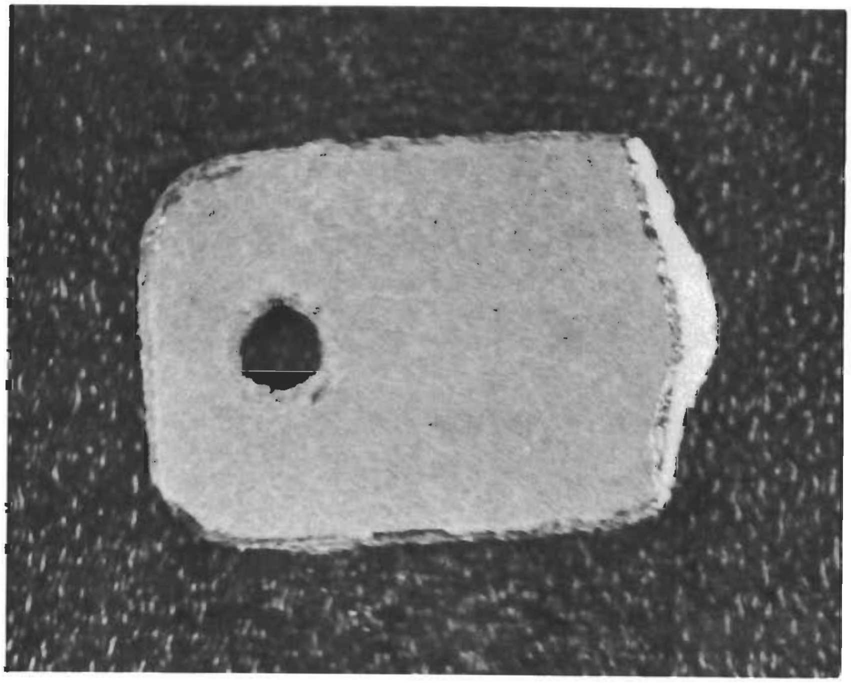
Silicide-Base Coatings on Tantalum Alloys

Silicide-base coatings were evaluated on the three tantalum alloys of major interest, Ta-10W, Ta-10Hf-5W, and Ta-30Cb-(5 to 10)V, and on two binary alloys, Ta-5V and -7.5V. In general, silicide coatings were much more protective to these alloys, especially to the Ta-Cb-V alloy, than to tantalum. The coated alloys also exhibited good self-healing qualities. Details on the application and evaluation of the silicide-coated alloys are presented in the following sections.



3X N400

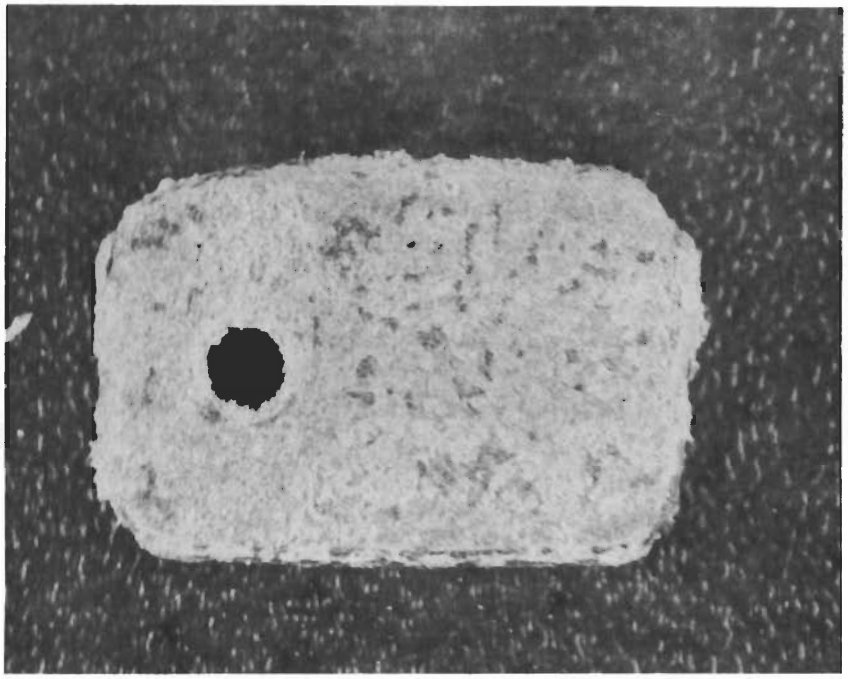
a. Exposed at 1200 F, Average Cyclic Life 100 Hours



3X N401

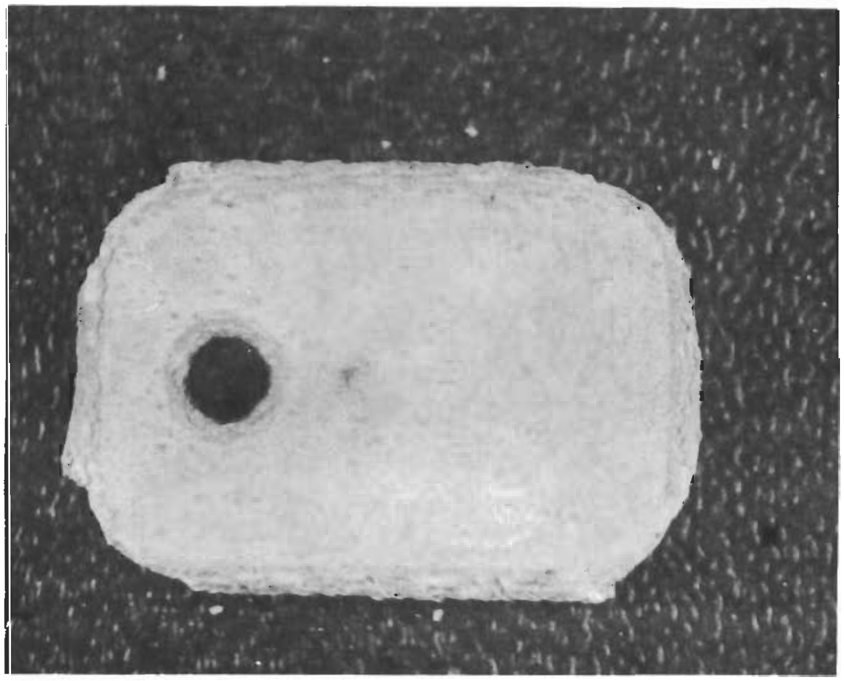
b. Exposed at 1500 F, Average Cyclic Life 25 Hours

FIGURE 9. Si-3Mn COATED TANTALUM AFTER CYCLIC EXPOSURES AT 1200 TO 2700 F



3X N402

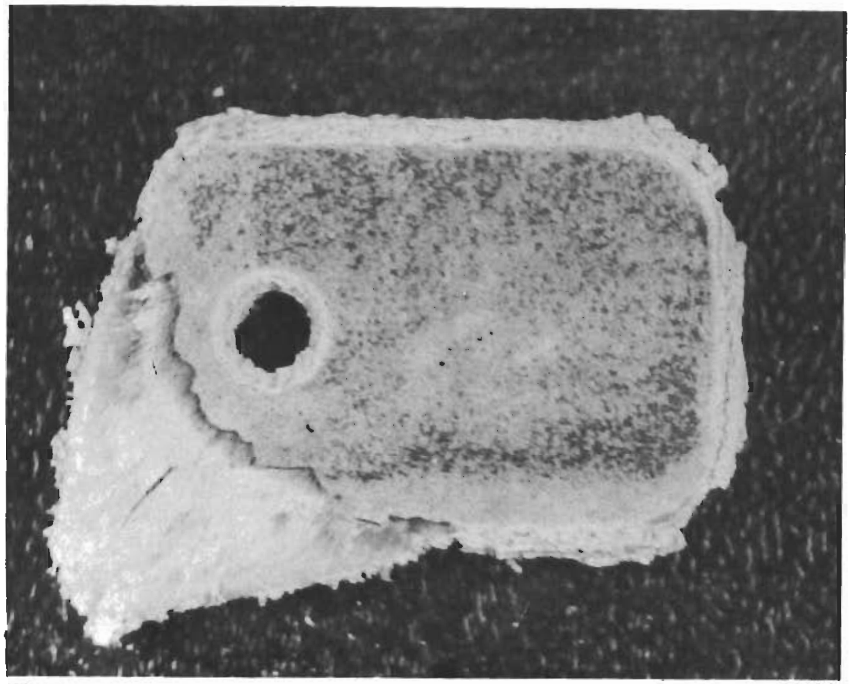
c. Exposed at 1800 F, Average Cyclic Life 3 Hours



3X N403

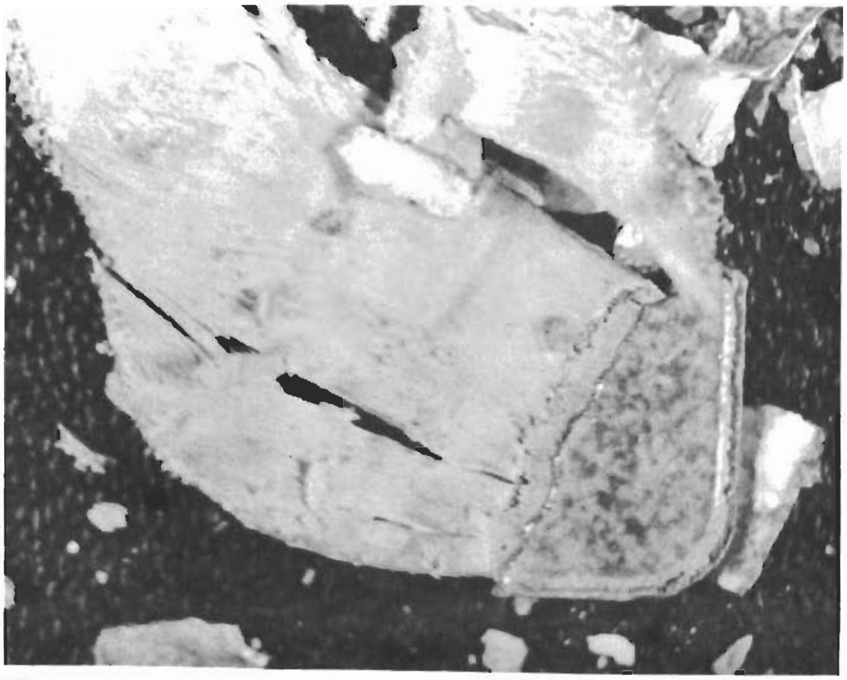
d. Exposed at 2200 F, Average Cyclic Life 100 Hours

FIGURE 9. (CONTINUED)



3X N404

e. Exposed at 2500 F, Average Cyclic Life 11 Hours



3X N405

f. Exposed at 2700 F, Average Cyclic Life 4 Hours

FIGURE 9. (CONTINUED)

Coatings on Ta-10W

Straight silicide and four modified silicide coatings were evaluated on Ta-10W, as shown in Tables 10 and 11. Although single-cycle deposition was studied only briefly, the two-cycle deposition method appears superior, as for coating unalloyed tantalum.

In comparison with unalloyed tantalum, the straight silicide, aluminum-modified silicide, and manganese-modified silicide coatings are moderately more protective to Ta-10W. This is seen by comparison of the cyclic oxidation data at 2500 and 2700 F, given in Table 8. The most protective of these three coatings is the manganese-modified silicide, which exhibited an average cyclic life of 10 hours at 2700 F, in comparison to an average of 4 hours for a similar coating on unalloyed tantalum. At temperatures from 1200 to 2200 F, no significant differences in behavior were noted in comparison with coated unalloyed tantalum. These data, given in Table 8, show that, as with tantalum, the accelerated "pest" oxidation is particularly detrimental at 1800 F.

Although the improved protectiveness of Si-8Mn coating is attributed partially to its higher manganese content, the generally better behavior of coated Ta-10W is probably associated with the relatively high volatility of WO_3.(14) It is believed that the volatilizing WO_3 is capable of fluxing the silica-rich oxide scale into a protective vitreous glass at slightly lower temperatures than are observed with unalloyed tantalum. Analyses of these silicide coatings, given in Table 12, showed that 3 to 7 weight per cent tungsten was present in the coatings.

Especially noteworthy are the self-healing qualities exhibited by the straight silicide, aluminum-modified silicide, and manganese-modified silicide coatings at 2500 F and by the latter coating at 2700 F. Whereas none of these coatings were self-healing on tantalum, all three were protective for 4.5 hours at 2500 F when defected by a 0.04-inch hole through the coating on one side. The improved self-healing qualities are taken as further evidence of the beneficial effects of tungsten in the substrate. Typical defected samples after oxidation at 2500 and 2700 F are shown in Figure 10.

Neither the Si-85B coating nor the Si-8Ti-8Al coating appeared particularly attractive for protecting Ta-10W, as seen in Table 11. An attempt to siliconize over aluminum on Ta-10W was unsuccessful as observed previously with unalloyed tantalum (see Table 7).

Coatings on Ta-10Hf-5W

The three coatings of major interest, straight silicide and the modifications with aluminum and manganese, were evaluated on the Ta-10Hf-5W alloy. Data on the application and protectiveness of these coatings are given in Tables 8, 10, and 11. Analyses of the coatings are given in Table 12.

Growth of the coatings during pack cementation was slightly slower than similar coatings on tantalum and Ta-10W. This was interpreted as a result of the hafnium content of the substrate. The microstructure of the straight silicide coating also showed a small zone of fine precipitate near the alloy/silicide interface, as seen in Figure 11. This is in contrast to the "clean" coatings obtained on tantalum, Figure 2, and on Ta-10W.

TABLE 10. SINGLE-CYCLE DEPOSITION OF SILICIDE COATINGS ON TANTALUM ALLOYS

Charged Coating Composition, at. %	Carrier[a]	Amount of Coating: Average Weight Gain, mg/cm^2	Amount of Coating: Average Thickness Increase, mil/side	Amount of Coating: Coating Thickness, mil/side[b]	Average Static Coating Life at Indicated Temperature, min[c]: 2500 F	Average Static Coating Life at Indicated Temperature, min[c]: 2700 F
			Ta-10W			
100Si	NaCl	13.6	1.3	2.7	--	75(2)
Si-50Al	NaCl	3.7	0.8	2.3	--	20(2)
			Ta-10Hf-5W			
100Si	NaF	20.4	2.2	3.3	--	40(2)
Si-50Al	NaF	14.2	1.6	--	--	400(2)
			Ta-5V			
100Si	NaCl	18.1	2.2	3	--	160(2)
			Ta-7.5V			
100Si	NaCl	13.1	1.5	2.5	--	165(2)
			Ta-30Cb-5V			
100Si	NaF	18.7	2.1	4	>360(1)	>360(1)
Si-50Al	NaF	21.5	2.0	3	>480(1)	420(1)
			Ta-30Cb-10V			
100Si	NaF	18.5	2.2	3.4	--	>420(1)
Si-50Al	NaF	11.7	1.8	1.6-2.6	--	>480(1)

(a) All coatings were deposited for 16 hours at 2200 F.

(b) Coating thicknesses were measured metallographically.

(c) Numbers in parentheses indicate number of samples in each average life.

TABLE 11. TWO-CYCLE DEPOSITION OF

Calculated or Charged Coating Composition, at.%	Analyzed Coating Composition, at.%	Al_2O_3 Filler Particle Size	4-Hour Cycle Charged Coating Composition, at.%	Carrier	Temp, F	Average Coating Weight Gain, mg/cm^2
						Ta-
100Si	--	Unsized	100Si	NaCl	2200	2.8
	--	5 mil	100Si	NaF	2200	18.3
	100Si	5 mil	100Si	NaF	2200	22.4
Si-50Al	--	Unsized	Si-50Al	NaCl	2200	2.3
	--	5 mil	Si-50Al	NaF	2200	10.7
	Si-5Al	5 mil	Si-50Al	NaF	2200	11.2
Si-Al	--	Unsized	100Al	KI	2200	14.3
Si-85B	--	5 mil	100B	NaF	2200	6.5
Si-17Mn	Si-8Mn	5 mil	100Mn	NaF	1800	13.1
Si-8Ti-8Al	--	Unsized	Ti-50Al	NaCl	2200	1.6
						Ta-10
100Si	100Si	5 mil	100Si	NaF	2200	13.0
Si-50Al	Si-6Al	5 mil	Si-50Al	NaF	2200	9.8
Si-15Mn	Si-5Mn	5 mil	100Mn	NaF	1800	13.7
						Ta-30
100Si	100Si	5 mil	100Si	NaF	2200	15.5
Si-50Al	Si-9Al	5 mil	Si-50Al	NaF	2200	12.0
Si-14Mn	Si-8Mn	5 mil	100Mn	NaF	1800	13.6

(a) Coating thickness estimated from coating weight gain.
(b) Numbers in parentheses indicate number of samples in average.
(c) Cyclic oxidation life; see Table 13 for results at lower temperatures.
(d) Coating was partly oxidized during deposition.

