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COATINGS FOR TANTALUM-BASE ALLOYS

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(Prepared under Contract No. AF 33(657)-7909
by Battelle Memorial Institute, Columbus, Ohio;
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FOREWORD

This report was prepared by Battelle Memorial Institute under USAF Contract No. AF 33(657)-7909, BPS No. 62(6899-7312)-731201. 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 January 1 through December 31, 1962.

ABSTRACT

Silicide coatings, applied by pack cementation, were evaluated on a variety of tantalum alloys including Ta-10W, Ta-30Cb-7.5V, and Ta-8W-2Hf. Modification of the silicide, by diffusion with the underlying substrates, resulted in significant differences in oxidation behavior. Similar effects were obtained by incorporating aluminum, boron, and manganese additions in the silicide coating. Of the modifiers studied, vanadium was found to be most beneficial in improving the protective life of silicide coatings at low as well as high temperatures. Straight silicide coating of Ta-30Cb-7.5V alloy had no detrimental effect on room-temperature properties and provided useful lives in dynamic as well as static oxidation testing at temperatures to 3000 F. Modifications of the silicide with boron and vanadium show further improvements in static oxidation performance at temperatures from at least 1800 through 2900 F.

This technical documentary report has been reviewed and is approved.

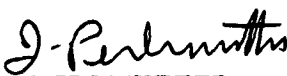

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INTRODUCTION

This report describes the work done during the second of 2 years of development of protective coatings for tantalum-base alloys. The first year's work* was initiated with a literature survey to determine what coating systems had the best potential for protecting tantalum alloys. This was followed by an experimental program which explored some of the more promising coating systems and methods of application.** The best results during the first year's program were obtained with silicide coatings applied by the pack-cementation method. The protectiveness of these coatings was attributed to the formation of a glassy silicate scale. Furthermore, the degree of vitrification and protectiveness of the silicate scale was promoted by the presence, either as a component of the coating or alloy substrate, of elements forming low melting oxides, i. e., aluminum, boron, manganese, vanadium, tungsten, and molybdenum.

The second year's work was therefore concentrated on the optimization of silicide coatings modified with the most promising additions from the prior work: aluminum, boron, and manganese, using tantalum alloys of greatest current interest. These substrates included the Ta-10W, Ta-30Cb-7.5V, and Ta-8W-2Hf alloys.

Additional work included a survey of the effect of alloy substrate composition on the behavior of silicide coatings as well as experimentation with other potential glass-forming additions to silicide coatings.

SUMMARY

Two-cycle silicide coatings were applied to 17 tantalum-base alloys and their oxidation performance was evaluated by cyclic oxidation testing at 2700 and 1800 F. At 2700 F, the test results ranked the substrate additions in order of decreasing benefit as follows: vanadium, molybdenum, tungsten, and hafnium. At 1800 F, only those alloys containing vanadium were resistant to failure in 100 hours of cyclic exposure.

Silicide coatings, both straight and modified with various amounts of aluminum, boron, manganese, vanadium, or chromium, were applied to Ta-10W, Ta-30Cb-7.5V, and Ta-8W-2Hf alloy substrates using a two-cycle, pack-cementation technique. Six combinations, Si-Mn and Si-V on Ta-10W, Si and Si-B on Ta-30Cb-7.5V, and Si and Si-Mn on Ta-8W-2Hf, showed 2700 F, cyclic oxidation lives ranging from 3 to 18 hours. Evaluation of these coating systems at 1800 F again showed the beneficial effects of vanadium on extending oxidation lives to at least 100 hours. The combination of boron with vanadium in the modified silicide coating on Ta-30Cb-7.5V showed outstanding resistance at both 1800 and 2700 F.

* "Development of Protective Coatings for Tantalum-Base Alloys", Battelle Memorial Institute, ASD Technical Report 61-676 on Contract No. AF 33(616)-7184, March, 1962.

**Aluminide and beryllide coatings for tantalum alloys were excluded from study since these were investigated separately on a complementary program at the General Telephone and Electronics Laboratories under Contract No. AF 33(616)-7462.

Manuscript released by the authors 28 February 1963 for publication as an ASD technical documentary report.

Application of the Si-V and Si-B coatings to Ta-10W and Ta-30Cb-7.5V, respectively, resulted in bend embrittlement of the substrate. Evidence found later indicates that the embrittlement of the Ta-10W occurred as a result of calcium contamination.

The straight Si coating on the Ta-30Cb-7.5V alloy was further characterized by furnace oxidation, torch, and tensile testing. This coating system had an oxidation life of >100 hours at 1200 to 2200 F except at 2000 F where oxidation failure occurred in 25 to 50 hours. Average lives of 8 and 13 hours were achieved at 2700 and 2900 F, respectively. Coated samples also survived ten 1/2-hour cycles in torch tests at 1800, 2500, and 2700 F, and two cycles at 3000 F. Tensile tests showed that the coating was not detrimental to room-temperature properties and was also protective during 1-1/2 per cent deformation at 2200 F.

MATERIALS AND PROCEDURES

Alloy Substrate Materials

Three tantalum alloy sheet substrates were used extensively in the program. These include the commercial Ta-10W alloy and two advanced experimental alloys, Ta-30Cb-7.5V and Ta-8W-2Hf.

The Ta-10W alloy was purchased from the National Research Corporation (NRC) as 40-mil-thick sheet. The Ta-30Cb-7.5V alloy was also acquired from NRC, but was in the form of two 1/2-inch-thick forged slabs having a Bhn of 232 to 248. The slabs were vacuum annealed 1 hour at 2400 F and rolled at 800 F, in air, to 40-mil thickness at Battelle.

The Ta-8W-2Hf alloy was received as 20-mil-thick sheet from the Westinghouse Research Laboratories.

Chemical analyses on the three substrate alloys are given in Table 1 which show that the actual composition of each alloy is close to the intended values.

TABLE 1. CHEMICAL ANALYSES OF TANTALUM-BASE ALLOY
SUBSTRATE MATERIALS

Element	Composition, weight per cent		
	Ta-10W ^(a)	Ta-30Cb-7.5V ^(b)	Ta-8W-2Hf ^(a)
Tungsten	9.6		7.5
Columbium	--	31.1	--
Vanadium	--	5.9	--
Hafnium	--	--	1.8
Carbon	0.0014	0.005	--
Oxygen	0.0050	0.0143	0.0018
Nitrogen	0.0036	0.009	0.0039
Chromium	<0.0010	--	--
Copper	<0.0005	--	--
Molybdenum	<0.0040	--	--
Iron	0.0012	--	--
Hydrogen	--	0.00034	--

(a) Supplier's analysis.

(b) Battelle's analysis.

The substrate material used for the study of the effect of substrate composition in Phase 2 consisted of the shoulder sections of broken tensile sheet specimens generated by the work on Contract No. AF 33(616)-7688.

Procedures

Three sizes of specimens were used. These included 1/2 by 3/4-inch tab samples for cyclic and static oxidation tests, 1/2 by 2-inch blanks for torch tests, and tensile test blanks approximately 1/2 by 3 inches. For each type of sample, all corners were machined to a 1/8-inch radius, surfaces ground through 400 grit, and edges and corners carefully rounded. All specimens were brightened and smoothed by pickling in a nitric-sulphuric-hydrofluoric-acid solution and then vacuum annealed to effect recrystallization, i. e., 1 hour at 2200 F for the Ta-30Cb-7.5V alloy, and 1 hour at 2700 F for the Ta-10W and Ta-8W-2Hf alloys.

Samples were coated in sets of three in mild steel cans 2 inches in diameter and 1-1/4 to 5 inches long, depending on specimen length. Pack compositions varied* but consisted generally of 10 to 40 weight per cent coating element, 0.5 to 3 weight per cent halide carrier, with the balance of -100 + 140 mesh Al_2O_3 . Caps were held on the cans with a friction fit and a small hole was punched in one end to relieve any pressure generated during heat up.

The packs were heated in a horizontal tube furnace under a flow of argon. Where two or more coating cycles were used, a fresh pack mix was used for each cycle.

For cyclic furnace oxidation tests at 1200 to 2900 F, coated specimens were laid across the upper edges of zirconia boats, heated in still air in an electric furnace at test temperature for a given time, cooled to room temperature, weighed, turned over, and then returned to the furnace for the next cycle. Specimens were considered failed when they showed rapid localized oxidation. Length of the exposure cycles varied from 1 to 25 hours, with the longer times being used at lower temperatures.

Static furnace oxidation tests consisted of uninterrupted exposure at 2700 F with continuous automatic recording of weight change. Specimens were considered failed when a sharp upward inflection occurred in the weight-gain curve.