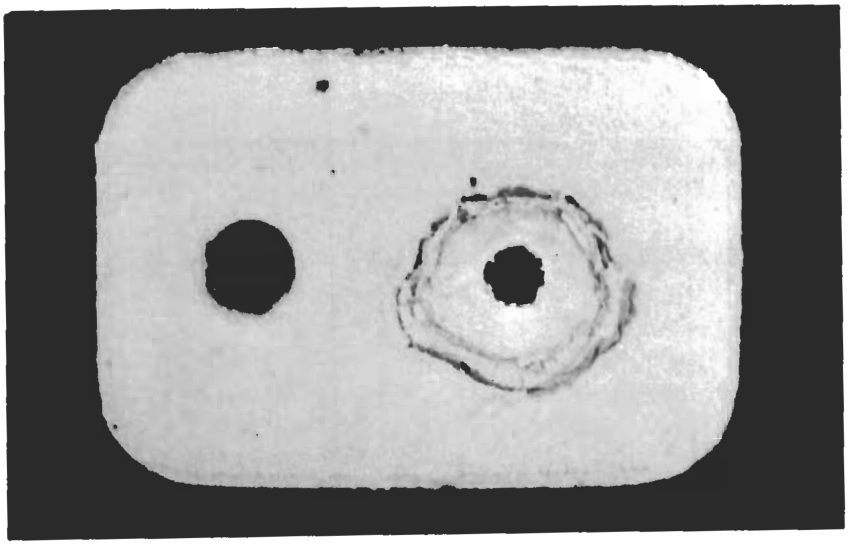
SILICIDE COATINGS ON TANTALUM ALLOYS

12-Hour Cycle				Total Coating Weight Gain, mg/cm^2	Estimated Coating Thickness, mils/side(a)	Average Static Coating Life at Indicated Temperature, min(b)	
Charged Coating Composition, at.%	Carrier	Temp, F	Average Coating Weight Gain, mg/cm^2			2500 F	2700 F
10W							
100Si	NaCl	2200	9.1	11.9	--	270(1)	95(2)
100Si	NaF	2200	11.7	30.0	--	--	310(2)
100Si	NaF	2200	13.6	36.0	5.8	600(2)(c)	270(2)(c)
Si-50Al	NaCl	2200	3.6	5.9	--(d)	--	40(1)
Si-50Al	NaF	2200	11.8	22.5	--	--	480(2)
Si-50Al	NaF	2200	10.8	22.0	3.5	220(3)(c)	250(3)
100Si	NaCl	2200	-6.6	7.7	--(d)	--	>345(1)
100Si	NaF	2200	3.0	9.5	--	60(1)	90(2)
100Si	NaF	2200	31.8	44.9	7.3	>1200(2)(c)	250(2)(c)
100Si	NaCl	2200	6.0	7.6	--(d)	--	35(1)
Hf-5W							
100Si	NaF	2200	6.6	19.6	3.2	480(2)(c)	120(2)(c)
Si-50Al	NaF	2200	7.7	17.5	2.8	570(2)(c)	240(2)(c)
100Si	NaF	2200	38.8	52.4	8.4	870(2)(c)	450(2)(c)
Cb-5V							
100Si	NaF	2200	10.7	26.2	4.2	>1200(4)(c)	540(4)(c)
Si-50Al	NaF	2200	8.7	20.7	3.3	>1200(4)(c)	200(4)(c)
100Si	NaF	2200	43.5	57.1	8.9	>1200(3)(c)	290(3)(c)

TABLE 12. SPECTROGRAPHIC ANALYSES OF COATINGS ON TANTALUM ALLOYS

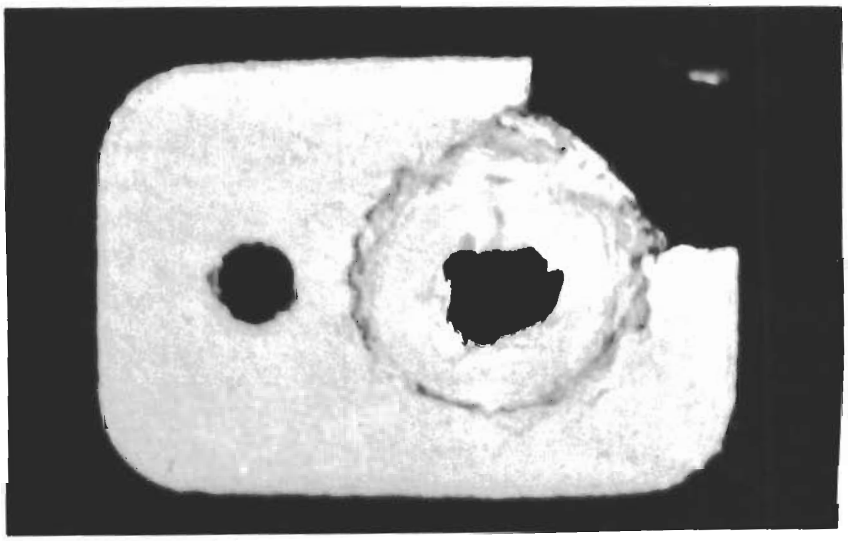
Charged or Calculated Coating Composition, at. %	Deposited Coating Composition, at. %	Carrier	Weight of Coating, mg/cm^2	Analysis of Coating, wt. %(a)							
				Ta	W	Hf	Cb	V	Si	Al	Mn
				Ta-10W							
100Si	100Si	NaF	36.0	30-60	3	--	--	--	30-50	0.3	--
Si-50Al	Si-5Al	NaF	22.0	30-60	5	--	--	--	30-50	2	--
Si-17Mn	Si-8Mn	NaF	44.9	51	7	--	--	--	36	--	6
				Ta-10Hf-5W							
100Si	100Si	NaF	19.6	30-60	3	10	--	--	20-40	0.3	--
Si-50Al	Si-6Al	NaF	17.5	30-60	3	9	--	--	20-40	2	--
Si-15Mn	Si-5Mn	NaF	52.5	47	3	9	--	--	37	--	4
				Ta-30Cb-5V							
100Si	100Si	NaF	26.2	20-50	-	--	30	5	20-40	0.5	--
Si-50Al	Si-1Al	NaF	21.5	20-60	-	--	10-30	2	15-40	0.2	--
Si-50Al	Si-9Al	NaF	20.7	20-50	-	--	35	5	20-40	3	--
Si-14Mn	Si-8Mn	NaF	57.1	24	-	--	33	4	33	--	6
				Ta-30Cb-10V							
100Si	100Si	NaF	18.5	20-40	-	--	20-40	15	42	--	--
Si-50Al	Si-2Al	NaF	11.7	20-60	-	--	10-30	5	15-40	0.5	--

(a) Analyses are considered accurate to ±25 relative per cent.



3X N427

a. Si Coated Ta-10W, Average Cyclic Life 4.5 Hours at 2500 F

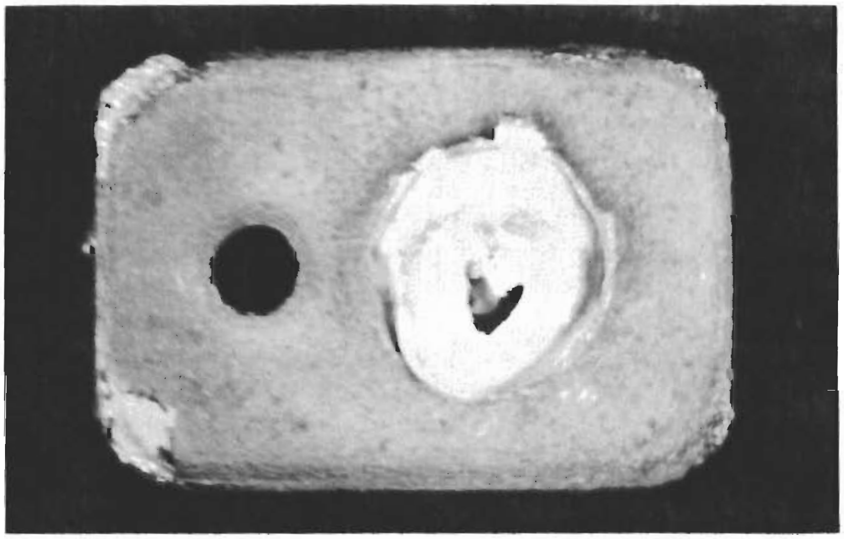


3X N428

b. Si-5Al Coated Ta-10W, Average Cyclic Life 4.5 Hours at 2500 F

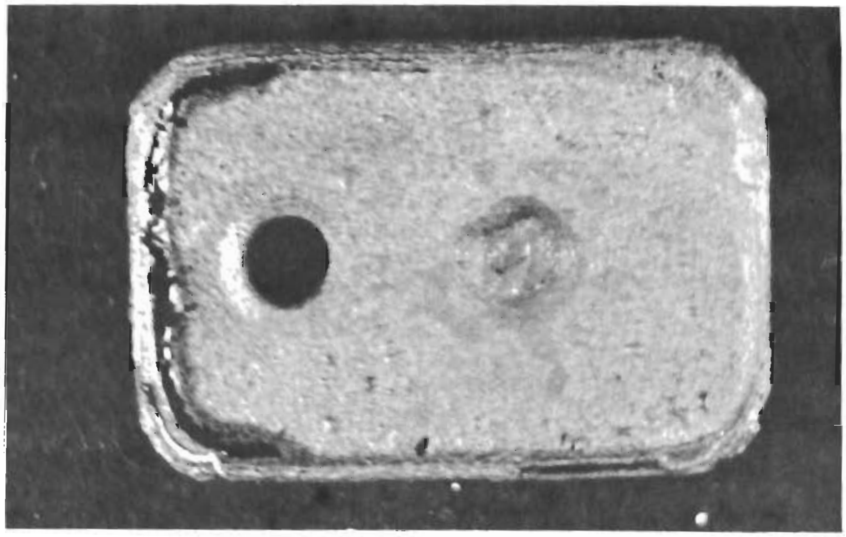
FIGURE 10. COATED Ta-10W AFTER DEFECT OXIDATION EXPOSURES AT 2500 AND 2700 F

Coatings were defected by a 0.04-inch-diameter hole halfway through center of sample before exposure.



3X N429

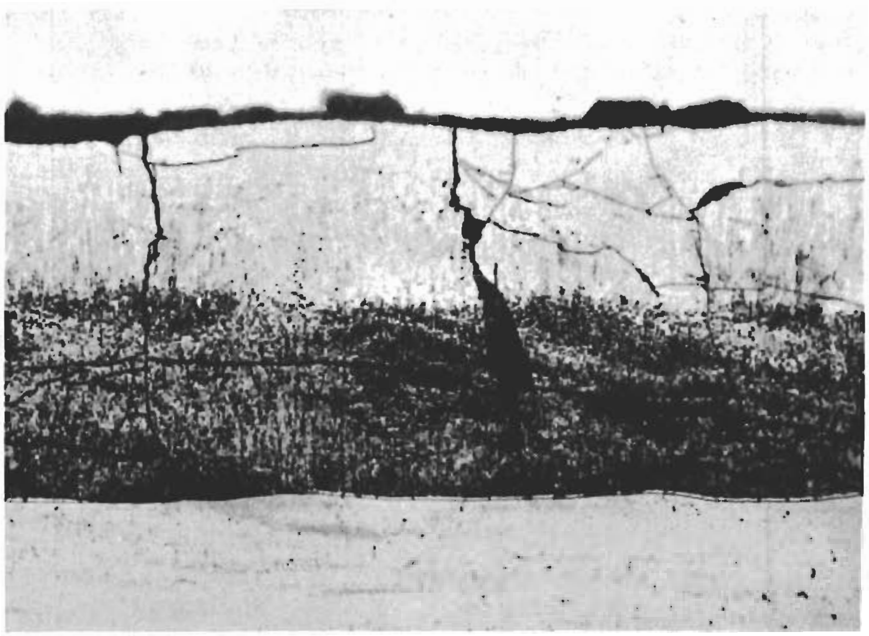
c. Si-8Mn Coated Ta-10W, Cyclic Life 4.5 Hours at 2500 F



3X N430

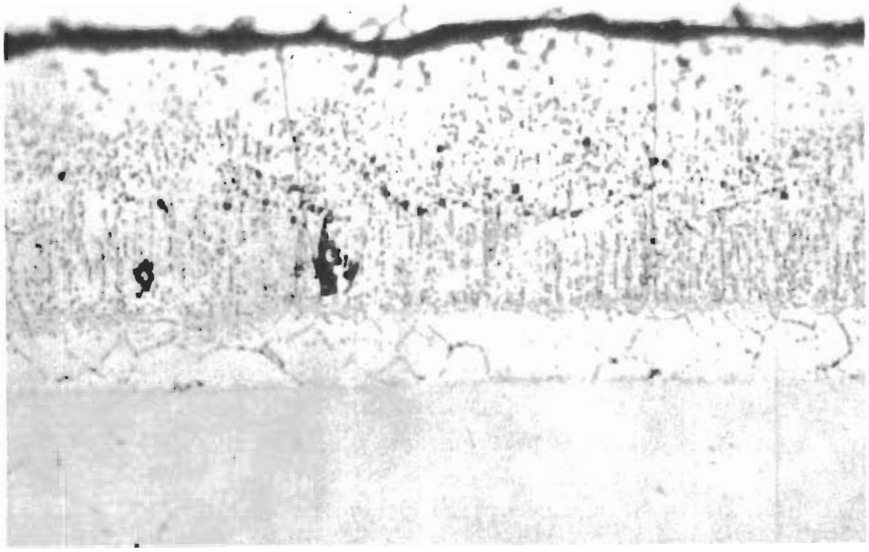
d. Si-8Mn Coated Ta-10W, Average Cyclic Life 10 Hours at 2700 F

FIGURE 10. (CONTINUED)



600X P-1

a. As Coated With Si, 3.3 Mils



600 X P-32

b. Si-Al Coated, Exposed 8 Hours at 2700 F, 3 Mils

FIGURE 11. COATED Ta-10Hf-5W AS COATED AND AFTER STATIC EXPOSURE AT 2700 F

Moderate differences in oxidation behavior were also noted for Ta-10Hf-5W as compared with the two previous substrates. Oxidation weight-gain curves of Si-Al coated Ta-10Hf-5W and Si-Al coated tantalum are compared in Figure 12. The weight gains for the coated alloy are appreciably lower than those for coated tantalum, indicating the presence of a more protective scale. A micrograph of Si-Al coated and exposed Ta-10Hf-5W, Figure 11b, also shows the absence of appreciable oxidation attack on the coating.

The cyclic and defect oxidation behavior of the straight silicide, aluminum-modified, and manganese-modified silicide coatings on Ta-10Hf-5W are compared in Table 8. The aluminum-modified silicide coating, analyzed as Si-6Al, affords excellent protection through the region of low-temperature accelerated "pest" oxidation. This is apparently a result of the combined hafnium and aluminum in the coating. At 2500 and 2700 F, the Si-6Al coating was slightly better than the straight silicide coating but slightly inferior to the Si-5Mn coating. The Si-6Al coated alloy after exposure at 1200 to 2700 F is shown in Figure 13.

All three coatings showed good self-healing properties at 2500 F but none were good at 2700 F, as shown by the data of Table 8. The defected samples after exposure are shown in Figure 14.

The differences in behavior between coated Ta-10Hf-5W and coated tantalum are attributed to the effects of hafnium and tungsten oxides on the properties of the silica-rich scale formed on exposure. Although the SiO_2-HfO_2 ceramic phase diagram has not been determined, small additions of TiO_2 and ZrO_2 lower the melting point of SiO_2 from 1715 C (3120 F) to 1550 C (2820 F) and 1675 C (3050 F), respectively(11, 13). It appears reasonable that HfO_2 additions would also lower the fusion point, especially in the presence of Al_2O_3. These effects, coupled with the melting point and volatility effects of WO_3, are believed to promote the formation of a vitreous silicate scale which is more protective than the less-vitreous scale formed on coated unalloyed tantalum.

Coatings on Ta-V and Ta-Cb-V Alloys

Straight silicide and the aluminum-modified and manganese-modified silicide coatings were evaluated on two binary alloys, Ta-5V and Ta-7.5V, and on two ternary alloys, Ta-30Cb-5V and Ta-30Cb-10V. The Ta-30Cb-(5-10)V alloys have been shown to possess an excellent combination of low-temperature ductility and fabricability and high-temperature strength(1), and, along with the Ta-10Hf-5W alloy, are under further evaluation under Contract AF 33(616)-7452.

Straight silicide coatings were applied to the two binary alloys, Ta-5V and Ta-7.5V, by single-cycle deposition using NaCl as carrier, as indicated in Table 10. Although the lives exhibited by these coated samples were not exceptional, the appearance of the samples after oxidation differed from that of silicide-coated tantalum. The Ta-7.5V alloy, shown in Figure 15, had droplets of a black phase, tentatively identified as a V_2O_5-SiO_2 mixture which was liquid at 2700 F.

The coated Ta-Cb-V alloys had exceptional oxidation resistance at all temperatures in the range 1200 to 2700 F. In initial static oxidation studies, no failures were

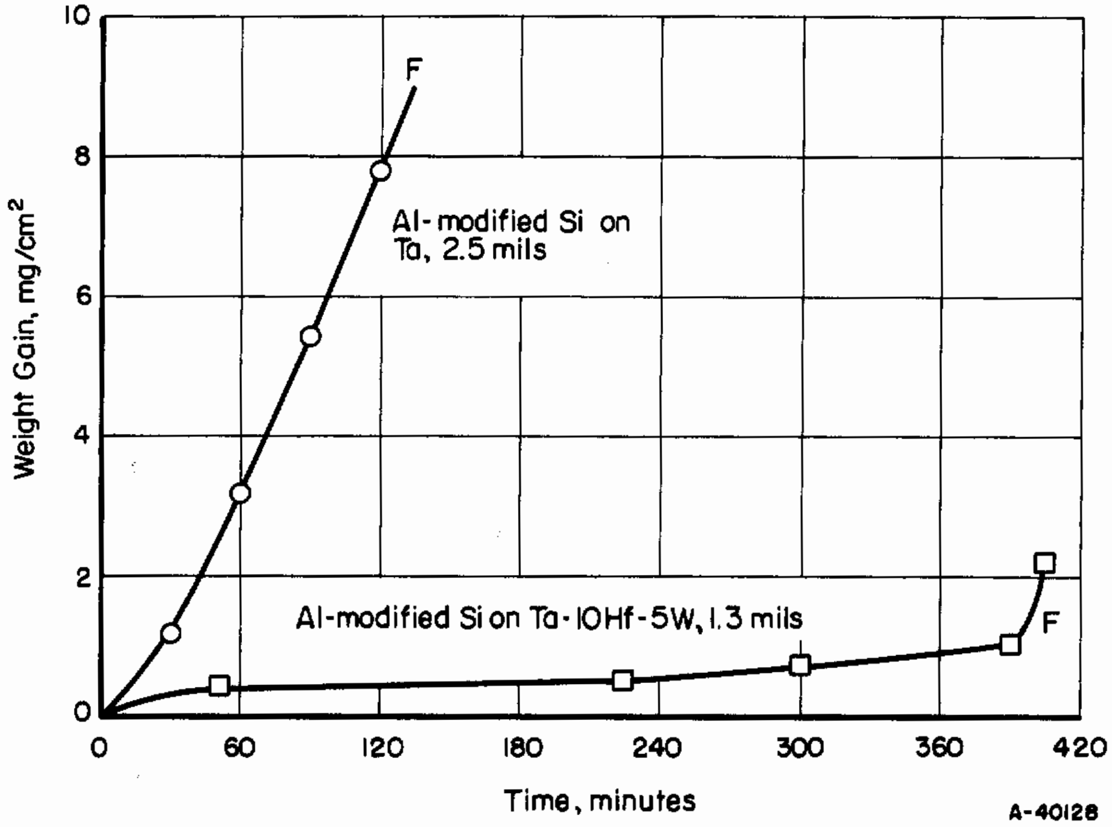
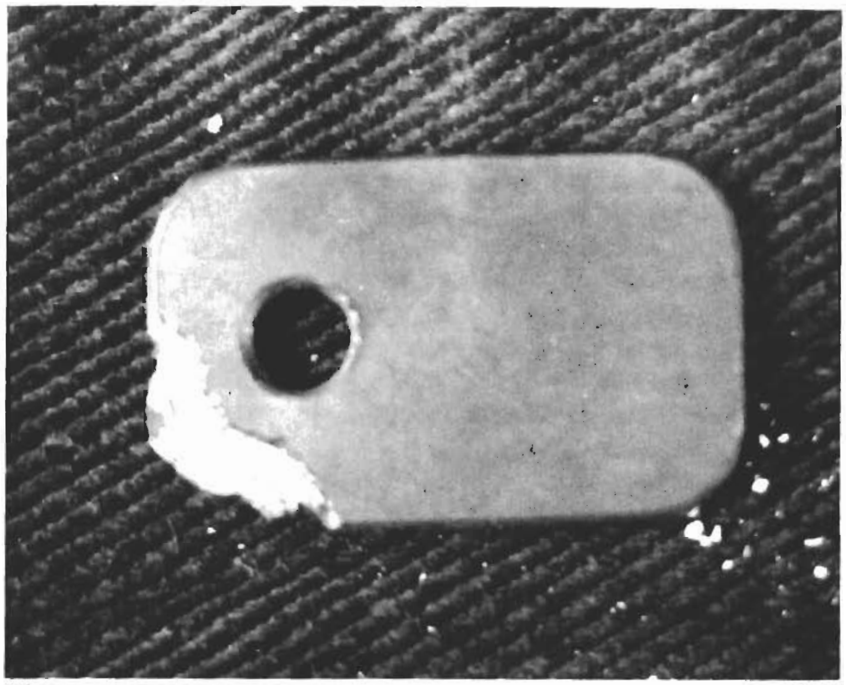
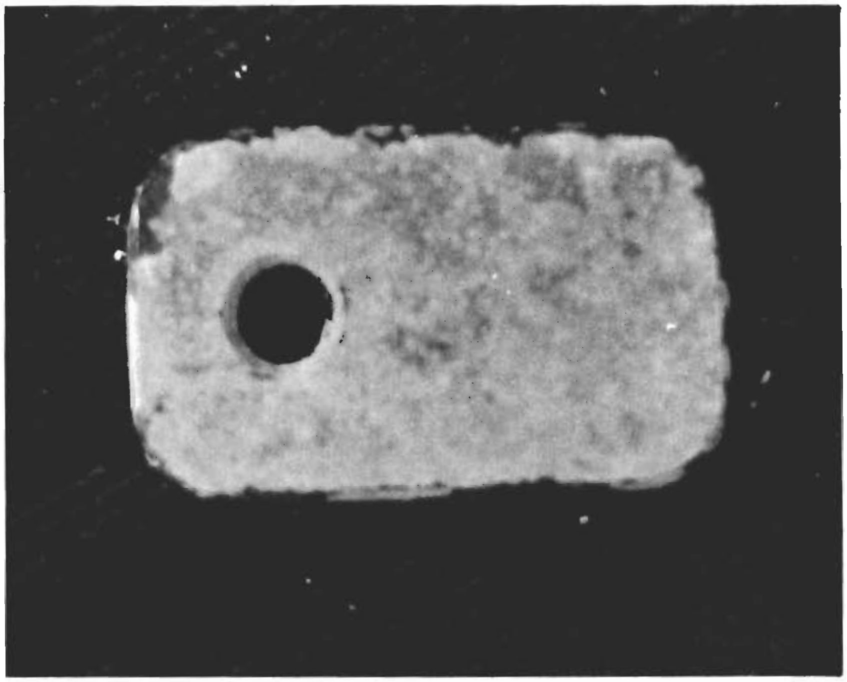


FIGURE 12. WEIGHT-GAIN OXIDATION CURVES FOR Si-Al COATED Ta-10Hf-5W AND Si-Al COATED TANTALUM AT 2700 F

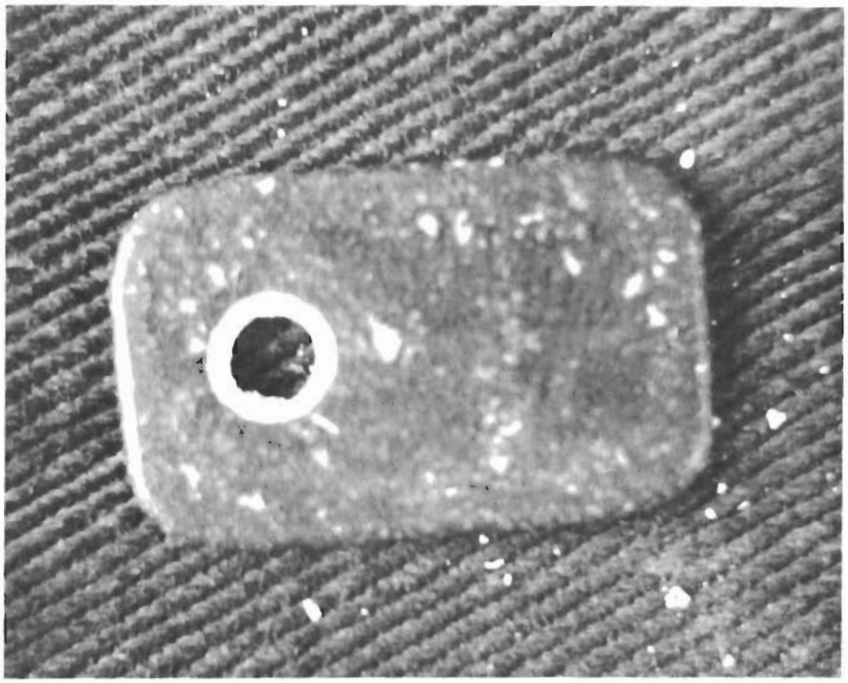


a. Exposed at 1200 F, Cyclic Life 100 Hours



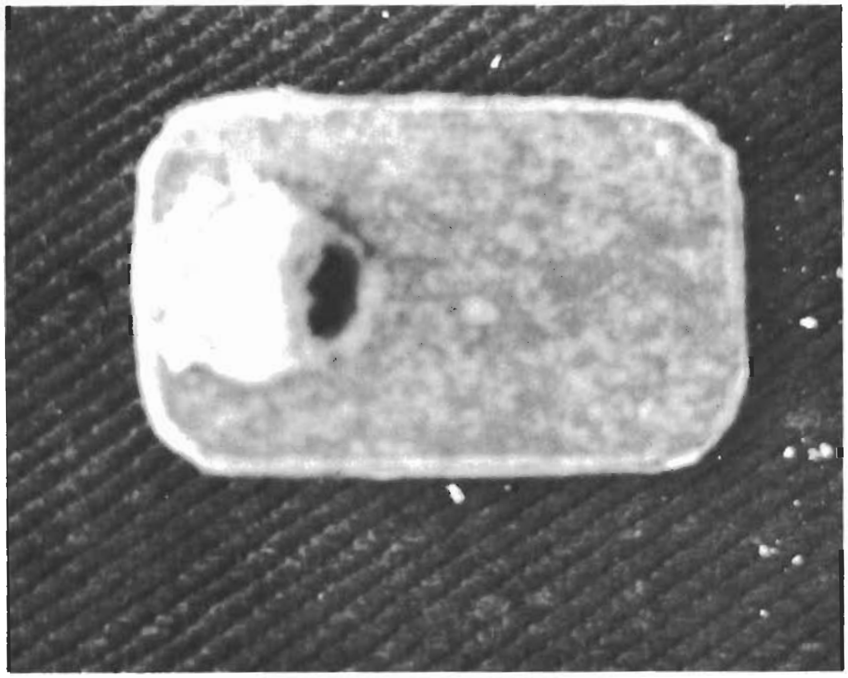
b. Exposed at 1500 F, Cyclic Life Greater Than 100 Hours

FIGURE 13. Si-6Al COATED Ta-10Hf-5W AFTER CYCLIC EXPOSURES AT 1200 TO 2700 F



3X N422

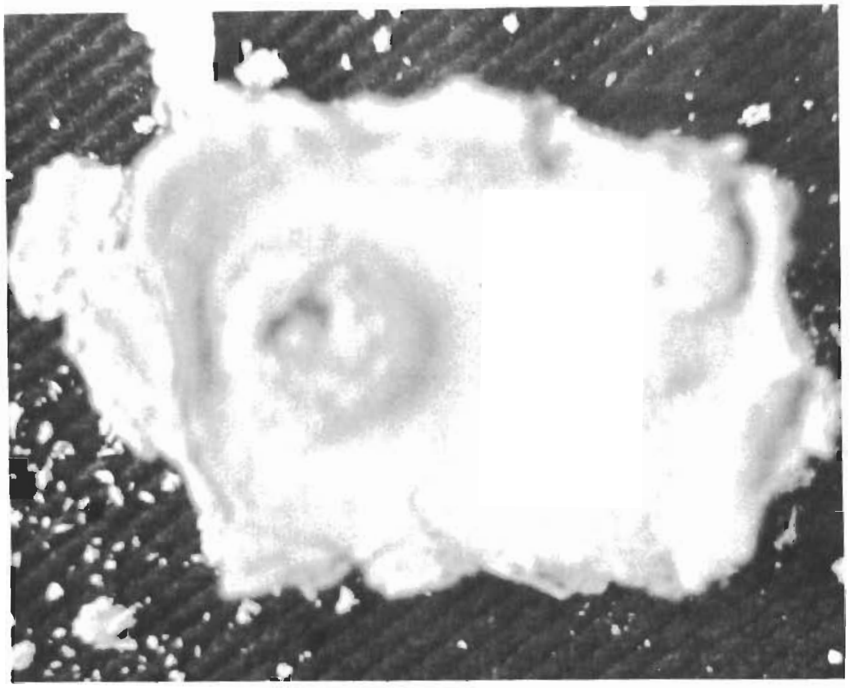
c. Exposed at 1800 F, Cyclic Life Greater Than 100 Hours



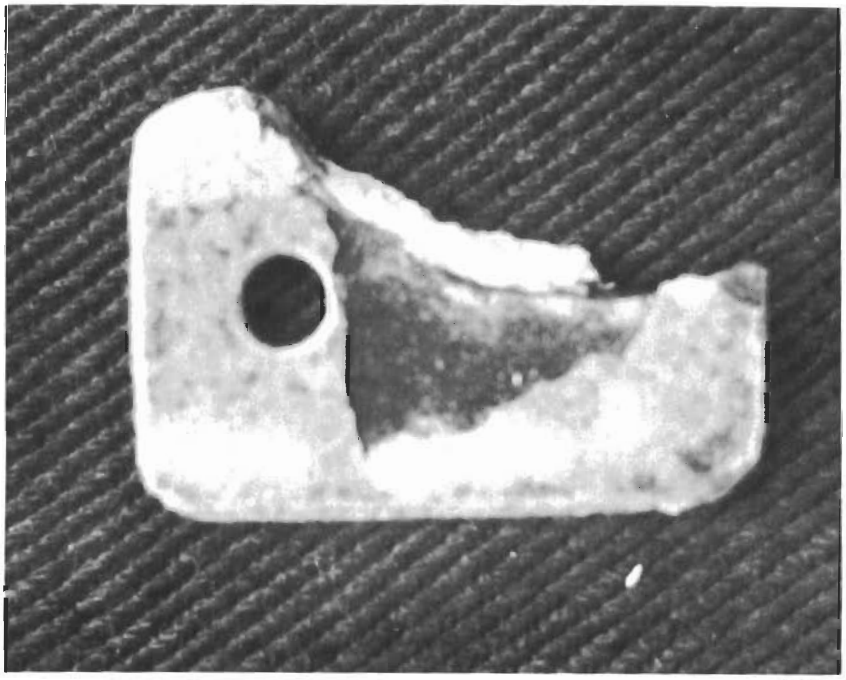
3X N423

d. Exposed at 2200 F, Cyclic Life 55 Hours

FIGURE 13. (CONTINUED)

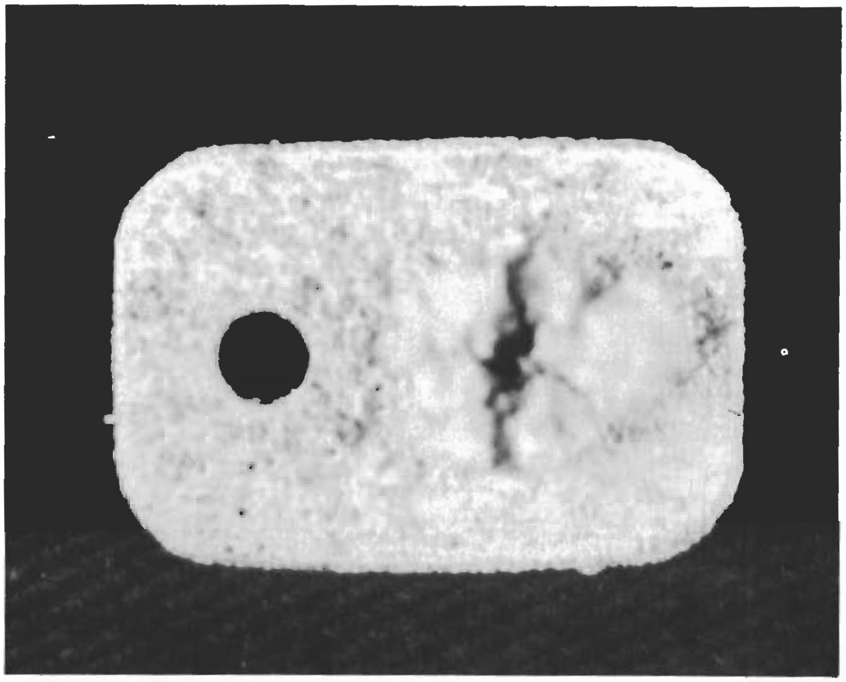


e. Exposed at 2500 F, Average Cyclic Life 9.5 Hours



f. Exposed at 2700 F, Average Cyclic Life 4 Hours

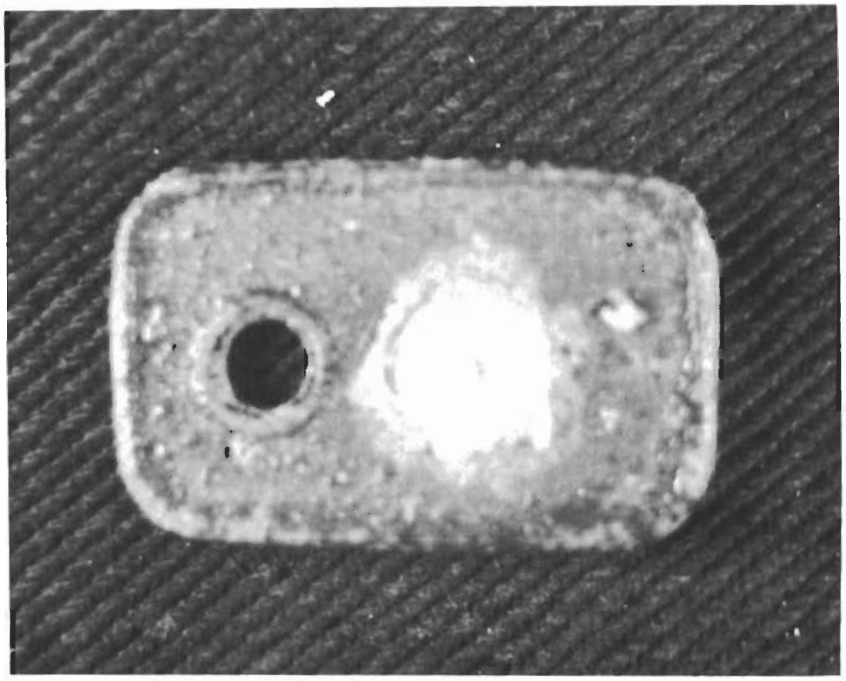
FIGURE 13. (CONTINUED)



a. Si Coated, Cyclic Life 9.5 Hours at 2500 F

b. Si-6Al Coated, Cyclic Life 4.5 Hours at 2500 F

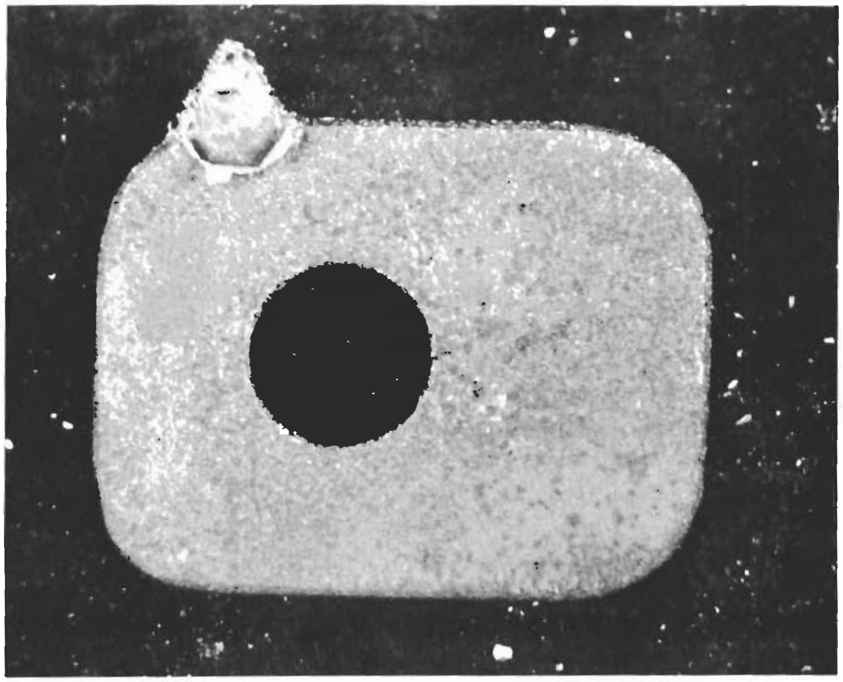
FIGURE 14. COATED Ta-10Hf-5W AFTER DEFECT OXIDATION EXPOSURES AT 2500 F



3X N439

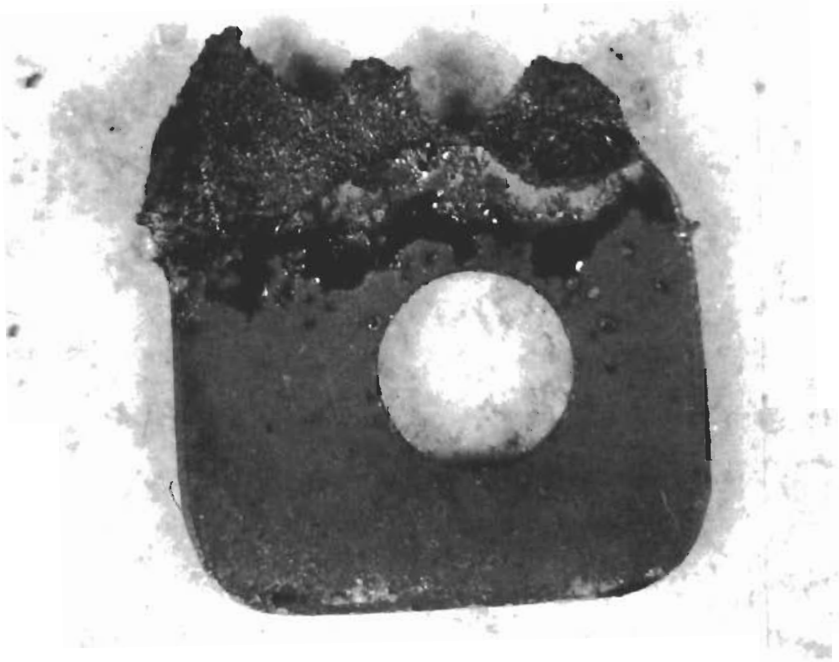
c. Si-5Mn Coated, Cyclic Life 4.5 Hours at 2500 F

FIGURE 14. (CONTINUED)



3X N340

a. Ta-5V, Failed After 135 Minutes' Static Exposure



3X N341

b. Ta-7.5V, Failed After 150 Minutes' Static Exposure

FIGURE 15. SILICIDE-COATED Ta-5V AND Ta-7.5V AFTER STATIC EXPOSURES AT 2700 F

observed after 8 hours at 2500 F and only one failure (after 7 hours) in four samples at 2700 F (see Table 10). The low weight gains on oxidation, as seen in Figure 16, indicated the formation of a very protective scale. Similarly, comparison of the microstructure before and after exposure, shown in Figure 16, revealed no detectable loss of coating by oxidation. Analyses of the coating, given in Table 12, showed that significant amounts of columbium and vanadium had diffused into the coating. These elements apparently saturate the disilicide at elevated temperatures and, on cooling, produce the precipitate visible in Figure 17.