Defect resistance was tested by ultrasonically drilling a hole through the coating on one side of the specimen to expose the substrate. Two sizes of defect were used, these being 0.040 and 0.020 inch in diameter.

EFFECT OF ALLOY SUBSTRATE COMPOSITION ON OXIDATION PERFORMANCE OF SILICIDE COATINGS

Eighteen alloy substrates were coated with two-cycle, unmodified silicide coating and screened for oxidation performance in 2700 and 1800 F cyclic testing. The latter

*Pack compositions for all coating runs are detailed in Appendix I.

temperature was of interest as this was the temperature at which accelerated failures had occurred in silicide coatings tested on the previous contract.

In preparing these samples, the pack mix consisted of 48 grams of Al_2O_3 , 10 grams of silicon, and 1 gram of NaF. Two cycles, consisting of 4 and 12 hours each, were used at 2000 or 2200 F.

As a means of control in coating preparation, it was of some interest to study the correlation of coating thickness to unit coating weight. This was done for a variety of tantalum substrates coated with both straight and modified silicides. Representative data from these samples are cross plotted in Figure 1. These data show a linear relationship with a coating weight of 5 to 6 mg/cm^2 being equivalent to 1 mil of coating thickness.

Oxidation Behavior

Initially, 9 of the 18 alloys were coated at 2000 F and had coatings 1.5 to 2.6 mils thick. Since these coating thicknesses were less than desired, additional samples of these and the 9 remaining alloys were coated at 2200 F. As noted in Table 2, this resulted in coating thicknesses ranging from 3.2 to 6.0 mils. Table 2 lists the coating thicknesses and 2700 F cyclic lives obtained on both sets of samples. Within the two sets of coating thicknesses, the alloys are listed in order of decreasing life in the 2700 F cyclic test.

As shown by these data, in almost every instance doubling the coating thickness generally increased the cyclic 2700 F oxidation resistance by at least twofold. By prolonging life at 2700 F, the thicker coatings served better to differentiate the effects of the various substrate additions. The general effects of substrate composition on the oxidation resistance are illustrated in Figure 2.

On the basis of binary additions, the test results gave a ranking of substrate additions in order of decreasing benefit as follows: vanadium, molybdenum, tungsten, and hafnium. Hafnium could probably be considered detrimental since, on the basis of prior work, unalloyed tantalum with the same coating would be expected to have a life of 2 to 2-1/2 hours in this test. Five of the six alloys containing hafnium had lives shorter than this.

In the ternary combinations, the results generally agreed with the effects shown by the binary additions. Thus, the longest lives were obtained with the vanadium-molybdenum and vanadium-tungsten substrates, with alloys containing tungsten and molybdenum also showing a significant degree of improvement. Again, ternary combinations of hafnium with molybdenum or tungsten had less resistance to oxidation than unalloyed tantalum.

The curves showing weight gain versus time at 2700 F for these coated samples fell into two different types. Thus, the curves for the Ta-5Mo-5V and Ta-30Cb-7.5V alloys were parabolic, showing total weight gains on the order of 2 to 4 mg/cm^2 after 5 to 10 cycles. Also, specimens of both of these alloys had a definite over-all glassy appearance. The curves for the other alloys were generally linear and showed weight

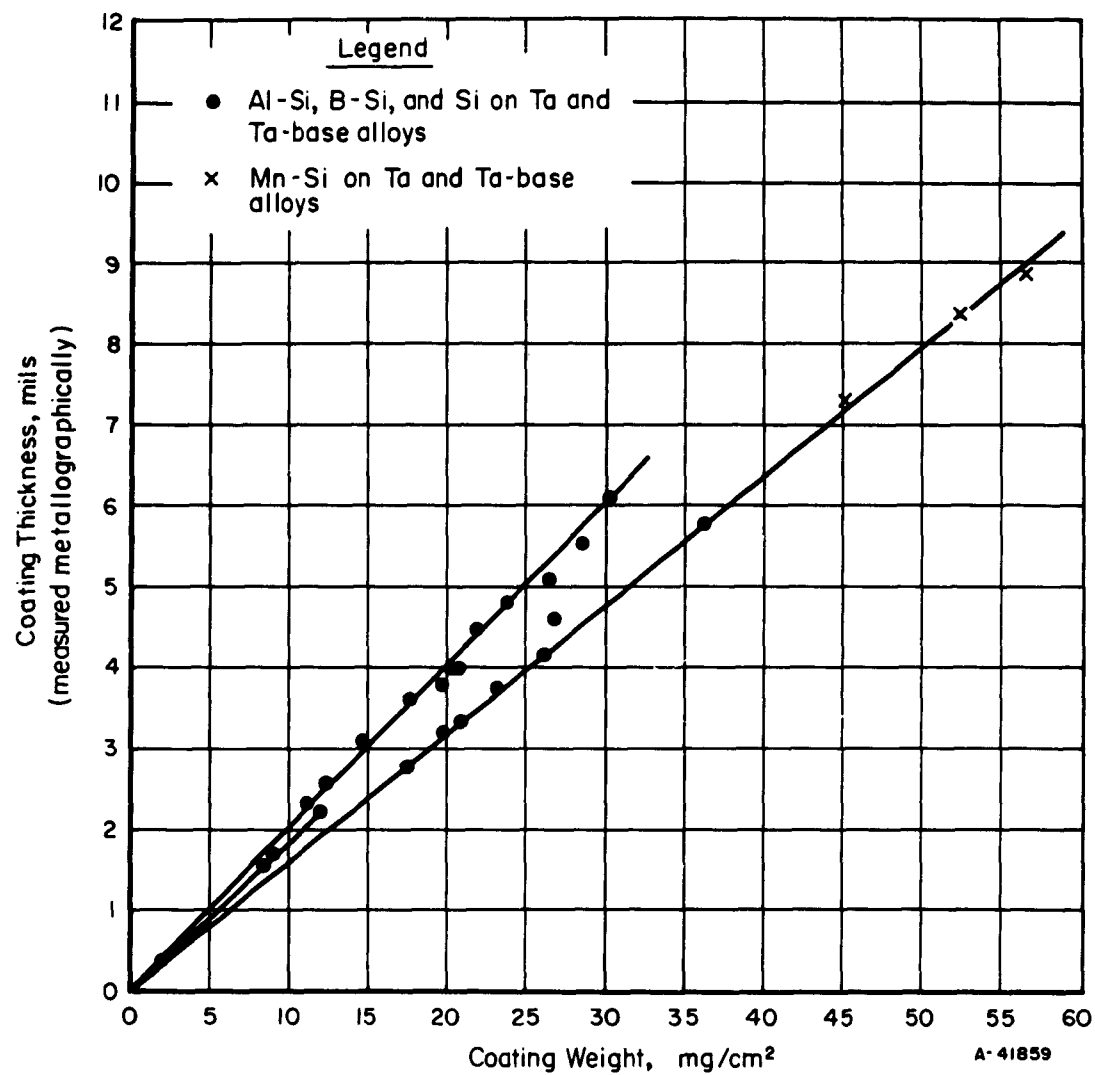


FIGURE 1. COATING THICKNESS VERSUS UNIT WEIGHT FOR SILICIDE COATINGS ON TANTALUM AND TANTALUM-BASE ALLOYS

TABLE 2. EFFECT OF SUBSTRATE COMPOSITION ON OXIDATION RESISTANCE OF TWO-CYCLE SILICIDE COATINGS

Substrate Alloy Content, weight per cent				Tested at 2700 F			Tested at 1800 F		
				Total Coating Weight, mg/cm ² (a)	Coating Thickness, mils./side(b)	Cyclic Oxidation Life, hours(c)	Total Coating Weight, mg/cm ² (a)	Cyclic Oxidation Life, hours (d) (Individual Specimens)	
V	Mo	W	Hf						
Unalloyed tantalum									
5	5	--	--	22.1	--	--	2.5(e)	16.1	25 to 52, 25 to 52
7.5	--	30Cb	--	26.5	4.6	5, 11	8	24.8	>100, >100
5	--	5	--	19.7	3.8	3, 9	6	25.2	>100, >100
5	--	--	--	20.8	4.0	5, 5	5	28.9	52 to 75, >100
5	--	--	--	20.5	4.0	4, 5	4.5	21.4	>100, >100
--	5	--	--	26.4	5.1	4, 4	4	--	--
--	2.5	10	--	23.9	4.8	4, 4	4	28.1	8 to 25, 25 to 30
--	5	7.5	--	30.1	5.6	4, 4	4	18.6	3 to 8, 3 to 8
--	5	5	--	26.1	4.9	3, 4	3.5	29.4	3 to 8
5	--	10	--	18.9	3.2	3, 3	3	30.2	3 to 8, 25 to 52
--	--	--	--	27.5	6.0	3, 3	3	--	--
--	10	--	--	24.7	5.5	3, 3	3	27.4	3 to 8, 3 to 8
--	--	5	5	24.6	4.6	3, 3	3	--	--
--	--	5	--	20.4	4.6	2, 2	2	19.4	3 to 8, 8 to 25
--	7.5	--	5	27.8	--	1, 1	1	--	--
--	5	--	5	16.3	3.8	<1, <1	<1	--	--
--	--	--	5	17.3	3.8	<1, <1	<1	--	--
--	--	5	10	24.2	4.6	<1, 1	<1	--	--
--	--	10	5	22.9	4.6	<1, 1	<1	--	--
Coated at 2000 F									
--	5	7.5	--	11.2	2.3	2, 2	2	--	--
5	--	5	--	9.2	1.7	2, 2	2	--	--
--	2.5	10	--	12.3	2.6	2, 2	2	--	--
5	5	--	--	11.0	2.4	2, <1	1	--	--
--	--	10	5	9.1	1.8	<1, 2	1	--	--
--	5	5	--	9.4	1.5	1, <1	<1	--	--
--	5	--	--	10.4	2.2	<1, <1	<1	--	--
--	10	--	--	8.5	1.6	<1, <1	<1	--	--
--	7.5	--	5	9.6	2.0	<1, <1	<1	--	--

(a) Average of two specimens.

(b) Measured metallographically on one specimen.

(c) Number of 1-hour periods survived.

(d) Times denote the period during which failure occurred.

(e) Data from prior contract, No. AF 33(616)-7184; average of four specimens

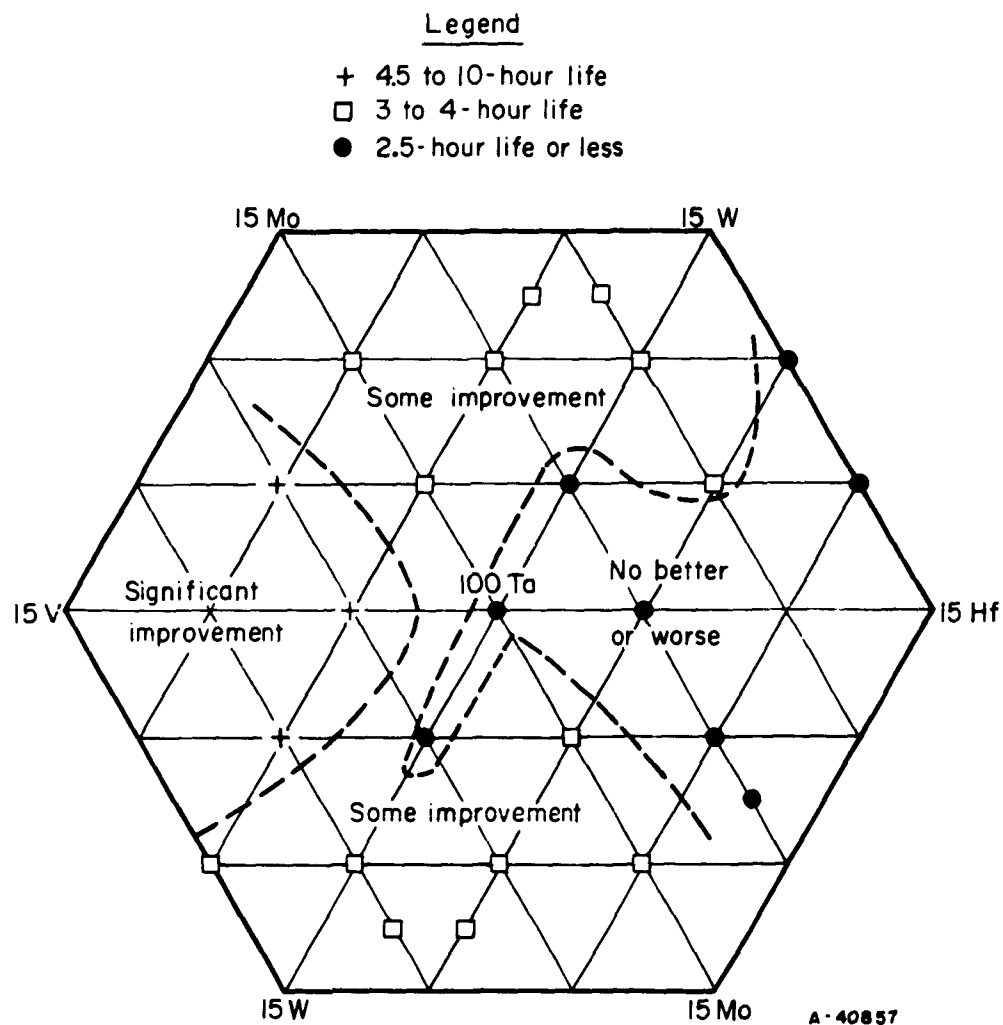


FIGURE 2. EFFECT OF SUBSTRATE COMPOSITION ON THE 2700 F CYCLIC OXIDATION LIFE OF SILICIDE-COATED TANTALUM

gains ranging from 1 to 3 mg/cm²/hr for those samples which survived three or more cycles. Most of these samples, including unalloyed tantalum and the ternary alloys containing hafnium, showed some evidence of glass formation. This tendency, however, was not shown in the silicide-coated Ta-5Hf alloy which developed a flaky, nonadherent oxide on exposure at 2700 F.

The extremely beneficial effect of vanadium in the substrate on improving 1800 F cyclic life is immediately apparent on inspecting Table 2. Thus, four vanadium-bearing alloys (including Ta-5V, Ta-5V-5Mo, Ta-5V-5W, and Ta-30Cb-7.5V) were the only samples to resist accelerated oxidation failure at this temperature. Also, seven of the eight samples representing these four alloys survived the full 100-hour exposure.

Weight-gain curves for these particular alloy samples are illustrated in Figure 3. Each of the curves, excepting those for the Ta-30Cb-7.5V alloy, are characterized by an initially rapid weight gain within 24 hours' exposure after which the weight remained essentially constant. The total weight gains shown by these samples after 100-hour exposures were also quite low (2 to 5 mg/cm²). By comparison, the curves for the Ta-30Cb-7.5V alloy were parabolic in nature over the 100-hour period and both samples showed slightly higher total weight gains (14 to 15 mg/cm²). Subsequent rechecks on other silicide-coated Ta-30Cb-7.5V alloy samples have not only confirmed this type of behavior at 1800 F but further indicate it is unique to this coating system. Thus, three of six samples tested gave 1800 F weight-gain curves which agreed well with the cubic relationship $m^3 = kt$, where m represents the weight gained (mg/cm²) in time, t (hours).