The coated Ta-30Cb-5V alloys had excellent resistance to "pest" oxidation. The lives of samples coated with silicide, Si-9Al, and Si-8Mn were all in excess of 100 hours at 1800 F, the temperature at which accelerated "pest" oxidation was most severe on the other silicide-coated samples of unalloyed tantalum, Ta-10W, and Ta-10Hf-5W. Samples coated with silicide and Si-8Mn after exposures at 1200 to 2700 F are shown in Figures 18 and 19, respectively.

The cyclic resistance of this alloy was superior to that of coated tantalum, Ta-10W, or Ta-10Hf-5W. At 2500 F, the life was in excess of 20 hours for all three coatings, while at 2700 F, average lives of 9 and 4.8 hours were observed for the silicide and Si-8Mn coatings, respectively.

Superior defect oxidation resistance was also observed for the Si-8Mn coated alloy at both 2500 and 2700 F. The oxide formed on all three coatings, especially the Si-8Mn, appeared to have been viscous during exposure and effectively retarded oxidation at the defected point. The defect samples after exposure are shown in Figure 20.

The effectiveness of these silicide-base coatings is believed related, as for Ta-10W and Ta-10Hf-5W, to the properties of the oxides of the substrate alloy additions, columbium and vanadium. Both Cb_2O_5 and V_2O_5 have moderately low melting points, 1460 C (2660 F) and 660 C (1220 F), respectively. In addition, V_2O_5 has a relatively high volatility. Thus, these oxides may be expected to flux the SiO_2 formed on exposure into a vitreous glass at elevated temperatures. The photomicrographs of Si-coated Ta-30Cb-5V, shown in Figure 18, indicate that glass-formation probably occurs at 2200 F and higher. The mechanism of low-temperature improvement may be similar, although it is not apparent from visual examination of the exposed samples.

Bend and tensile tests indicated that the Ta-30Cb-5V alloy suffered little or no loss in ductility as a result of coating application or exposure. Tensile data, presented in Table 13, show that the room-temperature strength and ductility are unaffected by coating or exposure at 2700 F, although a decrease in ductility was noted at 2200 F after a 4-hour exposure at 2700 F. Room-temperature bend tests showed 0 T bend ductility for samples exposed up to 8 hours at 2700 F.

Aluminum-Base Coatings

Aluminide coatings were applied to tantalum by pack cementation and by hot dipping and diffusing. Data on aluminide coatings applied by pack cementation are given in Table 14.

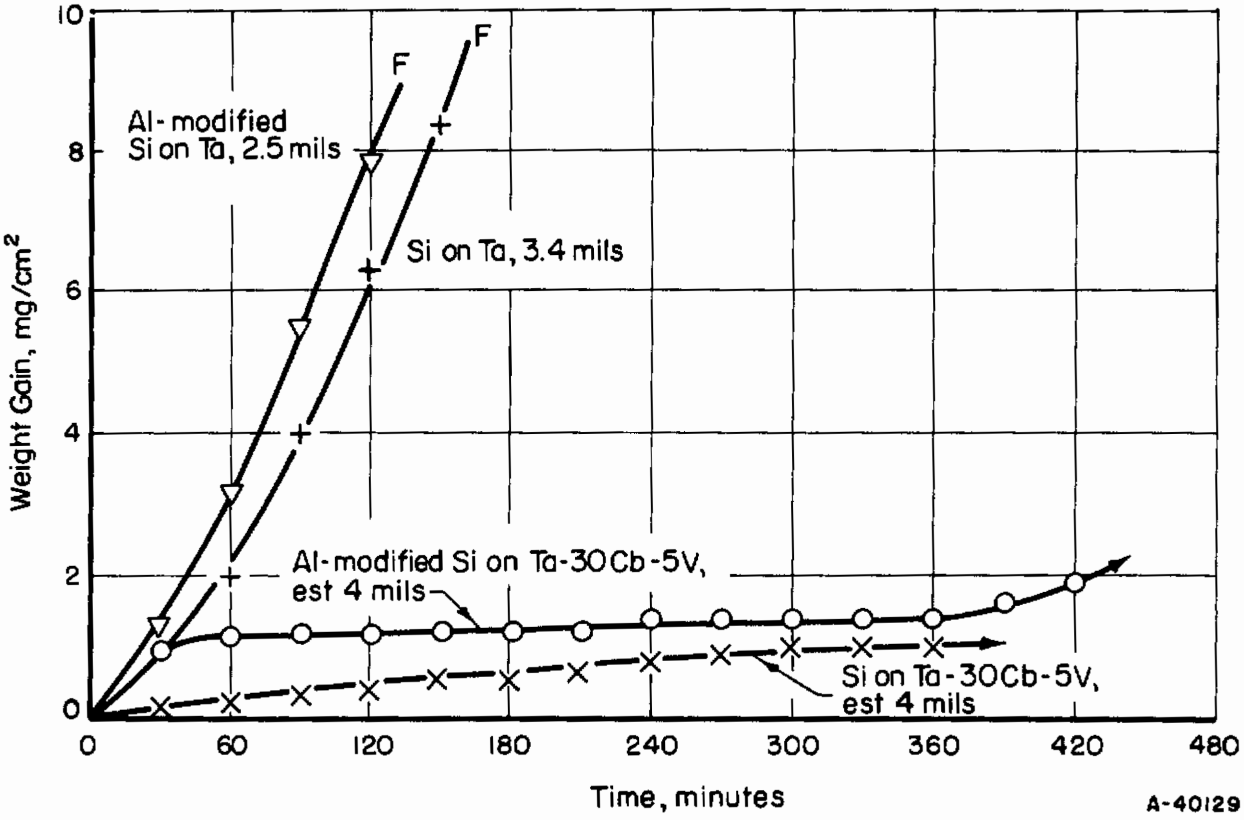
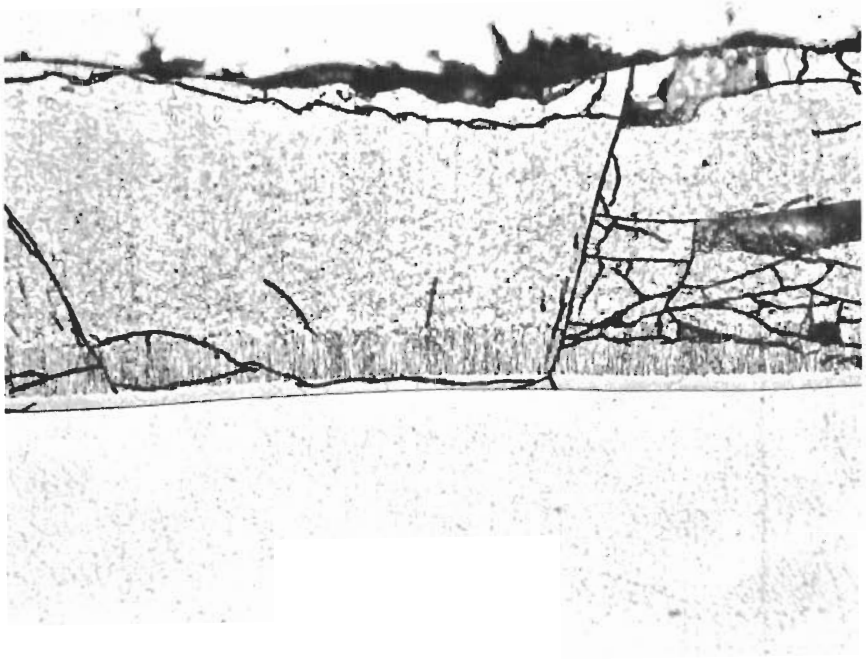
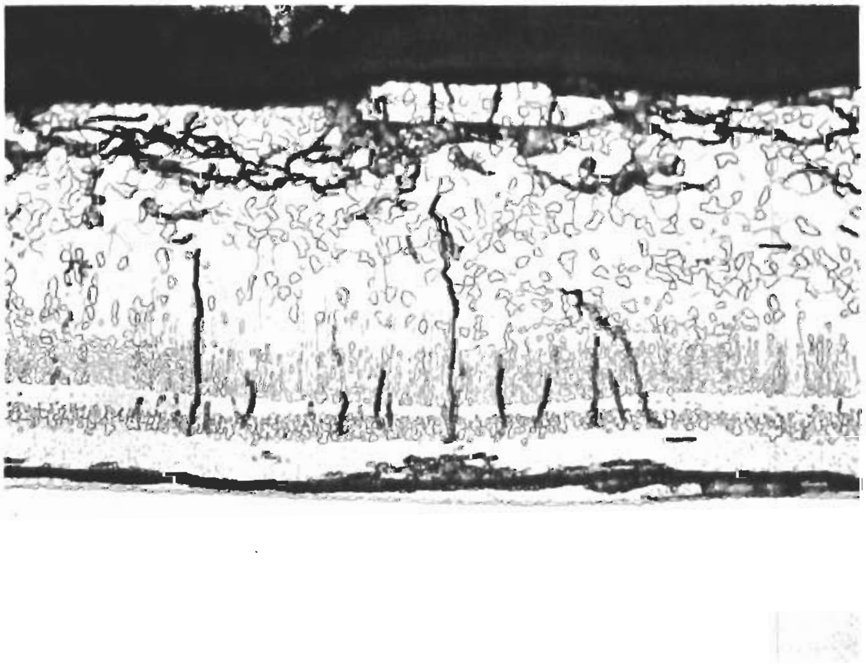


FIGURE 16. OXIDATION WEIGHT-GAIN CURVES FOR SILICIDE AND Si-Al COATED TANTALUM AND Ta-30Cb-5V AT 2700 F

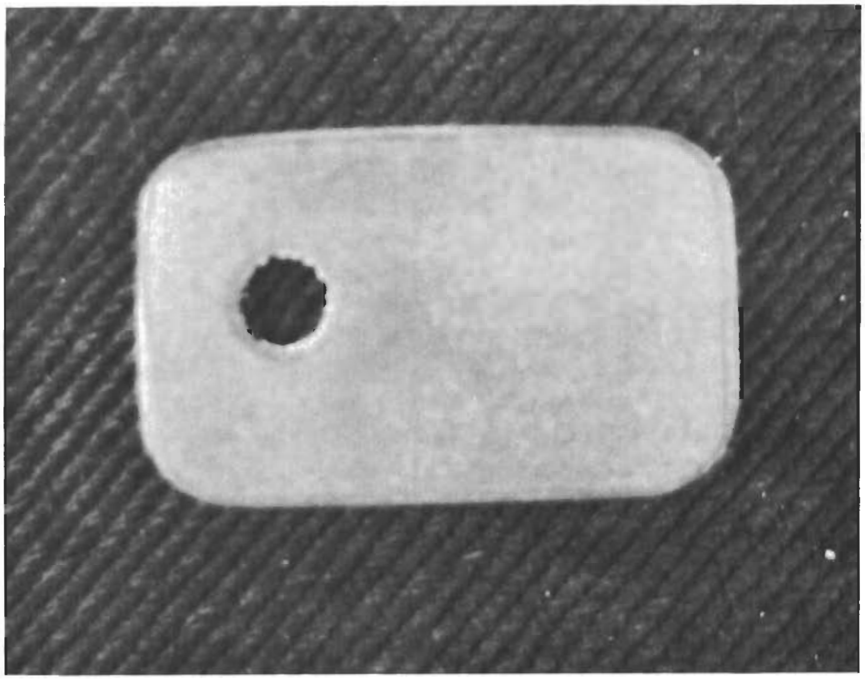


a. As Coated, 3.2 Mils



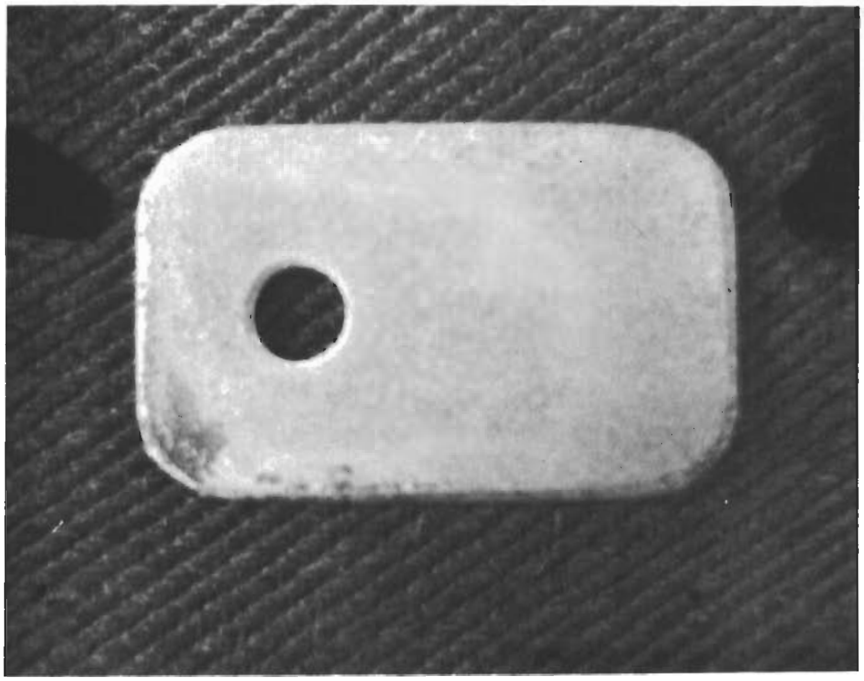
b. Exposed for 7 Hours at 2700 F, 4.1 Mils

FIGURE 17. SILICIDE-COATED Ta-30Cb-10V AS COATED AND AFTER EXPOSURE AT 2700 F



3X N406

a. Exposed at 1200 F, Cyclic Life Greater Than 100 Hours



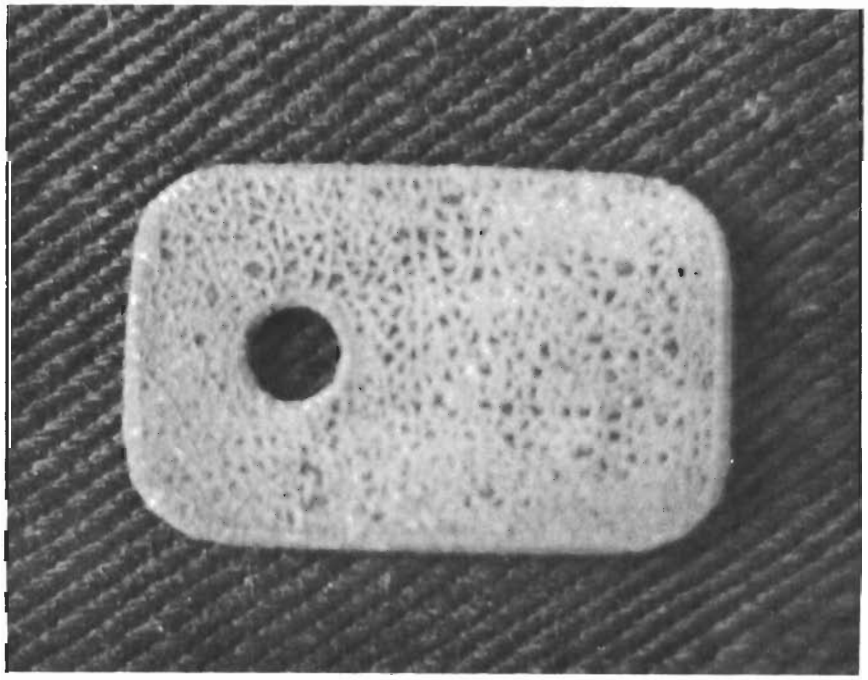
3X N407

b. Exposed at 1500 F, Cyclic Life Greater Than 100 Hours

FIGURE 18. SILICIDE-COATED Ta-30Cb-5V AFTER CYCLIC EXPOSURES AT 1200 TO 2700 F

3X N408

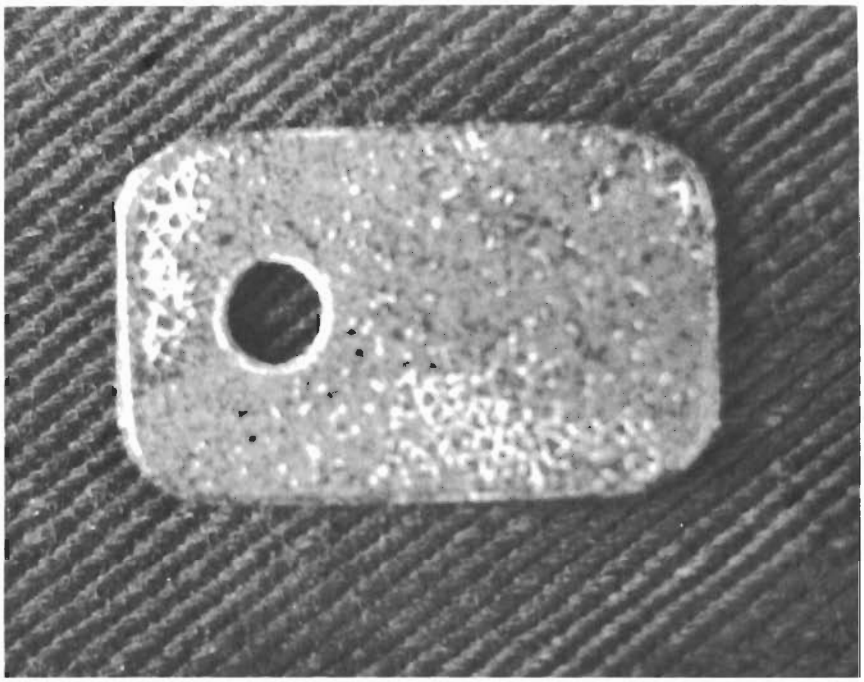
c. Exposed at 1800 F, Cyclic Life Greater Than 100 Hours



3X N409

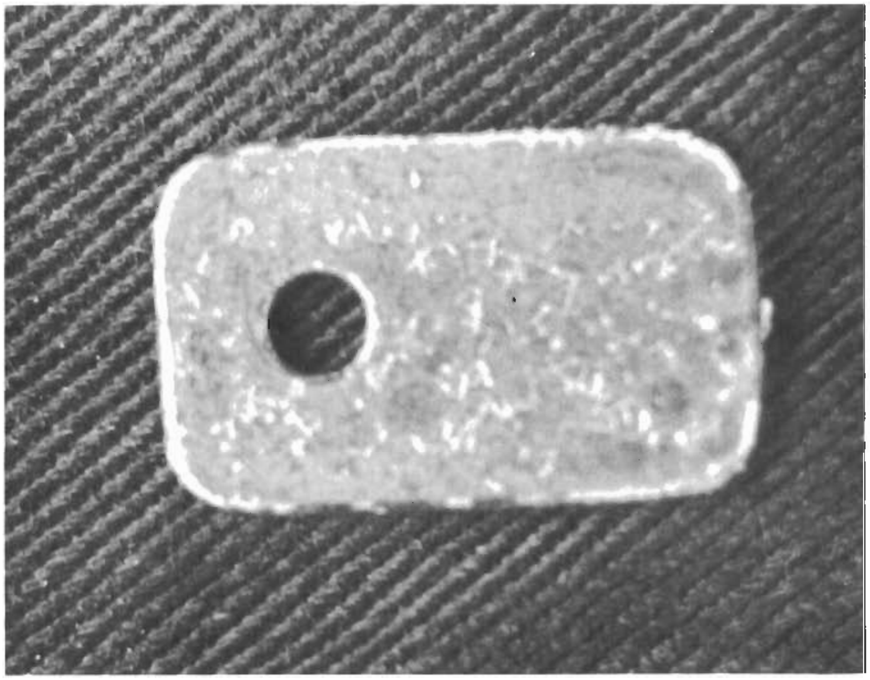
d. Exposed at 2200 F, Cyclic Life Greater Than 100 Hours