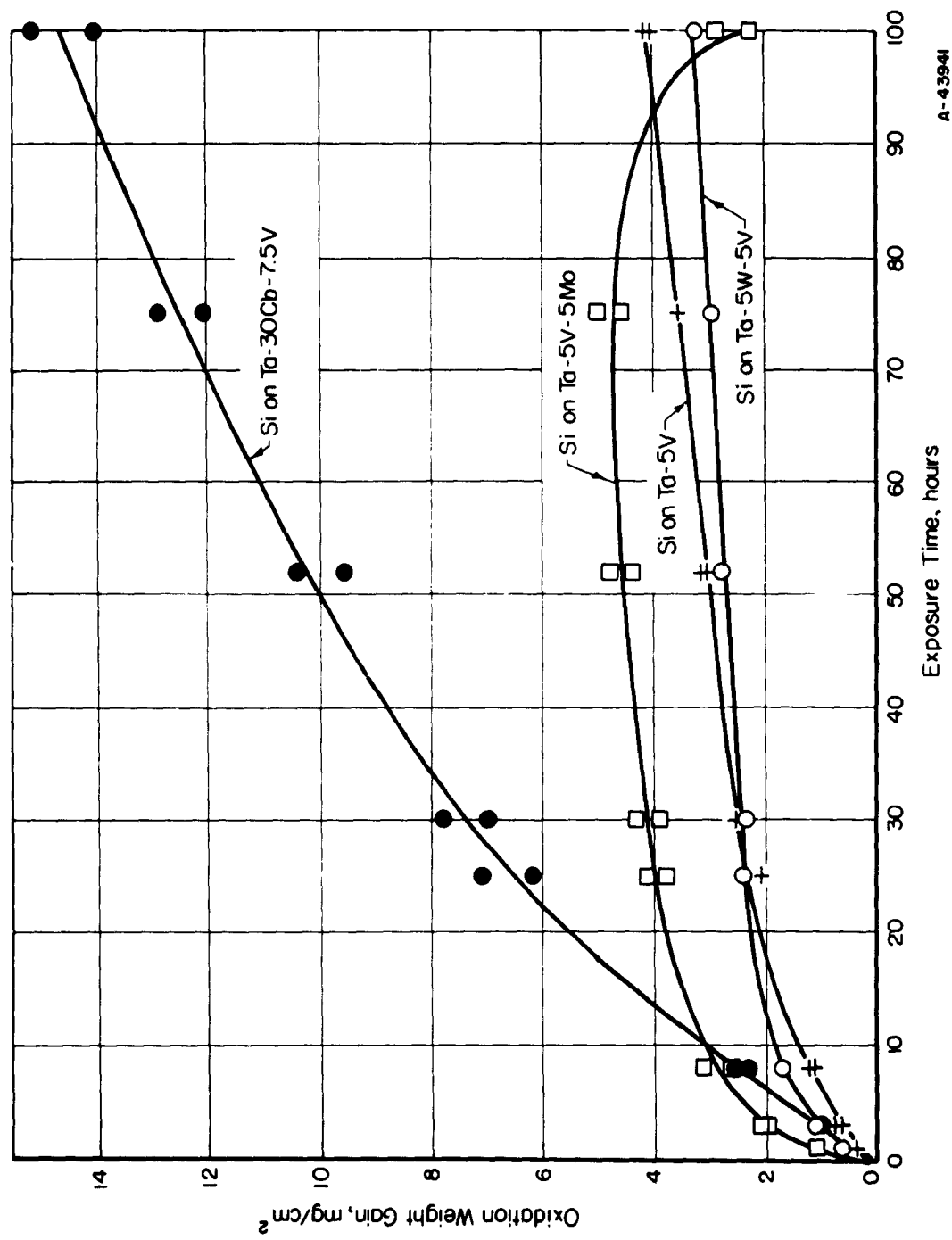
The fact that, of the vanadium-bearing alloys to survive the 100-hour 1800 F exposure, the Ta-30Cb-7.5V alloy was the only one to show a continuous weight gain strongly suggests this characteristic results from the moderately high columbium content of the alloy. It is perhaps significant to note that, of the four alloys to survive 100 hours' exposure at 1800 F, none contained molybdenum on tungsten in excess of 5 per cent. By comparison, the balance of the alloys which included Ta-5V-10W and various binary and ternary combinations of molybdenum and tungsten were subject to accelerated failure at 1800 F.

Metallography and Microprobe Analyses

In the as-coated condition, simple coating structures, of the type illustrated in Figure 4a, for unalloyed tantalum, were obtained on all of the alloy substrates containing binary and ternary combinations of tungsten, molybdenum, and vanadium. More complex appearing coating structures were observed on the Ta-30Cb-7.5V alloy and all of the alloys containing hafnium (Figures 5 and 6).

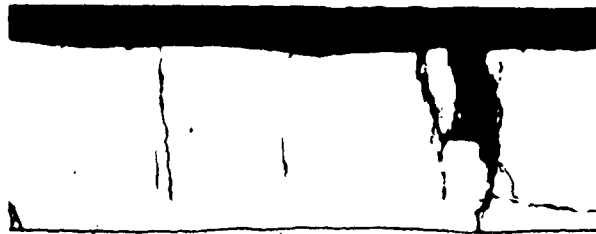
Electron beam microprobe analyses were conducted on selected specimens to aid in phase identification as shown in Table 3.

As coated, the thick silicide layer on unalloyed tantalum showed a silicon gradient ranging from a stoichiometric ratio of TaSi_{2.4} at the interface to TaSi_{2.8} near the edge. X-ray diffraction studies carried out during last year's work on a similarly prepared sample had structurally identified this phase as TaSi₂. Inasmuch as the present analyses



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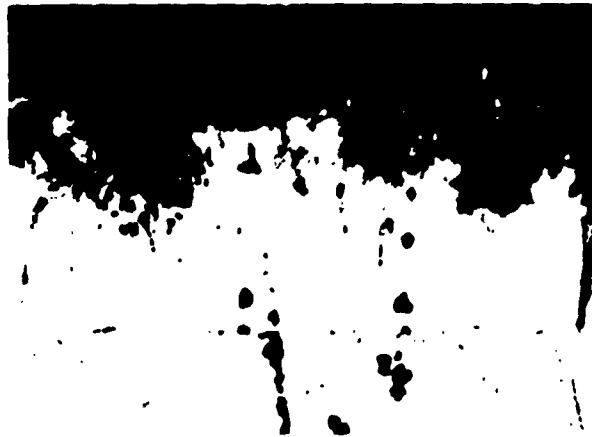
FIGURE 3. 1800 F CYCLIC OXIDATION WEIGHT GAINS OF SILICIDE-COATED TANTALUM-BASE ALLOYS



500X

N90836

a. As Coated at 2000 F (Sample No. 7)



500X

N90838

b. After Two 1-Hour Oxidation Cycles at 2700 F (Sample No. 8)

Note: Dark areas in lower center portion mark the sites of microprobe analyses.

FIGURE 4. TWO-CYCLE, UNMODIFIED SILICIDE COATING ON UNALLOYED TANTALUM



500X

N92956

a. As Applied (Specimen 536)

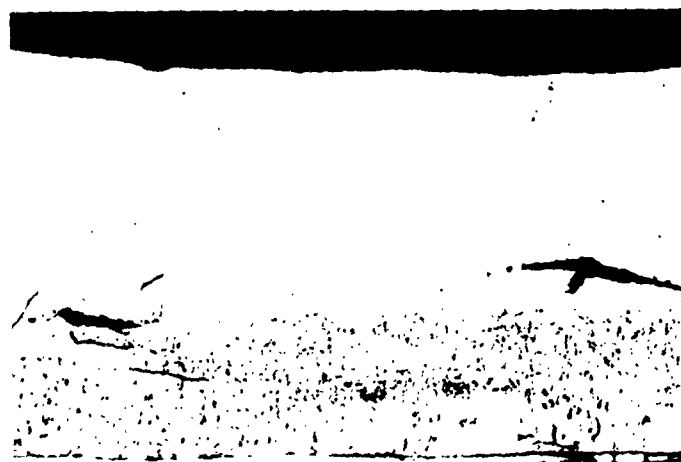


500X

N90832

b. Oxidized Ten 1-Hour Cycles at 2700 F (Specimen 51)

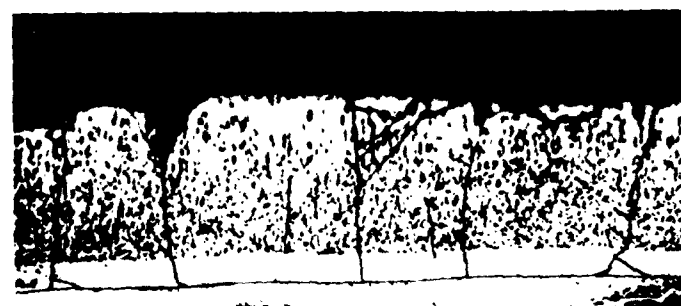
FIGURE 5. TWO CYCLE, UNMODIFIED SILICIDE COATINGS ON Ta-30Cb-7.5V, AS APPLIED AND AFTER OXIDATION AT 2700 F



500X

N90849

a. As Coated at 2200 F (Sample No. 76)



500X

N90851

b. After One 1-Hour Oxidation Cycle at 2700 F (Sample No. 77)

FIGURE 6. TWO-CYCLE, UNMODIFIED SILICIDE COATING ON Ta-10W-5Hf

TABLE 3. ELECTRON-BEAM MICROPROBE ANALYSES OF SILICIDE COATINGS ON TANTALUM AND TANTALUM ALLOYS

Nominal Substrate Composition, weight per cent	Condition	Element	Microprobe Analyses (a)							
			Substrate		Near Interface,		Near Interface		Coating	
			Center, weight per cent	Near Interface, weight per cent	Element	weight per cent	Weight Per Cent	Atomic Per Cent	Weight Per Cent	Atomic Per Cent
100Ta	As coated	Ta	100	100			73.3(b)	29.2	70.2(b)	26.4
		Si	0	0			27.7(b)	70.8	30.6(b)	73.6
Ta-30Cb-7.5V	Oxidized 1 hour at 2700 F	Ta	100	100			90.4(c)	69.5	72.4(d)	30.0
		Si	0	0			6.2(c)	30.5	26.4(d)	70.0
		Ta	61	61			50.3(c)	20.9	40.6(d)	11.8
		Cb	30.4	30.4			21.9(c)	17.8	19.3(d)	10.9
Ta-10W	As coated	V	7.1	7.1			7(c)	10.8	3.8(d)	3.9
		Si	0	0			19(c)	50.9	39.3(d)	73.4
		Ta	90	90			61.0(b)	22.3	61.0(b)	22.3
		W	10	10			7.4(b)	2.6	7.4(b)	2.6
Ta-5V	As coated	Si	0	0			32.0(b)	75.1	32.0(b)	75.1
		Ta	96.4	96.4			65.9(b)	25.0	65.9(b)	25.0
		V	2	2			1.2(b)	1.7	1.2(b)	1.7
		Si	0	0			32.0(b)	76.0	32.0(b)	76.0
Ta-10W-2.5Mo	As coated	Ta	87.6	87.6			62.6(b)	19.7	62.6(b)	19.7
		W	10.4	10.4			6.9(b)	2.1	6.9(b)	2.1
		Mo	2.6	2.6			2.1(b)	1.2	2.1(b)	1.2
		Si	0	0			37.9(b)	77.0	37.9(b)	77.0

(a) Values believed accurate to ± 2 weight per cent.

(b) Continuous single phase.

(c and d) Separate phases.

(in Table 3) are believed accurate to ± 2 weight per cent, it was not possible to reconcile the apparent disagreement in the stoichiometry of this phase as determined by these two methods of measurement. On high-temperature exposure, two subsilicide layers formed on the silicide-coated tantalum as illustrated in Figure 4b. The thickness (1 to 3 microns) of the lowest silicide layer adjacent to the substrate precluded microprobe analysis. However, the compositions of the two outer layers (given in Table 3) gave ratios of $\text{Ta}_{2.3}\text{Si}$ and $\text{TaSi}_{2.3}$ for the intermediate and outer layers, respectively. It was assumed that these phases corresponded to the accepted Ta_2Si and TaSi_2 phases. No evidence of the Ta_5Si_3 phase, which should appear as an intermediate layer to Ta_2Si and TaSi_2 , was found on this sample although admittedly an extremely thin layer of this phase could have escaped detection by the methods used.

The spot microprobe analyses (Table 3) of the silicide-coated alloy substrates led to the following observations:

- (1) During coating, each of the alloy substrate additions diffused into the silicide layers in about the same proportions as these occur in the substrate.
- (2) The thick "single-phase" coatings on the Ta-5V, Ta-10W, and Ta-10W-2.5Mo alloys and the outer silicide layer on the Ta-30Cb-7.5V alloy corresponded, stoichiometrically, to a modified TiSi_3 phase, i. e., $(\text{Ta}, 5\text{V})\text{Si}_{2.9}$, $(\text{Ta}, 10\text{W})\text{Si}_{3.0}$, $(\text{Ta}, 10\text{W}, 2.5\text{Mo})\text{Si}_{3.4}$, and $(\text{Ta}, 30\text{Cb}, 7.5\text{V})\text{Si}_{2.8}$.
- (3) The thin subsilicide layer formed on the Ta-30Cb-7.5V alloy has a ratio of $(\text{Ta}, 30\text{Cb}, 7.5\text{V})\text{Si}$ which probably corresponds to a modification of the Ta_5Si_3 phase.

Additional verification that the entire columnar structure in the outer silicide layer of the silicide-coated Ta-30Cb-7.5V alloy (Figure 5a) consisted of the single $(\text{Ta}, 30\text{Cb}, 7.5\text{V})\text{Si}_{2.8}$ phase was obtained by a microprobe traverse analysis across this phase.

NEW COATING SYSTEMS AND TECHNIQUES

Pack-Cementation Coatings

Nine metals, including cobalt, chromium, copper, iron, molybdenum, nickel, titanium, vanadium, and tungsten were selected as being of possible benefit as additions to silicide coatings. These metals were chosen on the basis of their tendency to form low-melting glasses (as determined by ceramic phase diagrams) and/or their observed effectiveness from the alloy substrate studies (i. e., V, Mo, and W).

Two series of two-cycle pack-cementation runs were made for each of the nine coating systems. In the first series, a silicide coating was applied initially in a 4-hour cycle and the various metals were applied later in a second 12-hour cycle. In the second series, initial coating with the metallic additions was attempted in the first 4-hour cycle.

Those samples successfully treated in this manner were subjected to a second, siliconizing cycle of 12 hours. In all instances, unalloyed tantalum was used as the substrate and 2200 F was used as the pack-cementation temperature. The coating data from these experiments are summarized in Table 4.

The attempts to deposit cobalt, copper, iron, molybdenum, nickel, and tungsten directly on tantalum were not successful, in that moderate to heavy weight losses (indicative of corrosive attack) resulted. On the other hand, thin coatings of chromium, titanium, and vanadium were obtained by this method.

Initially coating the tantalum with a silicide layer resulted in the apparent second-cycle transfer of appreciable amounts of cobalt, copper, iron, nickel, molybdenum, and tungsten, but not of chromium, titanium, or vanadium.

Visual and metallographic examination revealed that many of the coatings were partially oxidized, porous, or of extremely variable thickness, due to corrosive attack during deposition. The only coatings which exhibited any degree of integrity were those with cobalt and chromium over silicon and with silicon over cobalt, chromium, iron, titanium, and vanadium.

The following metallographic observations were made on these coatings:

Co over Si } Cr over Si }	Outer surface of silicide coating attacked
Si over Cr	0.1-mil-thick coating was deposited during the first cycle; the complete coating looked the same as unmodified silicide (single phase)
Si over Fe	0.6-mil-thick coating was deposited during the first cycle; the complete coating contained intermetallic phases at the interface and scattered through the coating
Si over Ti	0 to 0.2-mil-thick coating was deposited during the first cycle; complete coating looked the same as unmodified silicide (single phase)
Si over V	1-mil-thick, two-phase coating was deposited during the first cycle; complete coating had an intermetallic phase at the interface.

All of the two-cycle coatings were evaluated in 1-hour cyclic oxidation testing at 2500 F, with the results shown in Table 4. The only samples which survived a single cycle were the unmodified silicide controls and the vanadium- and chromium-modified silicide samples prepared by initially depositing silicon over vanadium and chromium. Each of these individual samples survived seven to nine cycles.

It was concluded from these experiments that pack-cementation coating techniques are not very favorable for the preparation of high-integrity, silicide coatings modifications containing copper, molybdenum, nickel, or tungsten. On the other hand, chromium- and vanadium-modified silicides, made by depositing the modifying element before siliconizing, offer some promise of obtaining improved oxidation resistance.

TABLE 4. TWO-CYCLE MODIFIED SILICIDE COATINGS ON UNALLOYED TANTALUM

Specimen Number	Coating Element	First Cycle (4 Hours at 2200 F)			Second Cycle (12 Hours at 2200 F)			Coating Thickness, mils/side(a)	2500 F Cyclic Life, hours(b)
		Carrier	Average Coating Weight Gain, mg/cm ²	Coating Element	Carrier	Average Coating Weight Gain, mg/cm ²	Total Coating Weight Gain, mg/cm ²		
94-95	Si	NaF	15.3	Co	NaCl	4.1	19.3	2.7	<1
97-98	"	"	13.1	Cr	KI	-6.5	6.7	2.5	<1
100-101	"	"	13.7	Cu	NaCl	17.2	31.0	2-3	<1
103-104	"	"	9.5	Fe	NaCl	13.4	23.1	1-2	<1
106-107	"	"	9.3	Mo	NaF	0.4	9.7	1-2	<1
109-110	"	"	8.9	Ni	NaCl	11.6	20.6	2	<1
111 & 113	"	"	9.7	Ti	NaF	-3.2	6.5	1-2	<1
114 & 116	"	"	8.9	V	NaF	-7.4	1.6	1.5	<1
118 & 119	"	"	8.3	W	NaF	15.0	23.2	0.1-1.4	<1
120-122	Co	NaCl	-24.3	Si	NaF	4.1	-14.2	2.6	<1
123-125	Cr	KI	0.7	Si	NaF	13.9	14.6	2.9	8-9
126-128	Cu	NaCl	5.6	(d)					
129-131	Cu	NaF	-25.3	(d)					
132-134	Fe	NaCl	-6.0	Si	NaF	26.3	20.8	0-15	<1
135-137	Mo	NaF	-33.0	(d)					
138-140	Ni	NaCl	-4.5	(d)					
141-143	Ti	NaF	0.9	Si	NaF	18.3	19.2	3.5	<1
144-146	Ti	NaI	0.4	(d)					
147-149	V	NaF	1.1	Si	NaF	20.3	21.5	3.2-4.5	7
168-170	W	NaF	-23.1	(d)					
171-173	W	NaCl	-0.5	Si	NaF	-4.7	-5.4	0.0-3.2	<1
175	Si	NaF	8.9	Si	NaF	5.3	14.2	2.5-3.0(c)	8-9

(a) Measured metallographically.

(b) One specimen tested.

(c) Estimated.

(d) Metallographic examination revealed that the tantalum had been attacked and no coating deposited.