FIGURE 18. (CONTINUED)



3X N410

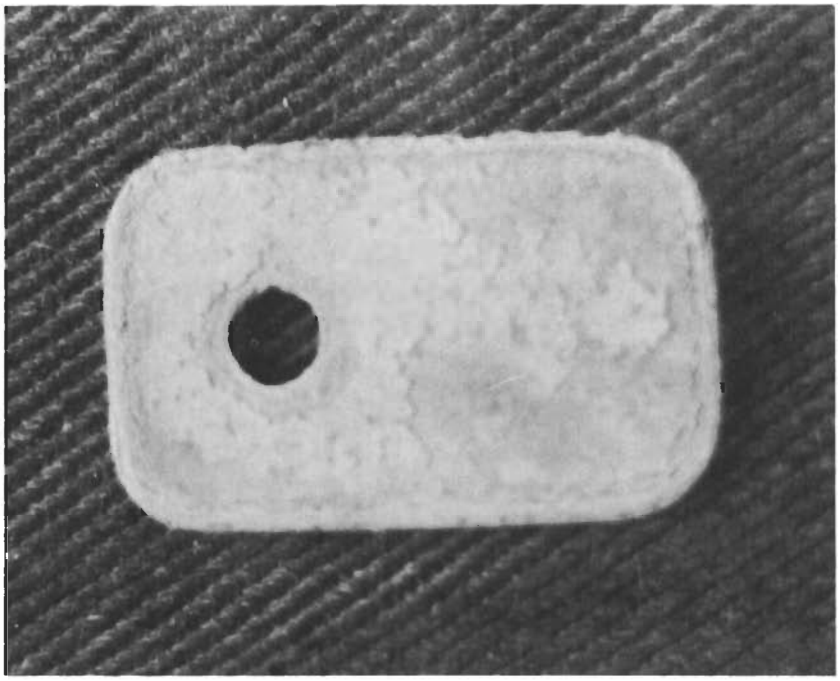
e. Exposed at 2500 F, Average Cyclic Life Greater Than 20 Hours



33X N411

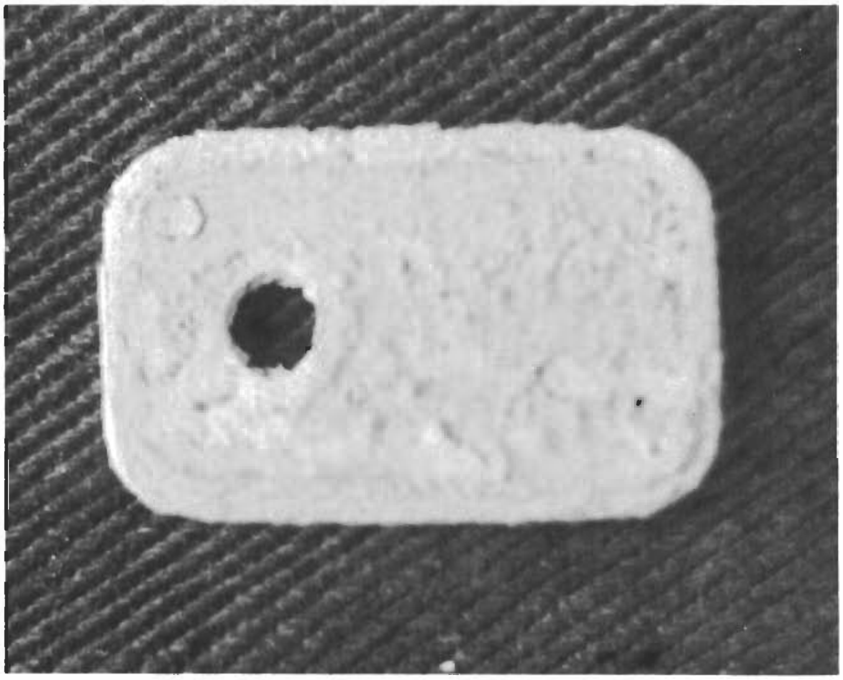
f. Exposed at 2700 F, Average Cyclic Life 9 Hours

FIGURE 18. (CONTINUED)



3X N413

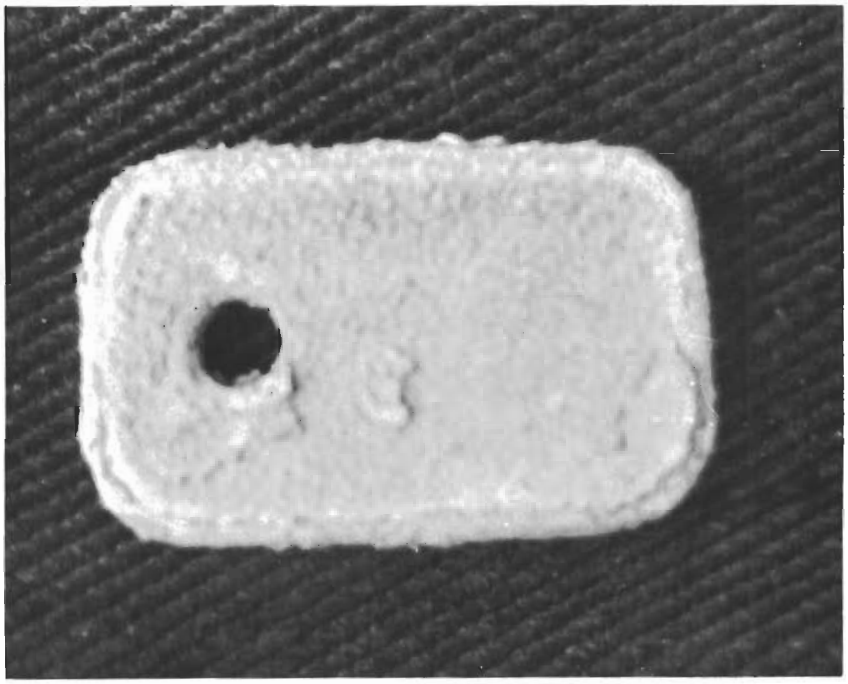
a. Exposed at 1200 F, Cyclic Life Greater Than 100 Hours



3X N414

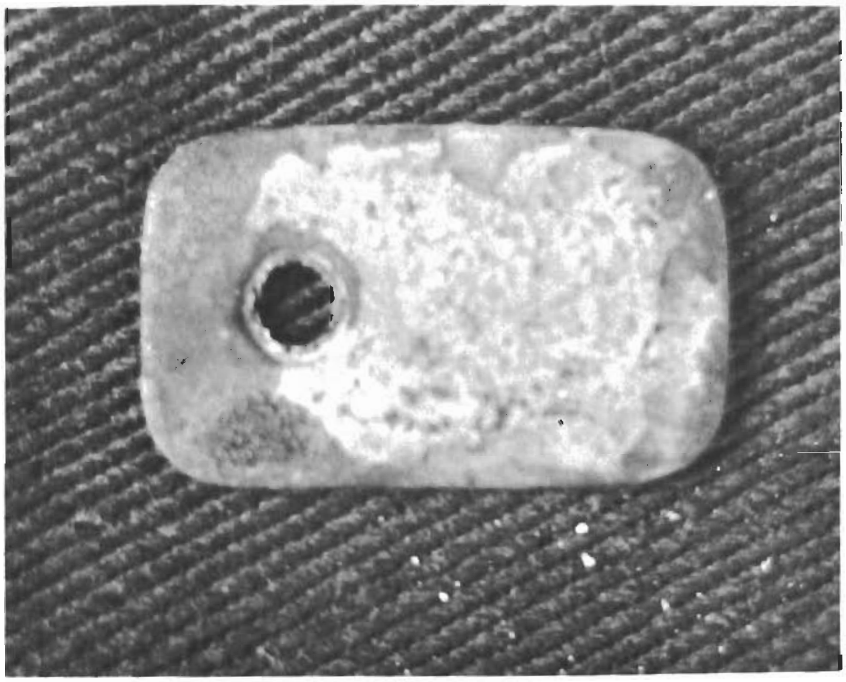
b. Exposed at 1500 F, Cyclic Life Greater Than 100 Hours

FIGURE 19. Si-8Mn COATED Ta-30Cb-5V AFTER CYCLIC EXPOSURES AT 1200 TO 2700 F



3X N415

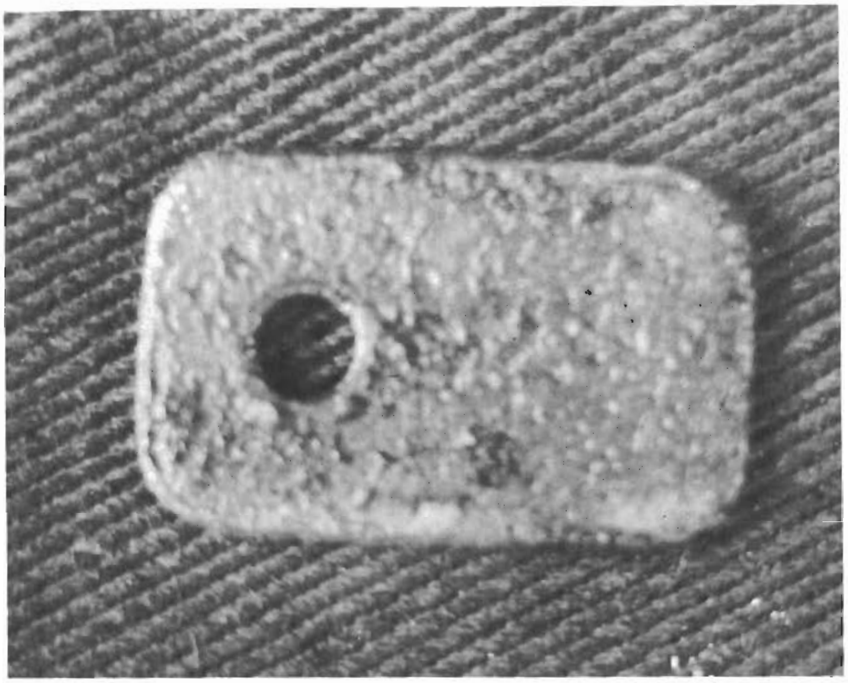
c. Exposed at 1800 F, Cyclic Life Greater Than 100 Hours



3X N416

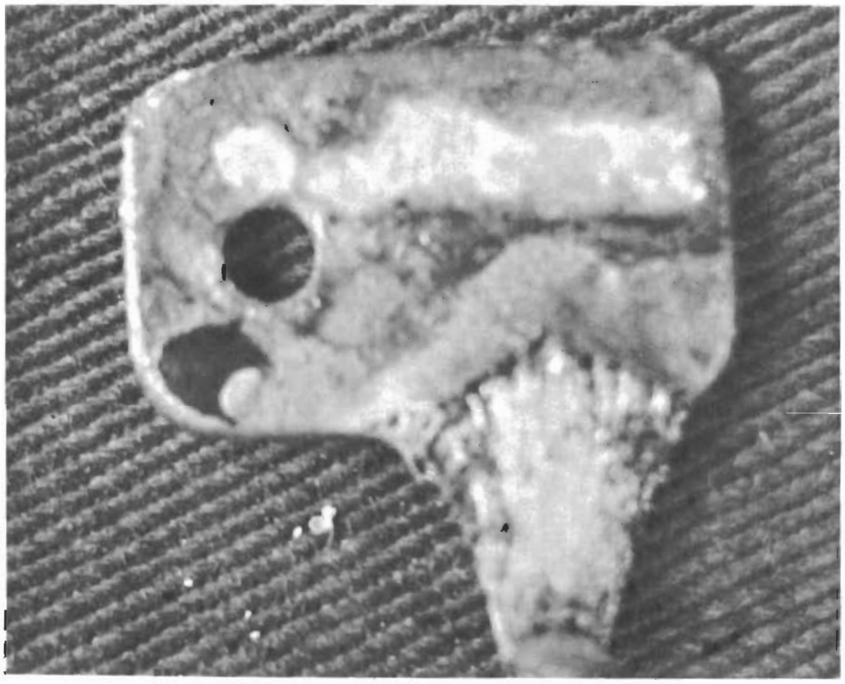
d. Exposed at 2200 F, Cyclic Life 30 Hours

FIGURE 19. (CONTINUED)



3X N417

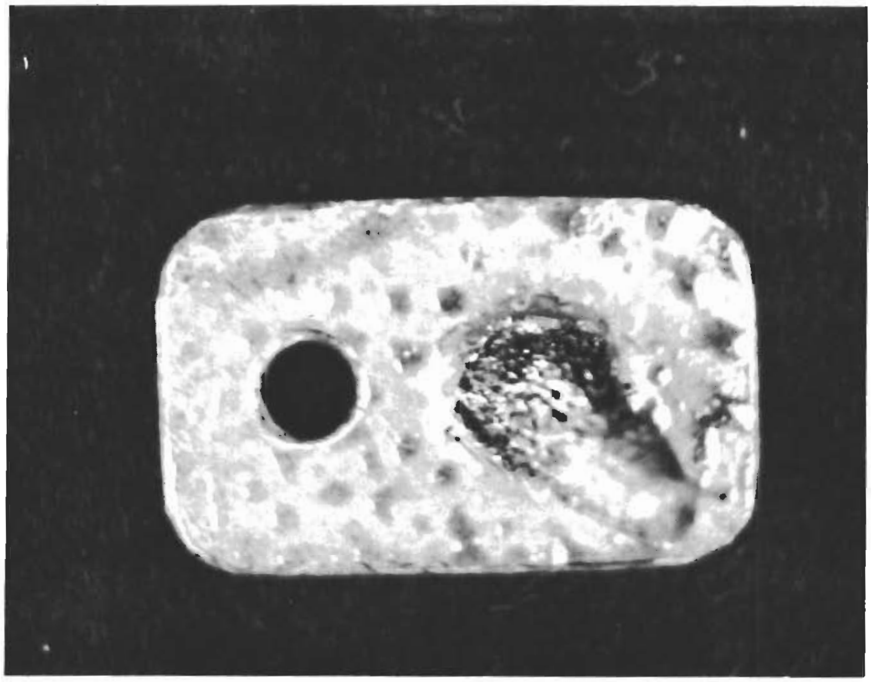
e. Exposed at 2500 F, Average Cyclic Life Greater Than 20 Hours



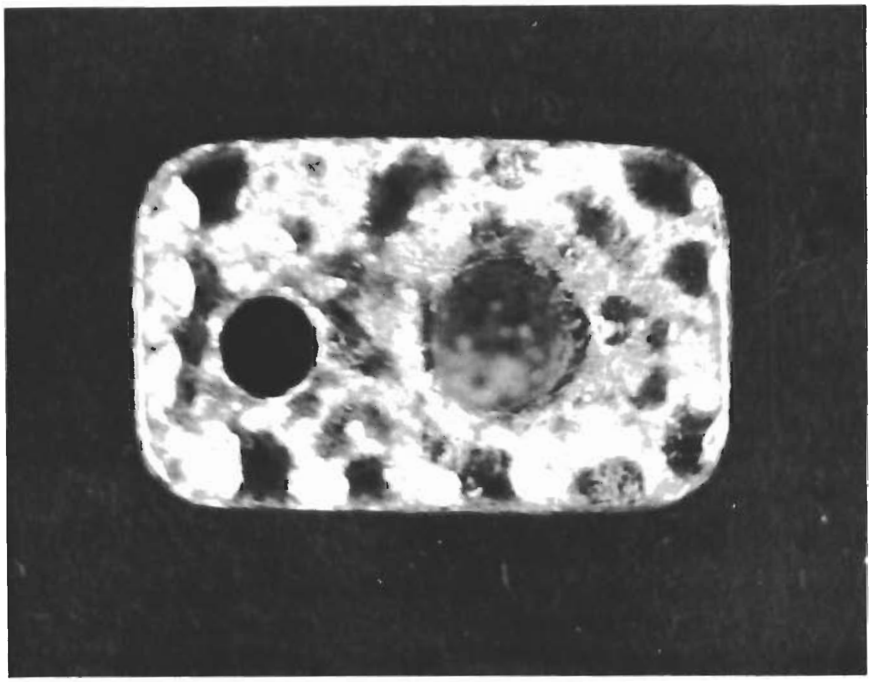
3X N418

f. Exposed at 2700 F, Average Cyclic Life 4.8 Hours

FIGURE 19. (CONTINUED)