These results with vanadium are consistent with the beneficial effects observed for vanadium introduced to the silicide via the substrate composition, as described earlier.

Paint and Sinter Techniques

A limited amount of work was done on the development of paint and sinter techniques for the application of silicide coatings. This included the evaluation of paint vehicles and experiments with various sintering conditions and coating compositions.

Three paint vehicles, collodion, lacquer, and glyptol resin, were used and applied by dipping, brushing, or spraying. For the initial purpose of vehicle evaluation, the only metal used in the coating was silicon. The specific mixtures and the methods of application feasible for each were as follows:

<u>Coating Mixture</u>	<u>Methods of Application</u>
(1) 10 cc collodion 5 cc methyl alcohol 10 g -200 mesh silicon	Dip and brush
(2) 100 cc lacquer 20 g -200 mesh silicon	Dip, brush, and spray
(3) 2 g white glyptol resin 7 cc diacetone alcohol 3 cc acetone 5 g -200 mesh silicon	Dip and brush

Each of the above combinations was used to produce coatings on 1/2 by 3/4-inch tab specimens of unalloyed tantalum. It was found necessary to use a rough surface to achieve adhesion of any of the coatings, so all specimens were ground to an 80 grit finish. After air drying, coating quality was rated on the basis of coating thickness and uniformity, edge and corner coverage, adhesion, and resistance to flaking and chipping. On the basis of the above criteria, the sprayed lacquer coatings appeared best. Dipping required the use of a supporting wire hook, and the resulting defect was considered detrimental to coating quality, even if touched up. Brushing produced coatings less uniform than sprayed coatings.

Coated specimens, both air dried and baked 1 hour at 400 F, were subjected to vacuum sintering treatments of 1 hour at 1900 or 2200 F. Specimens were charged into a tube furnace, the tube evacuated, heated to temperature in 2-1/2 to 3 hours, held for 1 hour, and furnace cooled. All the coatings flaked off and there was no significant diffusion reaction between the coatings and the substrate. The lack of adhesion was attributed to the evolution of gas from the paint vehicle during either evacuation and/or heat-up.

A subsequent experiment was designed to include the following process modifications:

- (1) Addition of metallic elements to the coating to produce liquid phases during the sintering operation to improve adhesion and diffusion between coating and substrate
- (2) Rapid heating rates to minimize flaking of the coating
- (3) A hydrogen atmosphere to reduce surface oxides on both the metal powders in the coating and on the substrate.

The coating mixtures chosen were:

16 g Si + 2 g V + 2 g Al/100 cc lacquer

16 g Si + 2 g V + 2 g Mn/100 cc lacquer

The metallic constituents were chosen on the basis of the beneficial effects demonstrated by V and Mn as modifiers for silicides in concurrent phases of this program as well as to produce liquid phases at the 2200 F sintering temperature, i. e., liquid aluminum or the Si-Mn eutectic.

Duplicate specimens of each coating were sintered in vacuum, using a relatively rapid heating rate, about 2 minutes to reach 2200 F. As before, coatings were non-adherent and did not react with the substrate. Specimens were also sintered in hydrogen, a rapid heating rate being achieved by charging the specimens into a furnace which was at 2200 F. It was possible to observe these specimens during the sintering treatment, and initially the coatings appeared adherent. However, after 45 minutes of sintering, the specimens showed evidence of progressive oxidation. After withdrawing and rapidly cooling in air, the specimens were almost completely oxidized. This was attributed to the back diffusion of oxygen into the hydrogen.

Although this work was not carried further, it is believed that the last experiment met some of the requisites for achieving successful coatings. These include provision for liquid-phase sintering, a rapid heating rate and atmosphere conducive to reduction of surface oxides and the minimization of gas evolution from the paint vehicle.

OPTIMIZATION OF MODIFIED SILICIDE COATINGS

The purpose of this phase of the program was to refine and optimize silicide coatings, using various modifying additions, so as to determine the best modified silicide coatings for each of the three alloys - Ta-10W, Ta-30Cb-7.5V, and Ta-8W-2Hf. Aluminum, boron, manganese, vanadium, and chromium were the modifying additions used.

The optimization program was organized to first screen a relatively large number of coating variations using 2700 F cyclic oxidation performance to select the two most outstanding coatings for each substrate. These two coatings were then evaluated in more detail to aid in the selection of an optimum coating for each substrate for advanced property evaluations.

Preliminary Screening

Five to six coatings were applied to each of the three alloy substrates as designated below.

Coating	Substrate Material		
	Ta-10W	Ta-30Cb-7.5V	Ta-8W-2Hf
Si	X	X	X
Al-Si	X	X	X
B-Si	X	X	X
Mn-Si	X	X	X
V-Si	X	--	X
V-B-Si	X	--	X
Cr-Si	--	X	--

In applying these coatings, a thickness of 3 to 5 mils per side was arbitrarily fixed as a target value. These thicknesses correspond, respectively, to total weight gains of 17 to 28 mg/cm². Thus, in order to explore wide ranges of composition for each of the silicide modifiers, coating times and/or temperatures were adjusted to meet these weight-gain values.

In all instances, two coating cycles were used to apply the coatings. Also, in line with experiences cited in a previous section of this report, the modifying elements were deposited in the first cycle with silicon being added in the second cycle.

Initially, the same carriers, coating times, and temperatures were used to apply a given coating to each of the alloy substrates. Table 5 summarizes the carriers, coating times, and temperatures used to apply the various silicide modifications. In most instances, the conditions cited in Table 5 were successful in achieving good-appearing coatings of the desired thickness. Some differences in deposition behavior

TABLE 5. SUMMARIZED COATING CONDITIONS FOR PREPARING MODIFIED SILICIDE COATINGS ON Ta-10W, Ta-30Cb-7.5V, and Ta-8W-2Hf SHEET^(a)

Coating System	First Cycle				Second Cycle ^(b)	
	Coating Element	Carrier	Time, hours	Temperature, F	Time, hours	Temperature, F
Si	Si	NaF	4	2200	12	2200
Si-Al	Al	KI	3/4 to 13-3/4	2200	14 to 24	2200
Si-B	B	NaF	3/4 to 13-3/4	1800	4 to 24	2200
			4	2200	4 to 8	2400
Si-Mn	Mn	NaF	2 to 12	1800	6 to 12	2200
Si-V	V	NaF	4 to 8	2400	12	2200
	V	NaCl	4 to 6	1800-2400	12	2200
Si-V-B	V-B	NaF	4 to 8	2400	12	2200

(a) See Appendix I for complete coating data on each alloy substrate.

(b) Second cycle consisted of applying silicon only using NaF as a carrier.

were observed with these coating systems. These are discussed separately in the pertinent sections of this report which follow. In addition, some generalizations on the application of modified silicide coatings to these alloy substrates are given in Appendix II.

Coatings on Ta-10W

In the as-coated condition, unmodified silicide coatings on Ta-10W exhibited a simple structure which consisted essentially of a thick outer layer of tantalum silicide with a thin (2 to 4 microns thick) underlayer of a subsilicide between the outer layer and the substrate. During oxidation, this system was characterized by the simultaneous formation of both glassy and porous, granular oxidation products. These coatings showed relatively rapid weight gains, as illustrated in Figure 7. Also, as shown in Table 6, the 2700 F cyclic oxidation life of the straight silicide coating on Ta-10W was moderately short, ranging from 2 to 4 hours.

The aluminum-modified silicide coatings on this alloy showed evidence of modification in that an additional phase, tentatively identified as an oxide, appeared in the outer zone of the coating at aluminum levels above 20 atom per cent (see Figure 8). This phase increased with increasing aluminum content above this level. This coating showed enhanced glass-forming tendencies relative to the straight silicide, but the glass did not prevent the eventual formation of porous oxidation products and general breakdown of the coating. The copious glass formed on these specimens tended to stick to the supporting boats, making weight-gain measurements erratic. One of the more consistent sets of weight-gain data, plotted in Figure 7, shows a slightly lower rate of increase than the straight silicide. Oxidation life, however, was not significantly different from that for the unmodified silicide.

The performance of the boron-modified silicide coating on Ta-10W was affected by difficulties in deposition. The thinner (1 to 2 mil thick) coatings were uniform in thickness and consisted of several layers, as shown in Figure 9. Increases in time and temperature for deposition of both boron and silicon were made in attempts to obtain coatings of greater thickness. This, however, resulted in a nonuniform microstructure, an example of which is shown in Figure 10. Although short-lived, this coating had a low rate of weight gain in oxidation and formed a thin uniform film of glass over the original coating on exposure at 2700 F.

The manganese-modified coatings on Ta-10W were slightly thinner and somewhat lower in manganese content than originally desired. Manganese modification of the silicide resulted in the complex coating illustrated in Figure 11. During oxidation, a brownish, vitreous scale formed which, in some cases, caused the specimens to stick to the supporting boat. The weight-gain data shown in Figure 7 were obtained from a specimen which showed no evidence of reaction with the boat. The longest 2700 F oxidation lives (3 and 5 hours, see Table 6) were obtained on coatings containing nominally 11 to 12 per cent manganese. However, the lives of these coatings were attributed more to their increased thickness than to manganese content since the coatings for samples of slightly lower and higher manganese content were only half as thick. On the basis of the low weight gains and good glass-forming tendencies, as well as the outstanding defect resistance demonstrated by this system in the prior year's work, this system was chosen for further evaluation.

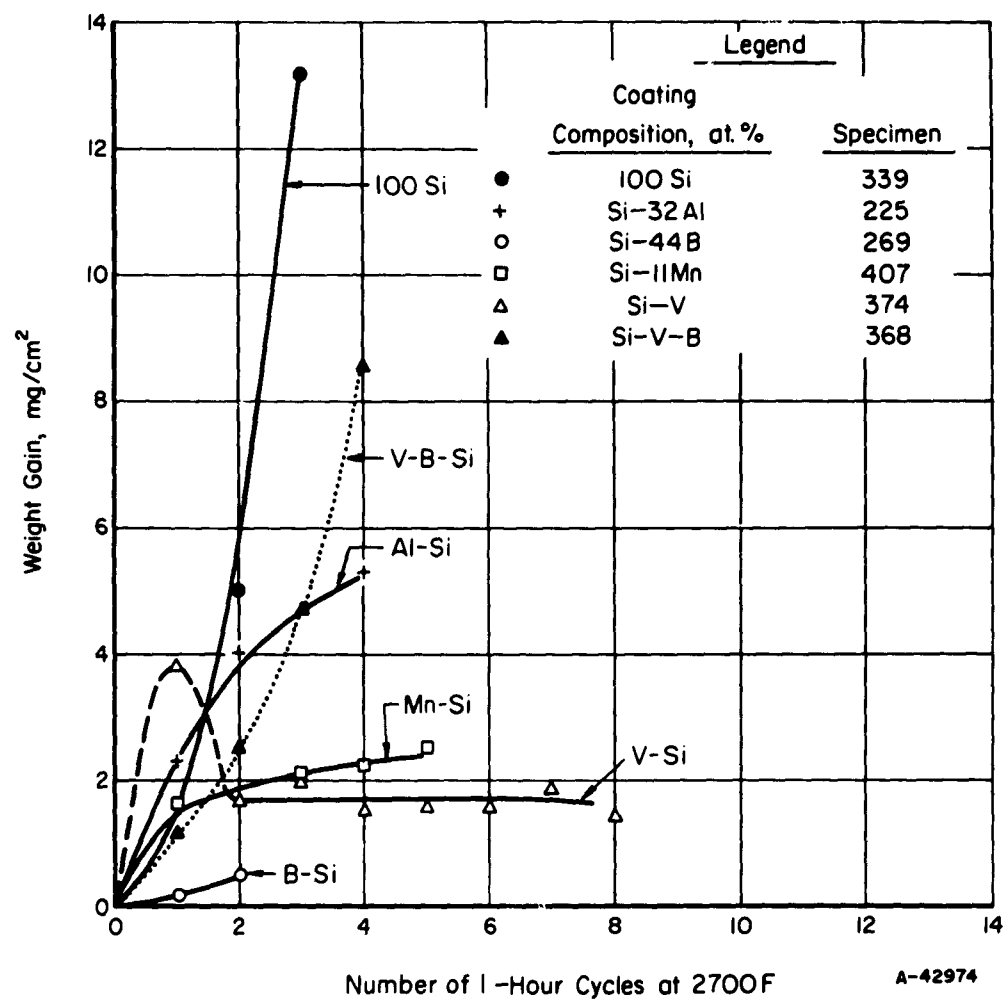


FIGURE 7. 2700 F CYCLIC OXIDATION WEIGHT GAINS OF MODIFIED SILICIDE COATINGS ON Ta-10W

TABLE 6. 2700 F CYCLIC OXIDATION LIVES OF MODIFIED SILICIDE COATINGS ON Ta-10W

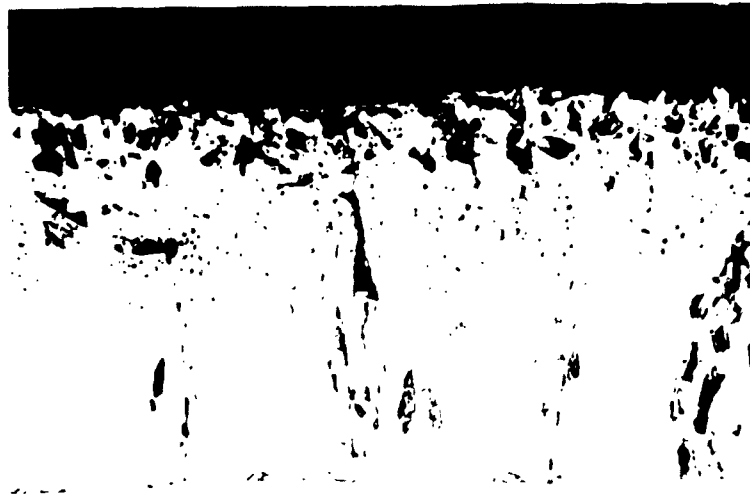
Coating System	Calculated Modifier Content ^(a) , at.% (Balance Si)	Coating Thickness ^(b) , mils/side	2700 F Cyclic Oxidation Life ^(c) , hours (Individual Specimens)
Si	0	4 to 5	2, 3, 3, 3, 4, 4
Si-Al	8	6	4
	17	5	4
	25 to 30	4 to 6	2, 3, 3, 3
	54	4	3
	89	7	3
Si-B	15 to 20	2-1/2	1, 1, 2
	20 to 30	1 to 3	<1, 1, 2, 2
	35	1 to 2	<1, <1
	40 to 50	1-1/2	<1, <1, 1, 1, 2
	65	2	<1
Si-Mn	3	2-1/2	<1, 2
	11 to 12	5	3, 5
	13 to 14	2	2, 2
	23 to 25	2-1/2	<1, 2
Si-V	-5 mg/cm ^{2(d)}	4-1/2	5
	-7 mg/cm ^{2(d)}	4-1/2	4, 10
	3.3 mg/cm ^{2(d)}	4-1/2	5
	1.5 mg/cm ^{2(d)}	4 to 5	2, 2
Si-V-B	-1.5 mg/cm ^{2(d)}	4	4, 4
	-0.2 mg/cm ^{2(d)}	3	2

(a) Calculated from weight gains during coating.

(b) Measured metallographically or estimated from coating weight.

(c) Number of 1-hour cycles survived without failure.

(d) Weight changes during first coating cycle.



500X

N91135

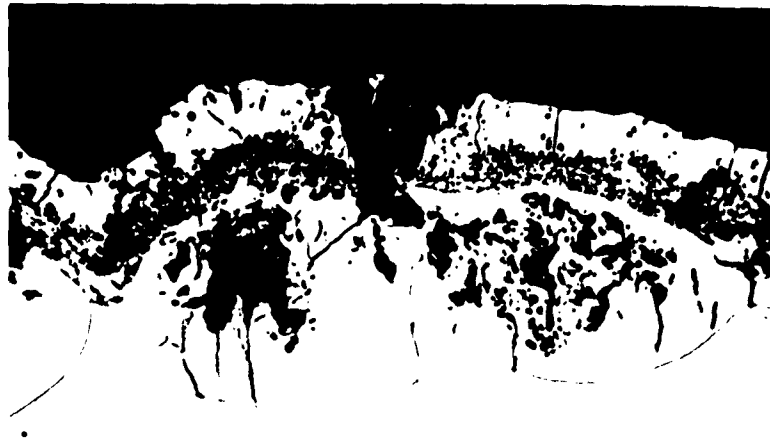
FIGURE 8. TWO-CYCLE Si-43 AT.% Al COATING ON Ta-10W, AS APPLIED (SPECIMEN 226)