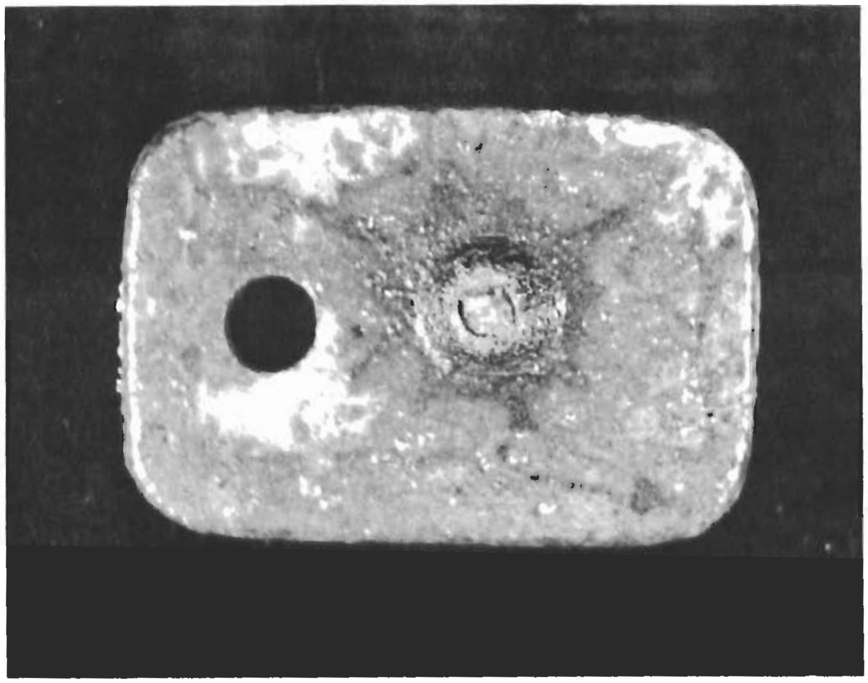


a. Si Coated, Average Cyclic Life 2 Hours at 2500 F

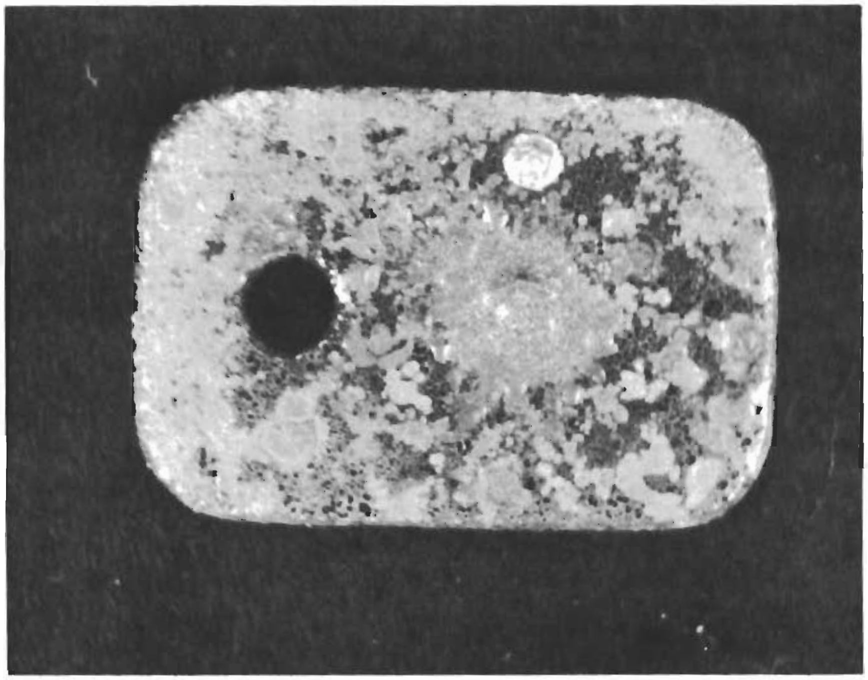


b. Si-9Al Coated, Average Life Less Than 1 Hour at 2700 F

FIGURE 20. COATED Ta-30Cb-5V AFTER DEFECT OXIDATION EXPOSURES AT 2500 AND 2700 F



c. Si-8Mn Coated, Average Cyclic Life 10 Hours at 2500 F



d. Si-8Mn Coated, Average Cyclic Life 10 Hours at 2700 F

FIGURE 20. (CONTINUED)

TABLE 13. TENSILE PROPERTIES OF UNCOATED, SILICIDE COATED, AND EXPOSED Ta-30Cb-5V AT ROOM TEMPERATURE AND 2200 F

Condition	Test Temperature, F	Yield Strength at 0.2% Offset(a), psi	Ultimate Strength(a), psi	Elongation in 1 Inch, per cent
Annealed, uncoated(b)	20	83,000	100,000	27
Silicide coated, 4.5 mils	20	84,100	101,000	21
Coated and exposed for 4 hours at 2500 F	20	79,500	95,400	20
Coated and exposed for 4 hours at 2700 F	20	79,500	93,800	20
Wrought, uncoated(c)	2200	27,200	33,800	58
Silicide coated, 4.5 mils	2200	--	32,300	40
Coated and exposed for 4 hours at 2700 F	2200	--	36,800	8

(a) Strength data for coated samples are based on core thickness only, and are corrected for metal consumed in forming coating.

(b) Average of three samples annealed 1 hour at 2300 F and evaluated on Contract AF 33(616)-5668.

(c) Average of two wrought samples evaluated on Contract AF 33(616)-7452. Samples are believed to have recrystallized during testing.

TABLE 14. SINGLE-CYCLE DEPOSITION OF ALUMINIDE-BASE COATINGS ON TANTALUM

Charged Coating Composition, at. %	Deposition Conditions(a)		Amount of Coating			Static Coating Life at Indicated Temperature(c), min		
	Temp, F	Carrier	Average Weight Gain, mg/cm^2	Average Thickness Increase, mil/side	Coating Thickness(b), mil/side	2200 F	2500 F	2700 F
				Straight Al Coatings				
100Al	2000	NH_4Cl	12.7	1.7	2.3	--	>330	>360
	2200	NaF	3.4	1.6	2.8(d)	--	<1	--
	2200	NH_4Cl	10.9	1.7	2.8	--	>300	<1
	2200	NaI	16.8	3.0	4.3	--	>450	3
	2200	KI	19.3	3.2	4.3	--	35	18
				Al-Cr Coatings				
Al-50Cr	2000	NH_4Cl+NaF	1.0	0.1	0.4(d)	--	1	--
	2200	KI	1.9	0.9	0.7	--	3	<1
		NaF	2.0	0.8	1.0(d)	--	75	<1
		NaCl	3.9	1.0	1.7	--	>360	1
		NH_4Cl	4.2	0.8	1.7	--	2	--
		NaI	5.8	1.1	2.7	--	95	<1
	2400	NaI	14.4	1.3	1.8	--	>390	>270
Al-75Cr	2000	NH_4Cl+NaF	0.3	-0.2	0.1	--	<1	--
	2200	NaI	0.6	0.5	0.1	--	<1	--
	2400	NaI	6.8	0.2	0.8	--	180	20
Al-14Ti	2130(e)	NH_4Cl	17.7	2.4	3.8	--	>360	--
Al-25Ti	2130(e)	NH_4Cl	6.4	0.9	1.3	120	16	--
Al-50Ti	2130(e)	NH_4Cl	4.2	0.9	0.9	20	<1	--
	2200	NaI	0.4	0.4	0.2	--	<1	--
Al-67Ti	2200	NaI	0.2	0.3	0.2	--	<1	--
Al-75Ti	2200	NaI	0.2	0.2	0.2	--	<1	--
	2200	NH_4Cl+NaF	1.9	0.2	0.2	--	<1	--

(a) Coating runs were for 16 hours in argon unless otherwise indicated.
(b) Coating thickness was measured metallographically.
(c) All exposures were single results.
(d) Coating was oxidized, uneven, and/or badly cracked.
(e) Coating run was 12 hours.

Several process variables for pack cementation were studied, including temperature and carrier. The thickest, but not most protective, aluminide coating was obtained with KI carrier at 2200 F. Best protection was afforded by an aluminide coating applied at 2000 F using NH_4Cl as carrier. Studies of these coatings were too brief to determine the reasons for the thicker coating not being more protective.

Microstructures of the aluminide coating as applied and after exposure at 2700 F are shown in Figure 21. Three intermetallic phases are present in the as-deposited coating. Although not identified, these phases are believed to be $TaAl_3$ (on the exterior), Ta_2Al, and Ta_3Al (next to the substrate). After exposure at 2700 F, the Ta_2Al and Ta_3Al phases thicken significantly at the expense of the $TaAl_3$ phase. The growth rates of the subaluminides are thus greater than those of the subsilicides, discussed earlier.

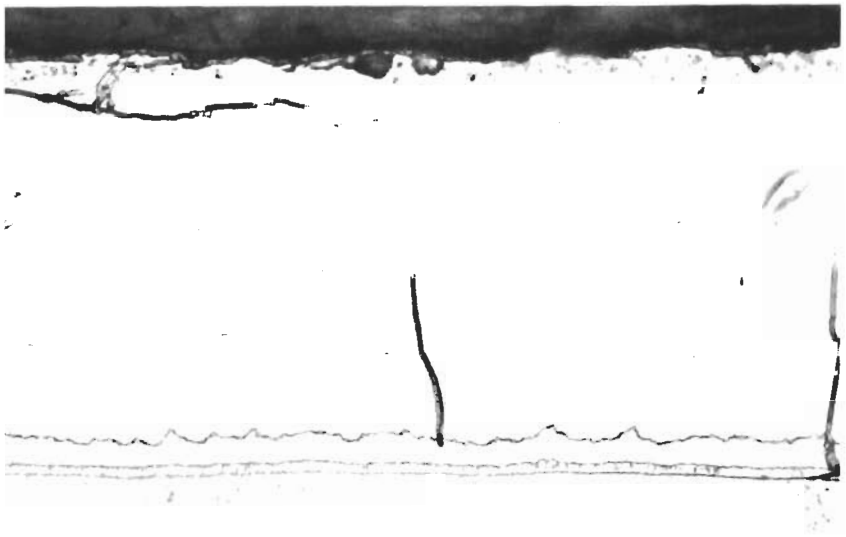
Oxidation weight-gain curves for aluminide-coated tantalum are parabolic, as seen in Figure 22. This behavior indicates that diffusion through a semiconducting Al_2O_3-rich scale is rate controlling. This is in contrast to the nonparabolic weight-gain curves observed for the protective silica-rich scales, e.g., on the Ta-Cb-V alloys (Figure 16). The vitreous silica scales are ionic conductors and have much slower diffusion rates than do the semiconducting scales. Several aluminide-coated tantalum samples after oxidation are shown in Figure 23.

Straight aluminide coatings were also applied by hot dipping and diffusing. Bath temperatures were varied from 1600 to 1900 F, and dipping times from 15 seconds to 5 minutes. The optimum dipping conditions were selected as 5 minutes at 1800 F with a flux of 45 per cent KCl-35 per cent NaCl-14 per cent Na_3AlF_3-6 per cent AlF_3. Slight variations in the dipping time or temperature, however, did not significantly affect the character of the coating.

The as-dipped samples were determined metallographically to contain one intermetallic phase in addition to free aluminum in the coating. The thickness of the intermetallic phase varied considerably over the individual samples, ranging up to 0.6 mil. The appearance of the intermetallic layer suggested that the outer portions were dissolving in the bath during dipping, as shown in Figure 21c.

The oxidation resistance of aluminum-dipped tantalum was evaluated as dipped and after heat treating in vacuum at 1700 and 2920 F. The as-dipped coating was protective for 1 hour at 2200 F but was not protective at 2500 F. Heat treating for 1 hour at 1700 F produced a coating structure similar to that obtained by pack cementation, although the dipped coating was porous. After 1700 F treatment, the dipped coating was protective for 3-1/2 hours at 2500 F. Heating for 1 hour at 2920 F, however, caused excessive growth of the subaluminides and rendered the coating nonprotective at 2500 F.

Aluminum-chromium and aluminum-titanium coatings were investigated by pack codeposition, as indicated in Table 14, and by two-cycle alternate deposition. The aluminum-chromium coatings deposited at 2000 and 2200 F showed some protection at 2500 F but generally appeared inferior to the straight aluminide coatings. The protectiveness was improved both at 2500 and 2700 F for the coatings deposited at 2400 F. These coatings were similar to the straight aluminide coating, both in microstructure and nature of oxidation weight-gain curve. Analysis of a nominal Al-50Cr coating, given in Table 9, showed the actual composition to be Al-16Cr. Thus aluminum, like silicon, appears to deposit preferentially to chromium during pack codeposition.



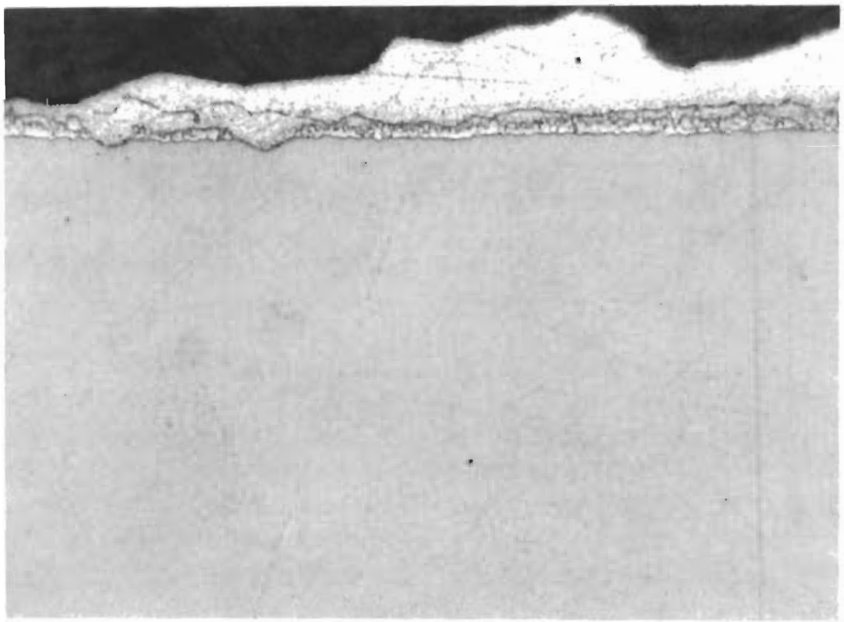
500X N75710

a. Coated at 2200 F by Pack Cementation, NaI Carrier, 4.3 Mil

500X N75083

b. Exposed for 360 Minutes at 2700 F

FIGURE 21. ALUMINIDE-COATED TANTALUM AS COATED AND AFTER STATIC EXPOSURE AT 2700 F



250X N71304

c. As-Hot-Dipped for 3 Minutes at 1900 F

FIGURE 21. (CONTINUED)

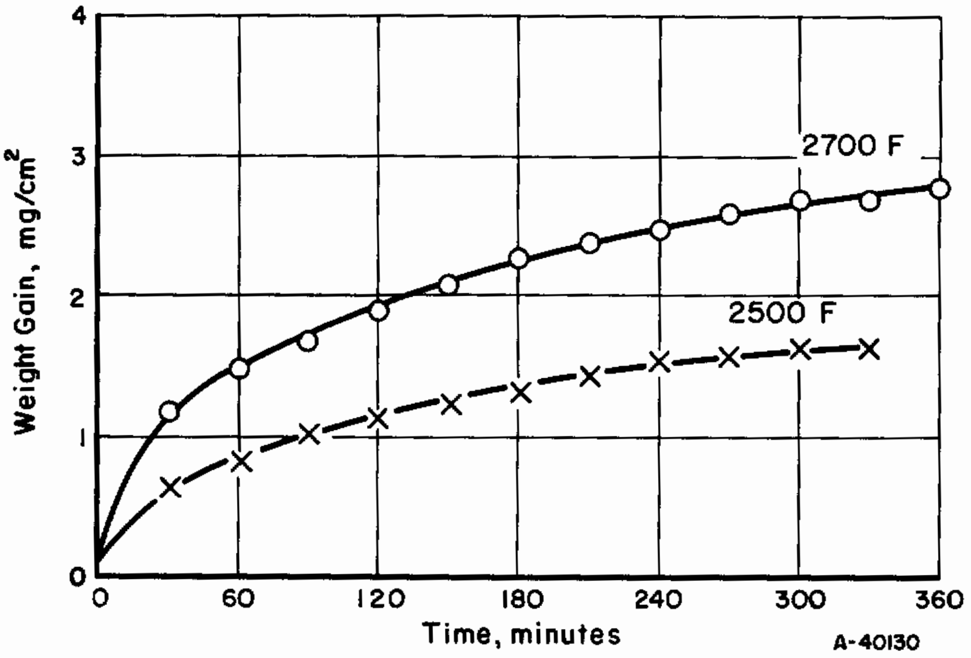
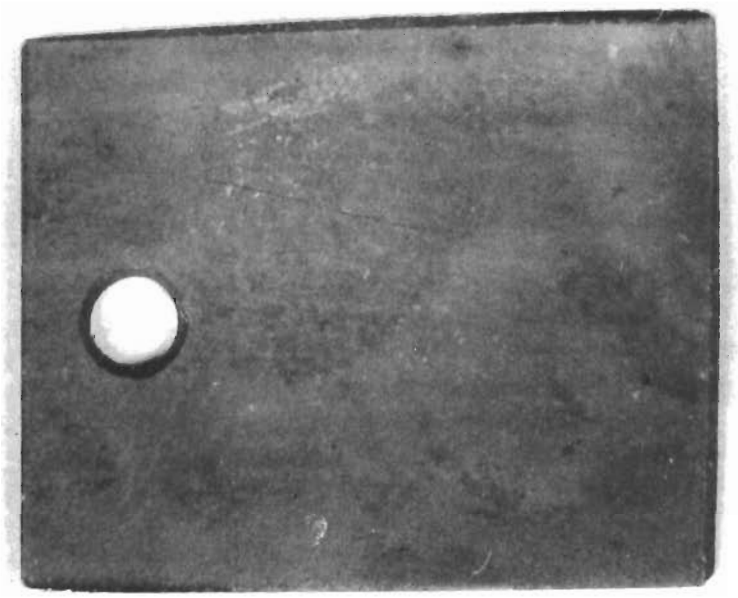
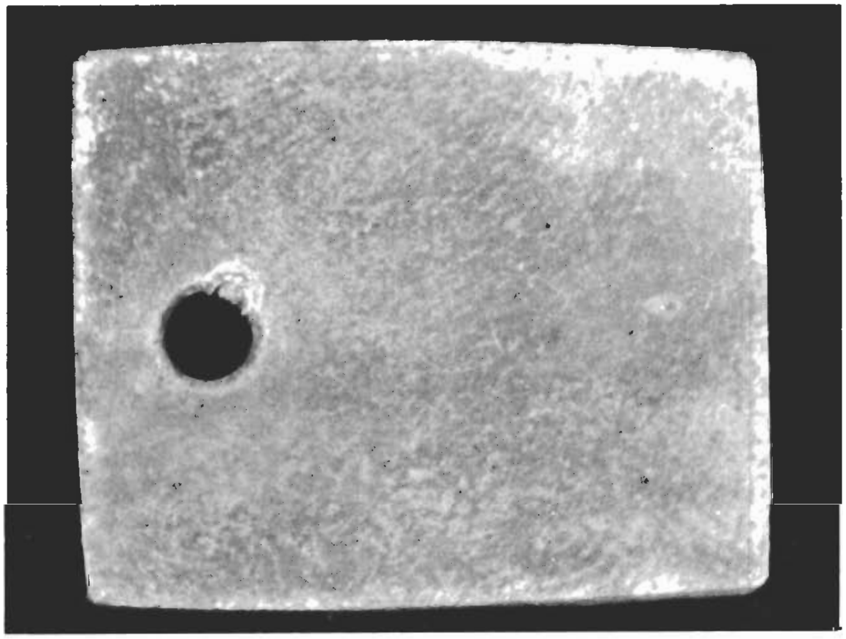


FIGURE 22. OXIDATION WEIGHT-GAIN CURVES FOR ALUMINIDE-COATED TANTALUM (2.3-MIL COATING)



3X N90

a. Exposed 330 Minutes at 2500 F, No Failure



3X N91

b. Exposed 360 Minutes at 2700 F, No Failure

FIGURE 23. ALUMINIDE-COATED TANTALUM AFTER STATIC EXPOSURES AT 2500 AND 2700 F

Coatings were applied by pack cementation at 2000 F.

Codeposition of Al-Ti coatings was evaluated, with results as presented in Table 14. Protective coatings were obtained at low titanium levels, but the coating rate and protectiveness decreased with increasing titanium content. Like Al-Cr, the oxidation behavior of the low Al-Ti coating was similar to that of the straight aluminide coatings, suggesting that the titanium content of these coatings is lower than nominal.

Aluminum-titanium coatings were also investigated briefly by two-cycle alternate deposition of aluminum and titanium. Aluminizing was conducted for 16 hours at 2000 F using NH_4Cl carrier, followed by subsequent titanizing under similar conditions. The composition of the coating was calculated from the weight gains during the two cycles to be Al-4Ti. The coating microstructure and protectiveness were similar to that of the straight aluminide coating.

Chromium, Hafnium, and Titanium Coatings

Coatings of chromium, chromium-titanium, hafnium, and titanium were applied to tantalum by pack deposition and codeposition, as shown in Table 15. Process variables evaluated include deposition temperature, carrier, and amounts of chromium and carrier in the pack.

Chromium coatings were difficult to apply because of the similar stabilities of chromium and tantalum halides. This caused both chromium and tantalum halides to volatilize during the deposition treatment and resulted in tantalum losses and relatively thin chromium coatings. The best carriers for chromium were NH_4Cl and NaI, although the coating thickness obtained with these carriers averaged only about 0.2 mil at 2200 F and were nonprotective at 2500 F. Increasing the chromium content of the pack from 25 volume per cent to 70 volume per cent doubled the weight of coating but it was still nonprotective. Increasing the amount of carrier from 2 weight per cent to 8 weight per cent had no significant effect on the deposition rate.

The microstructure of the chromium coating, shown in Figure 24, consisted of one intermetallic phase, presumably $TaCr_2$. On exposure at 2500 F, the coated samples failed generally rather than locally, as seen in Figure 25.

In addition to being difficult to deposit by pack deposition, chromium significantly hardens the tantalum substrate. Knoop hardness traverses, presented in Figure 26, show that chromium hardens tantalum to over 500 KHN at 2200 F and over 900 KHN at 2370 F. This results from the appreciable solid solubility of chromium in tantalum and the high hardness of Ta-Cr solid solutions. The diffusivity of chromium in tantalum at 2000 F was calculated from the hardness gradient in Figure 26 as 2×10^{-8} cm^2/sec, much higher than the estimated self-diffusivity of tantalum at 2000 F, 10^{-16} cm^2/sec.

Chromium-titanium-alloy coatings were applied by codeposition at 2200 and 2400 F, as noted in Table 15. These coatings also were difficult to deposit to appreciable thicknesses, although the amount of coating increased slightly with increasing deposition temperature and titanium content of the pack.

Hafnium and titanium coatings were applied at 2200 and 2400 F using various carriers, with results as presented in Table 15. The deposition rates of these two

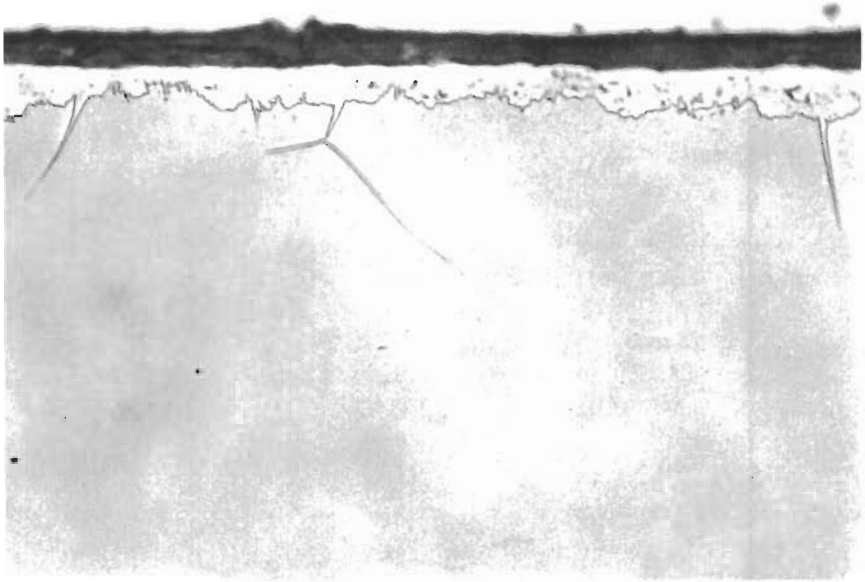
TABLE 15. SINGLE-CYCLE DEPOSITION OF CHROMIUM, HAFNIUM, AND TITANIUM-BASE COATINGS ON TANTALUM

Charged Coating Composition, at. %	Deposition Conditions[a]		Amount of Coating			Static Coating Life at Indicated Temperature, min		
	Temp, F	Carrier	Average Weight Gain mg/cm^2	Average Thickness Increase, mil/side	Coating Thickness[b], mil/side	2200 F	2500 F	2700 F
			Chromium-Base Coatings					
100Cr	1800	NH_4Cl	-1.5	0.02	--	--	--	--
	2000	NH_4Cl	-1.3	0.2	0.4	2	<1	--
	2200	NaF	-2.5	0.2	0.1[c]	--	<1	--
		NH_4Cl	-0.7	0.2	0.3	10	<1	--
		KI	0.6	0.3	0.1	--	<1	--
		NaI	1.0	0.4	0.1	--	<1	--
(50 vol % Cr)		NaI	1.2	0.3	--	--	--	--
(70 vol % Cr)		NaI	2.0	0.4	--	--	--	<1
(8 wt % NaI)		NaI	1.0	0.2	--	--	--	--
	2370	NH_4Cl	-1.0	-3.5	0.7	35	3	--
	2400	KI	0.7	0.3	0.3	--	<1	--
		NaI	0.9	0.3	0.2	--	<1	--
Cr-25Ti	2200	NH_4Cl+NaF	2.0	0.2	0.2	--	2	--
	2400	NaI	2.3	0.0	0.2	--	<1	--
Cr-50Ti	2200	NH_4Cl+NaF	2.3	0.1	0.2	--	2	--
	2400	NaI	2.7	0.1	0.3	--	<1	--
Cr-75Ti	2200	NH_4Cl+NaF	2.3	0.1	0.3	--	2	--
	2400	NaI	2.1	0.1	0.4	--	<1	--
			Hafnium Coatings					
100Hf	2200	NaI	0.2	0.4	0.04	--	<1	--
		NaF	1.8	0.3	0.2[c]	130	<1	--
	2400	NaI	1.3	0.0	0.6	--	<1	--
			Titanium Coatings					
100Ti	2000	NH_4Cl	1.4	0.4	0.2	--	<1	--
	2200	NaI	0.2	0.1	0.2	--	<1	--
		KI	0.3	0.0	0.1	--	<1	--
		NaI	0.4	0.3	0.3	--	<1	--
		NH_4Cl	2.0	0.5	0.2	--	<1	--
		NaCl	2.1	0.5	0.2	--	<1	--
		NH_4I	2.4	0.3	0.4	10	<1	--
		NaF	3.3	0.7	0.5	--	<1	--

TABLE 15. (Continued)

Charged Coating Composition, at. %	Deposition Conditions[a]		Amount of Coating			Static Coating Life at Indicated Temperature, min		
	Temp, F	Carrier	Average Weight Gain mg/cm^2	Average Thickness Increase, mil/side	Coating Thickness[b], mil/side	2200 F	2500 F	2700 F
			Titanium Coatings (Continued)					
(50 vol % Ti)	2200	NaCl	1.2	0.2	--	--	--	--
(70 vol % Ti)	2200	NaCl	1.8	0.3	--	--	--	--
(8 wt % NaCl)	2200	NaCl	2.2	0.2	--	--	--	<1
	2370	NH_4Cl	3.3	0.8	0.4	90	4	--
	2400	KI	0.4	0.2	0.2	--	<1	--
		NaI	0.9	0.6	0.4	--	<1	--

(a) All coating runs were for 16 hours in argon at the indicated temperature.
(b) Coating thickness was measured metallographically.
(c) Coating was partly oxidized during deposition.



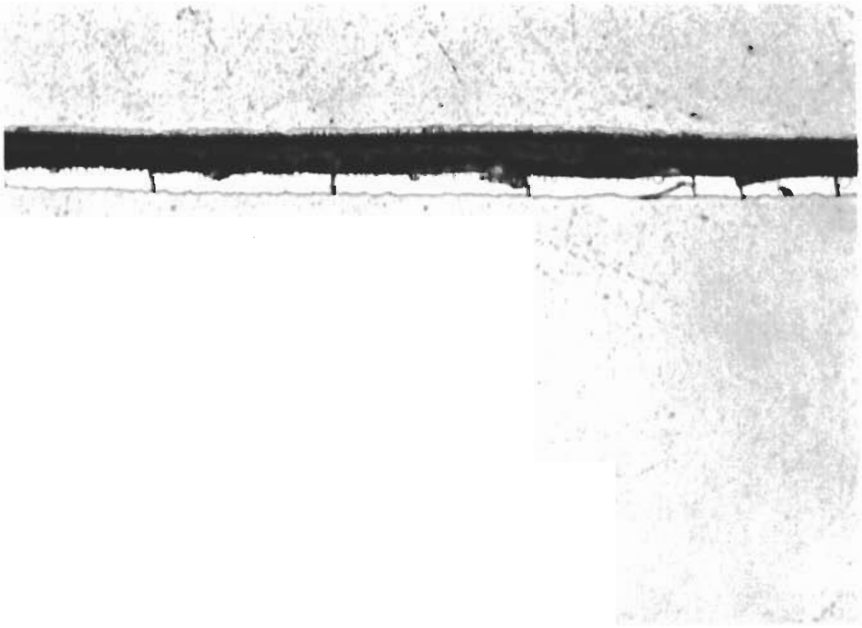
a. Chromium Coated Tantalum, 0.4-Mil Coating

b. Cr-50Ti Coated Tantalum, 0.2-Mil Coating

FIGURE 24. TANTALUM COATED WITH CHROMIUM, CHROMIUM-TITANIUM, HAFNIUM, AND TITANIUM

500X N77027

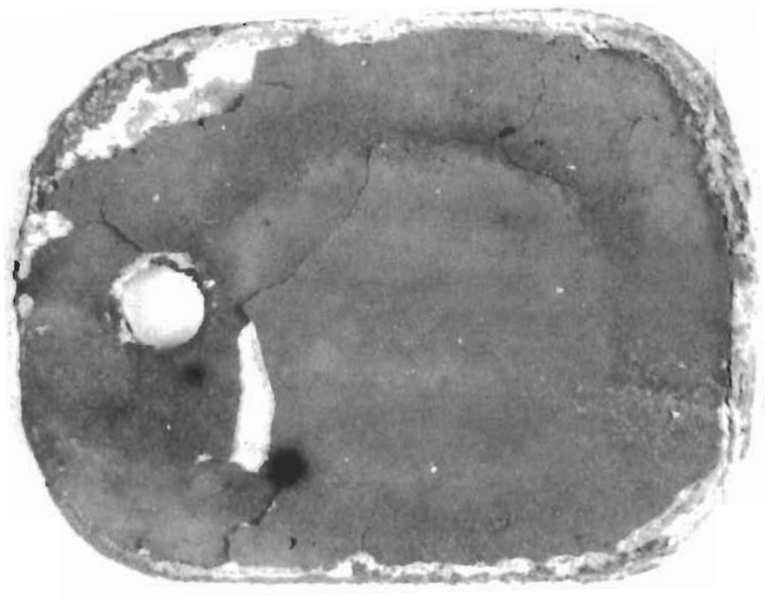
c. Hafnium Coated Tantalum, 0.6-Mil Coating, Cracked



500X N75709

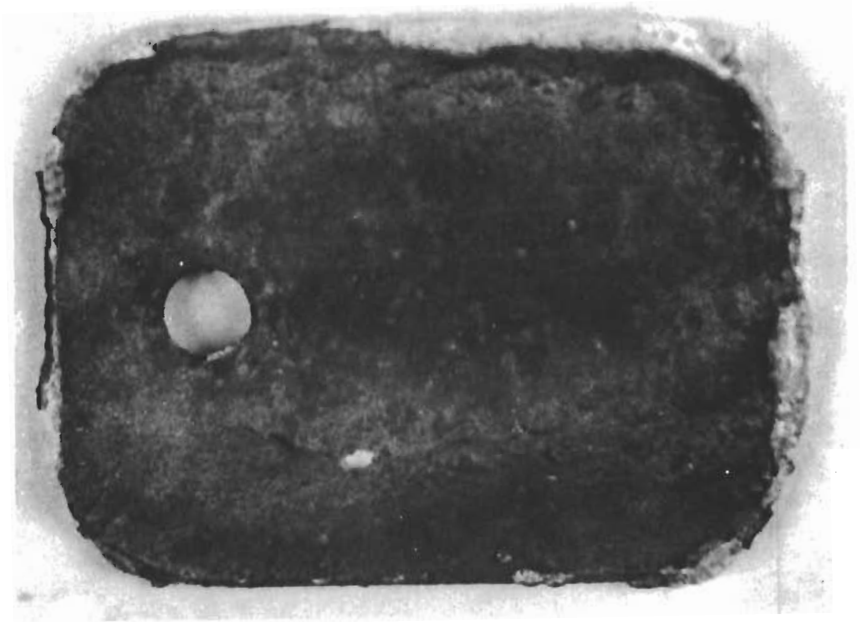
d. Titanium Coated Tantalum, 0.2-Mil Coating

FIGURE 24. (CONTINUED)



3X N176

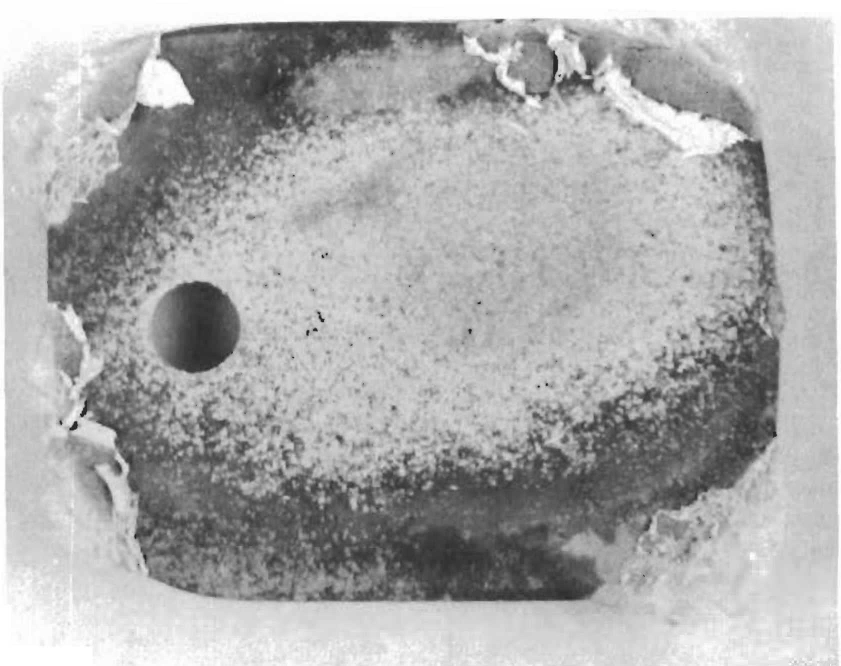
a. Chromium Coated Tantalum, Failed in 1 Minute



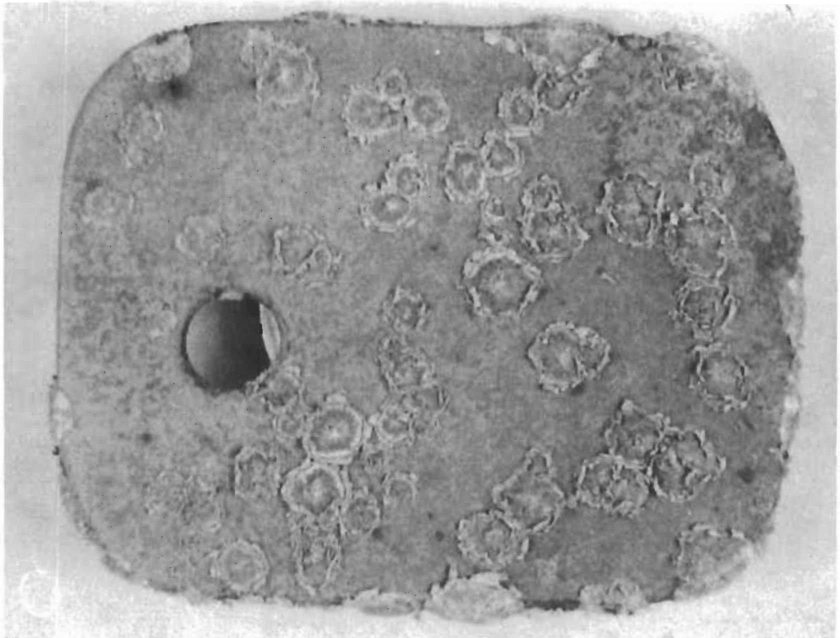
3X N110

b. Cr-50Ti Coated Tantalum, Failed in 2 Minutes

FIGURE 25. TANTALUM COATED WITH CHROMIUM, CHROMIUM-TITANIUM, HAFNIUM, AND TITANIUM AFTER EXPOSURE AT 2500 F



c. Hafnium Coated Tantalum, Failed in 1 Minute



d. Titanium Coated Tantalum, Failed in 1 Minute

FIGURE 25. (CONTINUED)

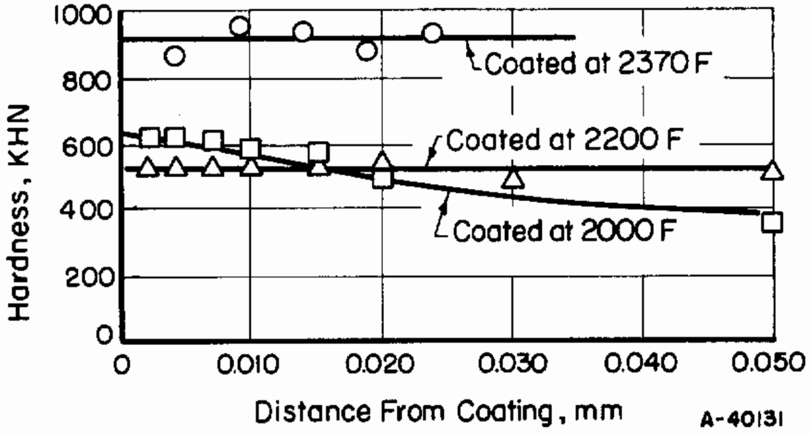


FIGURE 26. HARDNESS TRAVERSES ON TANTALUM COATED WITH CHROMIUM BY PACK DEPOSITION

metals, like chromium, were rather low, although no weight losses resulted from coating. The best carrier for both elements was NaF, which produced an 0.2-mil coating of hafnium and an 0.5-mil coating of titanium at 2200 F. Structures of these coatings, shown in Figure 24, consist of a single hafnium-rich or titanium-rich phase, since no intermetallics are present in systems of these metals with tantalum. No hardening was detected by Knoop traverses on tantalum coated with titanium at 2000 or 2200 F.

Some protection from hafnium and titanium coatings was obtained at 2200 F but none at 2500 F. Samples exposed at 2500 F are shown in Figure 25.

Al_2O_3-Base Coatings

Alumina coatings were applied to tantalum by flame spraying with Al_2O_3 using an oxyacetylene flame. Good adherence of the Al_2O_3 to the sand-blasted tantalum surface was obtained, and the Al_2O_3 was fused uniformly to a thickness of 3.4 to 6.6 mils. Metallographic examination, however, revealed a second thinner oxide layer, probably Ta_2O_5, between the tantalum substrate and the fused Al_2O_3 coating, shown in Figure 27.

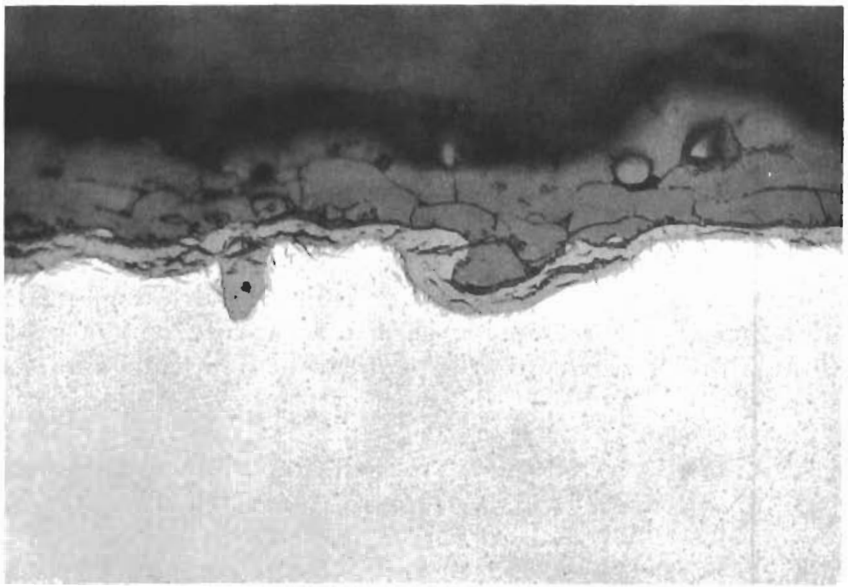
Air-oxidation tests at 2200 F were conducted on samples as coated and after treating for 1 hour in vacuum at 2190 F. In both instances, the alumina coating was unprotective, failing in less than 1 minute.

Limited studies were also conducted on impregnation of alumina coatings with glassy sealants, similar to the GE "System 400" coating. These studies consisted of painting a water slurry of a refractory silica-base glass powder onto the alumina coating, firing in vacuum at 2190 F, and dipping the flame-sprayed samples in ethyl silicate or water glass, followed by 2550 F firing. These three treatments all produced a vitreous surface on the alumina coating but none of the coatings were oxidation resistant at 2500 F.

Zinc Coatings

Zinc coatings were applied to tantalum both by hot dipping in molten zinc and by vacuum distillation.

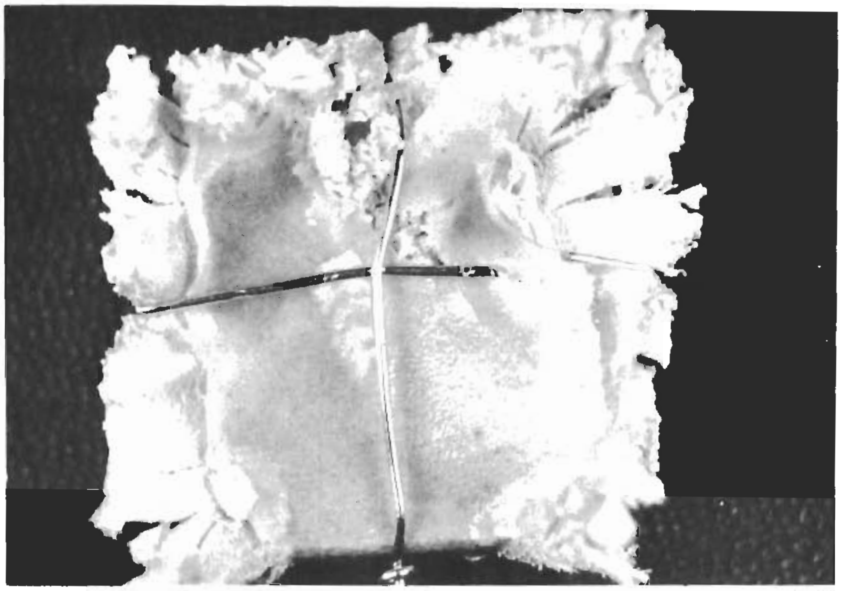
Hot dipping was conducted using zinc-bath temperatures of 1000 to 1200 F and dipping times of 15 seconds to 2 hours. Various fluxes, including ammonium chloride and three commercial fluoride-containing fluxes, were used on both the bath surface and sample surface to promote wetting and to improve coating uniformity. These studies, however, indicated that zinc-dipped coatings on tantalum are relatively nonuniform and are only mechanically adherent. The major problem appears to be absence of any reaction between the tantalum and the zinc to form intermetallics. The thin oxide film which forms on the tantalum as it is inserted into the bath also tends to prevent wetting by the zinc and results in uncoated areas. Attempts to improve the coating uniformity, by drawing the samples through a small set of rolls or by wiping with asbestos on removal from the bath, were unsuccessful.



250X N72139

a. Flame-Sprayed Al_2O_3 on Tantalum

Note Ta_2O_5 intermediate layer.



3X N68

b. Al_2O_3 Plus Sodium Silicate on Tantalum, Failed in 1 Minute at 2500 F

FIGURE 27. Al_2O_3 COATED TANTALUM

Thirteen zinc-coated samples were heated for 1 hour in air to promote formation and growth of tantalum-zinc intermetallics. A similar treatment is employed for producing columbium-zinc intermetallics on zinc-dipped columbium.(15) The zinc-coated tantalum specimens, however, suffered extensive oxidation during this treatment and did not appear to form any protective intermetallics on the surface.

Metallographic examination of several as-dipped zinc-coated samples revealed that no visible intermetallic layer had formed during dipping times up to 2 hours.

Three attempts were made to produce tantalum-zinc intermetallic surface layers by heating tantalum and zinc in an evacuated silica capsule at 1700 and 1900 F for 1-1/2 to 16 hours. No tantalum-zinc reaction to form intermetallics was observed in any of the three experiments.

It thus appears that the reaction of zinc with tantalum to form intermetallics is exceedingly slow, both at normal dipping temperatures (1000 to 1300 F) and at distillation temperatures (1700 to 1900 F).

DISCUSSION

Comparison of the experimental results on application and protective behavior of the various coatings evaluated allows logical correlations with other properties of the coating materials. These correlations are helpful in suggesting the most profitable lines for future studies in the development of protective, self-healing coatings for tantalum and other refractory metals.

Pack-Cementation Process

The pack-cementation process is an attractive method of coating application. The process is basically a chemical oxidation reduction reaction where the coating element is continually being removed by reaction with the substrate being coated. The probable reactions involved, for example, in the siliconizing of tantalum with NaF carrier may be written as follows:

(1) $6NaF_{(gas)} + 2Si_{(powder)} \rightleftharpoons Si_2F_{6(gas)} + 6Na_{(gas)}$

(2) $2Si_2F_{6(gas)} \longrightarrow 3SiF_{4(gas)} + Si\,(TaSi_2)$

(3) $3SiF_{4(gas)} + Si_{(powder)} \rightleftharpoons 2Si_2F_{6(gas)}$.

Reactions (1) and (3) involve conversion of the powdered silicon in the pack mix into volatile silicon trifluoride, while Reaction (2) involves oxidation of the trifluoride to the tetrafluoride at the $TaSi_2$ surface and reaction of the excess silicon with tantalum to form $TaSi_2$. The driving force for this particular coating reaction is removal of the silicon as $TaSi_2$, which is less easily oxidized than is elemental silicon. Assuming a sufficient supply of volatile Si_2F_6, the rate-controlling reaction may be expected to be the rate of removal of silicon or, in other words, the rate of diffusion of either silicon or tantalum in $TaSi_2$, whichever is faster.

Thus, the coating rate is seen to depend, first, on the availability of the coating material at the coated surface, and, second, on the interdiffusion rates of the coating element and the substrate in the coating.

The availability of the coating element at the coated surface depends greatly on the properties of the halide carriers and of the coating element halides. The properties of prime interest are the halide thermodynamic stabilities and boiling points. These properties are summarized in Table 16 for the elements of interest.

The relative thermodynamic stabilities of the carrier, the coating-element halides, and the tantalum halides determine the relative extents to which Reactions (1), (2), and (3) will proceed at equilibrium. The carrier should be slightly more stable than the coating-element halide in order to maintain a "reservoir" of halide for the coating reaction and to assure that a significant amount of coating-element halide will be available. Thus, NaF (95 kcal/g-atom), being slightly more stable than SiF_4 (80 kcal/g-atom), is superior for siliconizing to $BaCl_2$ (76 kcal/g-atom), which is significantly more stable than $SiCl_4$ (24 kcal/g-atom). Also, the coating-element halide must be more stable than the corresponding tantalum halide in order to prevent a simple exchange reaction at the tantalum surface. Chromium is difficult to deposit on tantalum because of the similar stabilities of their halides, which also resulted in tantalum losses during chromizing.

The boiling points, i.e., the volatilities, of the carriers and the coating-element halides influence the availabilities of the various halides for reaction. The carrier should have a boiling point slightly above the reaction temperature in order to provide a sufficient amount for reaction without volatilizing away too rapidly. The coating-element halide, however, should have a low boiling point in order to saturate the pack. The amount of coating-element halide is limited by its thermodynamic stability relative to that of the carrier, as indicated by Reaction (1) and discussed above.

It is seen from both experimental data and halide properties that satisfactory carriers for the various elements of interest are as listed below:

Coating	Melting Point, C	Carrier	Average Coating Thickness After 12 Hours at 2200 F, mils
Aluminum	660	KI	4.3
Silicon	1410	NaF	3.1
Titanium	1660	NaF	0.65
Chromium	1875	NaI	0.1
Hafnium	1975	NaF	0.3

As pointed out above, the coating rate depends both on the availability of the coating element at the coated surface and on the growth rate of the coating. Assuming sufficient availability, the growth rate may be expected to be rate determining. On the basis of qualitative interdiffusion relationships, the coating growth rates may be expected to be high for elements forming compounds with tantalum, and to decrease with increasing melting point of the compound element. These relationships are seen to hold for four

TABLE 16. PROPERTIES OF HALIDES AT 1500 K (2245 F)(16, 17)

Metal Ion	Free Energy of Formation of Indicated Halide, kcal/g-atom of halide				Boiling Point of Halide, F[(a)]			
	F	Cl	Br	I	F	Cl	Br	I
Ba^{2+}	115	76	65	54	4050	3510	3330	3150
Ca^{2+}	115	72	63	46	4550	3690	3330	2250
K^+	92	64	67	55	2700	2570	2520	2410
Na^+	95	63	61	49	3060	2670	2530	2380
NH_4^+	--	--	--	--	--	d 660	s1004	s1020
Ta^{2+}	68	22.5	--	8	--	2610	--	--
Al^{3+}	80	42.5	29	10	2340	840	870	790
Cr^{2+}	67.5	27	18	8	3870	2430	2070	1530
Hf^{4+}	86	47.5	29	17	1710	630	610	800
Si^{4+}	80	24	5	-8	-140	170	310	550
Ti^{4+}	78	35	20	8	540	280	450	720

(a) d indicates decomposes
s indicates sublimes.

of the five elements listed above. The low coating rate observed with chromium is most likely a result of the unfavorable thermodynamic stabilities of chromium halides, which complicate the coating reaction. The observations of linear siliconizing rates with NaCl carrier and parabolic siliconizing rates with NaF carrier tend to confirm the proposition that diffusion-controlled coating growth is rate determining if sufficient coating-element halide is available for reaction.

Protection Afforded by Silicide Coatings

Discussion of the protectiveness of the various coatings will be limited to the silicide-base compositions, since these are of greatest interest and were the major subject of this investigation. In addition to the three very basic criteria for selecting potential coating elements as discussed at the beginning of the survey section of this report, several other important criteria have become apparent during the experimental studies. These criteria, which are intended as general guides rather than firm requirements, include the following:

(1) Oxygen solubility in and diffusion through the coating should be as low as possible in order to minimize oxygen transfer to the substrate.

(2) The oxide(s) of the coating element(s) should be more stable thermodynamically than Ta_2O_5 so that the coating element(s) will oxidize preferentially.

(3) The coating, including its tantalum content, should be capable of forming a thin, adherent, protective scale in which diffusion (transfer) rates are very low.

(4) The coating element(s) should have either negligible solubility or hardening effects in the substrate.

(5) Growth rates of less oxidation-resistant tantalum-rich compounds, such as subsilicides and subaluminides, should be low.

Taking these criteria individually, it is seen that silicon, aluminum, and possibly chromium and glass-impregnated oxides meet Item (1), but titanium and hafnium do not. Silicon, aluminum, hafnium, and titanium meet the second criteria, while chromium and the glass-impregnated oxides would not oxidize preferentially to tantalum. Experimental data indicate that silicon and aluminum meet the third requirement most satisfactorily, although modifications of chromium, titanium, and hafnium coatings cannot be entirely ruled out. Chromium fails to meet the fourth requirement, have a solubility of about 15 atom per cent in tantalum and being a potent hardener, as seen in Figure 26. The fifth requirement, low growth rate of tantalum-rich compounds, appears best met by silicide coatings.

Thus, silicide and modified silicide coatings appear to satisfy these criteria to a greater extent than the other coatings evaluated in this study. The great advantage of silicide coatings, however, lies in the significant improvements in protectiveness available through alloying by additions to the coating and to the base.

Although the mechanisms by which silicide coatings oxidize have not been defined, it is possible to suggest reactions which qualitatively explain the observed behaviors. At 1200 F (650 C), $TaSi_2$ forms a thin oxide film which is protective for about 60 hours, while at 1500 F (820 C) and 1800 F (980 C), a porous oxide forms and the protective life decreases to about 35 hours and 3 hours, respectively, for approximately 3-mil coatings. It is believed that at 1200 F the film consists primarily of Ta_2O_5-saturated SiO_2. This film, by virtue of the high thermodynamic and physical stability of crystalline SiO_2, is able to form preferentially to Ta_2O_5 and remain adherent and protective. As the temperature is increased, however, silicon in the $TaSi_2$ layer oxidizes more rapidly, forming initially a protective SiO_2-rich scale over a subscale of SiO_2 in a matrix of unoxidized tantalum. After a period of time, breakdown of the protective scale occurs because the silicon needed for its replenishment has already been oxidized. As the scale becomes unprotective, tantalum in the $TaSi_2$ oxidizes to the depth at which unoxidized silicon is available, to re-form at least a partially protective scale.

As the temperature is raised to 2200 F (1200 C), the character of the oxidation product changes significantly, becoming appreciably more protective. This improvement is believed associated with vitrification of the SiO_2-rich scale and a sharp decrease in diffusion rates through the vitreous scale. It is known that silicon tends to form a vitreous scale on oxidation above 1830 F (1000 C).(7) Tantalum pentoxide is also a marginal glass former, and tendencies for the scale on tantalum to vitrify have been observed at 1830 F (1000 C) and 2190 F (1200 C).(18)

Further increases in the temperature, to 2500 F (1370 C) and 2700 F (1480 C), increase the tendency for the scale to vitrify, but to an insufficient extent to prevent oxidation of tantalum from $TaSi_2$ to porous, nonvitreous, high-temperature (alpha) form of Ta_2O_5. Thus, although scales may form on $TaSi_2$ at 2700 F which are visibly vitreous, microexamination of the cross sections shows oxidation of the underlying disilicide into porous Ta_2O_5 (see Figures 1 and 2).

Modification of the silicide coating and the resulting scale by additions to the coating itself or by alloying of the substrate have been shown experimentally in some cases to significantly improve the coating protectiveness, both at low and high temperatures. The effects of these additions appear directly related to the effects of their oxides in promoting vitrification of the SiO_2-rich scale.

The ability of an oxide to promote vitrification, or plasticity, of an SiO_2-rich scale may be correlated with the melting points of mixtures of the oxide with SiO_2, or, in the absence of a phase diagram, with the melting point of the new oxide itself. For purposes of discussion, the melting points of the oxides of additions studied in the current work are listed below:

Oxide	Melting Point, C
SiO_2	1713
Ta_2O_5	1890
B_2O_3	577
V_2O_5	660
MoO_3	795
Cb_2O_5	1460
WO_3	1470
MnO	1790
TiO_2	1860
Al_2O_3	2020
Cr_2O_3	2440

Those additions which were found to be beneficial include boron, vanadium, columbium, tungsten, and manganese. With the exception of MnO, which forms a low-melting eutectic with SiO_2 (Figure 5d), all of the oxides of the beneficial elements have lower melting points than SiO_2. (Molybdenum was apparently not codeposited with silicon; hence, its ineffectiveness.) The effectiveness of vitreous SiO_2 in protecting the underlying coating and substrate from oxidation is apparent from the photomicrographs of modified silicide coatings after exposure (Figures 7, 8, 11, and 17). These photomicrographs uniformly show only minor structural changes in the coating resulting from interdiffusion at high temperatures but show no consumption of the coating by oxidation. This is in distinct contrast to straight silicide coatings on tantalum, which exhibit considerable consumption by oxidation, Figure 2.

Improved low-temperature oxidation behavior is also exhibited by coatings which are able to form protective, (and presumably) vitreous scales. It is of interest to note that the best low-temperature behavior was observed on the coated Ta-Cb-V alloy, suggesting that the lower melting oxides are most effective at the lower temperatures.

The beneficial additions were also effective in promoting self-healing of defected silicide coatings at 2500 and 2700 F, with exception of the manganese-modified silicide coating on tantalum. Defect healing was observed on all three alloys investigated, with the manganese-silicide coating appearing best. The healing of defects appears associated not only with the formation of a vitreous silica scale, but further requires that the scale have a sufficiently low viscosity that it is able to flow into and flux the oxide forming at the defect.

It is thus apparent that the protectiveness of silicide-base coatings on tantalum is significantly affected by additions both to the coating and to the substrate. Static and cyclic protection is improved by additions which promote the formation of vitreous silicate scales, while self-healing is promoted by further alloying to decrease the viscosity of the scale. Future research might profitably be directed toward study of these and other silicide and nonsilicide systems where glass-forming tendencies in the scale may logically be expected.

CONCLUSIONS

The major conclusions from the current study may be summarized briefly as follows:

(1) Silicide and silicide-base coatings appear most attractive for protecting tantalum up to at least 2700 F, based on oxidation behavior of coated samples and prevention of substrate hardening.

(2) Coatings based on Al_2O_3, chromium, hafnium, titanium, and zinc are less attractive than silicide coatings.

(3) The cyclic and static oxidation resistance of silicide-base coatings may be improved by addition of manganese to the coating or of vanadium, columbium, or tungsten to the base. These promote vitrification of the silicate scale produced on exposure.

(4) Self-healing silicate scales are produced on exposure of silicide-coated alloys containing vanadium, columbium, or tungsten, all of which form low-melting oxides. Manganese additions to the silicide coating on these alloys further improve the self-healing abilities.

(5) The growth of coatings applied by the pack-cementation process is controlled by interdiffusion of the coating with the substrate, provided that supply of the coating element(s) as volatile halide(s) at the coating surface is sufficient. The choice of carriers for given coating element(s) is related to the thermodynamic stabilities and volatilities of the pertinent halides.

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Data on which this report is based are contained in Battelle Laboratory Record Books Numbers 16943, 17486, 17689, 17757, 17834, 17872, 18034, 18136, and 18586.

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