500X

N91147

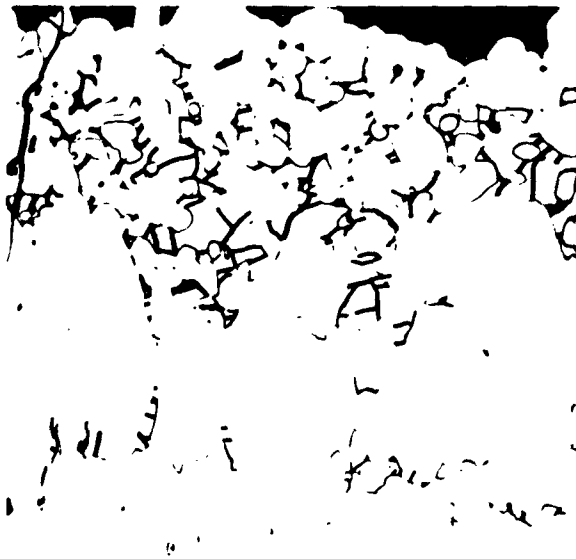
FIGURE 9. TWO-CYCLE Si-45 AT.% B COATING ON Ta-10W, AS APPLIED (SPECIMEN 268)



500X

N91413

FIGURE 10. TWO-CYCLE Si-22 AT.% B COATING ON Ta-10W, OXIDIZED FOR TWO 1-HOUR CYCLES AT 2700 F (SPECIMEN 255)



500X

N92954

FIGURE 11. TWO-CYCLE Si-20 AT.% Mn COATING ON Ta-10W, AS APPLIED (SPECIMEN 473)

Four different sets of conditions for first-cycle vanadium deposition were tried in preparing vanadium-modified silicides. As shown in Tables 5 and 15, the use of NaF and NaCl carriers and times of 4 to 8 hours at 1800 to 2400 F resulted in only minor weight changes. These varied from net gains of about 3.3 mg/cm² at 1800 F to net losses of about 7 mg/cm² at 2400 F. Examination of microstructures (Figure 12a) showed that even where the net weight change was negative, an appreciable amount of vanadium had entered the substrate and that the weight loss actually resulted from corrosive attack of the substrate surface. During the second coating cycle, siliciding leveled off the roughened surface produced in the first cycle and resulted in a coating of fairly uniform thickness. However, as shown in Figure 12b, after the second coating cycle, some areas in the substrate displayed what appeared to be a localized intergranular precipitate and/or crack network.

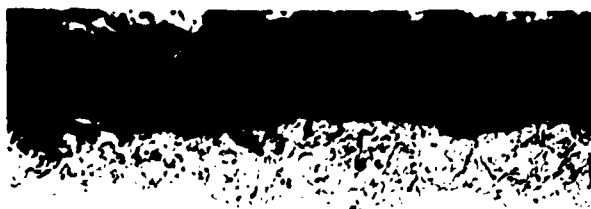
As shown in Table 6, the vanadium-modified silicide coatings on Ta-10W had the longest lives of any of the coatings tested on this substrate, i. e., up to 10 hours at 2700 F. The oxidation-weight-gain behavior of the vanadium-modified coating was, as illustrated in Figure 7, associated with the formation, in the initial cycles, of a thin uniform film of glass over the original coating after which there was no significant change in appearance. The long life, low rate of weight gain, and good glass-forming tendencies made this coating a candidate for further work.

The last coating screened for behavior on Ta-10W was based on a first cycle for the codeposition of vanadium and boron followed by a second siliciding cycle. Here, codeposition of vanadium and boron in the first cycle again resulted in corrosive attack of the substrate. Apparently, less vanadium was transferred (on the basis of microstructure) than where deposition of vanadium alone was attempted. Also, the oxidation weight gain increased rapidly with time (Figure 7) and the appearance of the oxidized specimen was similar to that of the unmodified silicide. It was concluded that, in these limited attempts to codeposit vanadium and boron, less vanadium was added to the silicide than where vanadium alone was deposited and that little or no boron was added to the coating.

Coatings on Ta-30Cb-7.5 V

Five silicide coating systems, including four modifications, were evaluated on this alloy substrate with the results summarized in Table 7.

Straight silicide coating with the standard two-cycle process resulted in coatings of uniform thickness. As coated, the structure of these coatings, illustrated in Figure 5a, consisted essentially of a single thick outer layer of extremely fine grain size over a layer of subsilicide. On oxidation exposure, the subsilicide layer increased in thickness and the structure in the outer layer coarsened, as shown in Figure 5b. This figure also shows the thin protective glass which formed at 2700 F as the only oxidation product prior to failure. The protective nature of the coating is indicated by the low rate of oxidation weight gain shown in Figure 13. Cyclic oxidation lives of 10 to 16 hours were obtained with coating thicknesses of 4 to 6 mils (Table 7). This combination of desirable glass-forming tendencies and low weight gain was attributed to modification of the silicide by interdiffusion of the silicide with vanadium (and possibly columbium) from the substrate.

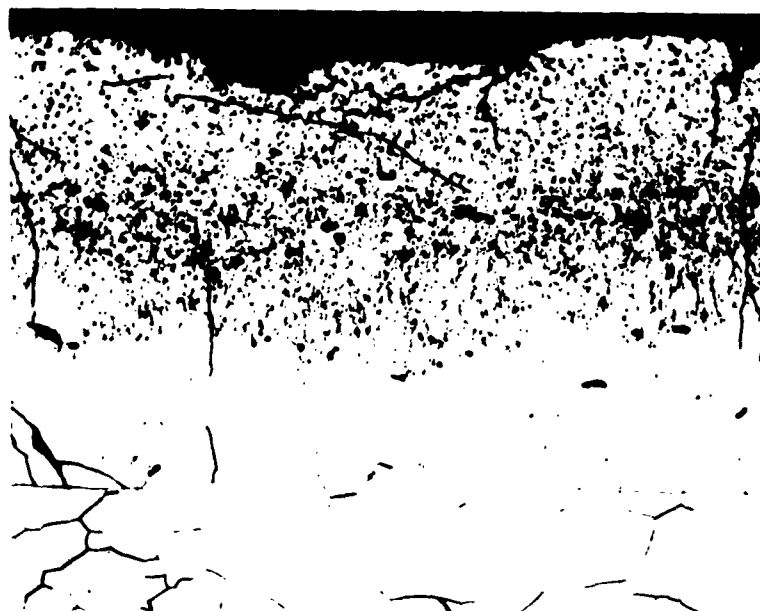


500X

N91830

a. First-Cycle Coating of V (Specimen 363)

First cycle weight change -5.5 mg/cm^2 .



500X

N92958

b. Second-Cycle Si-V Coating (Specimen 482)

First-cycle weight change -8.9 mg/cm^2 .

FIGURE 12. FIRST- AND SECOND-CYCLE STRUCTURES OF Si-V COATING ON Ta-10W

TABLE 7. 2700 F CYCLIC OXIDATION LIVES OF MODIFIED SILICIDE COATINGS ON Ta-30Cb-7.5V

Coating System	Calculated Modifier Content ^(a) , at. % (Balance Si)	Coating Thickness ^(b) , mils/side	2700 F Cyclic Oxidation Life ^(c) , hours (Individual Specimens)
Si	0	4	3, 4, 4, 10
		5	6, 6, 9, 10
		6	11, 16
Si-Al	20	4 to 5	2, 2
	30 to 35	4 to 5	2, 4
	35 to 45	4 to 5	3, 4
	60 to 65	4 to 5	3, 3
Si-B	13 to 17	3	16, 17
	30 to 40	2-1/2	<1, 1, 3, 16, 18
	57	5	>32 ^(d)
Si-Mn	8	2-1/2	<1
	13 to 14	2-1/2 to 3-1/2	<1, <1, <1
	18 to 19	3	<1, <1
	30	2-1/2	<1, <1
Si-Cr	9	3-1/2	<1, <1

(a) Calculated from weight gains during coating.

(b) Measured metallographically or estimated from coating weight.

(c) Number of 1-hour cycles survived without failure.

(d) This specimens subsequently survived 17 hours at 2900 F.

The aluminum-modified silicide coatings on Ta-30Cb-7.5V were evaluated over a fairly wide range of modifier contents and at relatively substantial thicknesses. Figure 14 illustrates the typical structure of these coatings. Comparison with Figure 5a shows that addition of aluminum resulted in modification of the outer coating layer which contains what appears to be entrapped oxides as well as cracks penetrating completely through the outer layer. The amount of "entrapped oxides" in the outer layer was proportional to the nominal aluminum content, and all of these coatings showed cracks penetrating through this layer. Oxidation lives were definitely inferior to the straight silicide on the same alloy. While the aluminum additions resulted in increased glass-forming tendencies, the resulting surface film was not as protective as where no aluminum was added. Thus, as shown in Figure 13, the Si-Al coated samples showed rapid weight gains during oxidation, relative to the straight silicide coatings.

The boron-modified silicide coating on this alloy had the longest 2700 F cyclic lives achieved in this program. The coatings on this alloy were uniform at all coating weights, in contrast to the results on the Ta-10W alloy. Figure 15a illustrates the structure of a nominal Si-13 at. % B coating and Figure 15b shows the effects of increased amounts of boron. It may be noted that even with the lowest boron content, intergranular

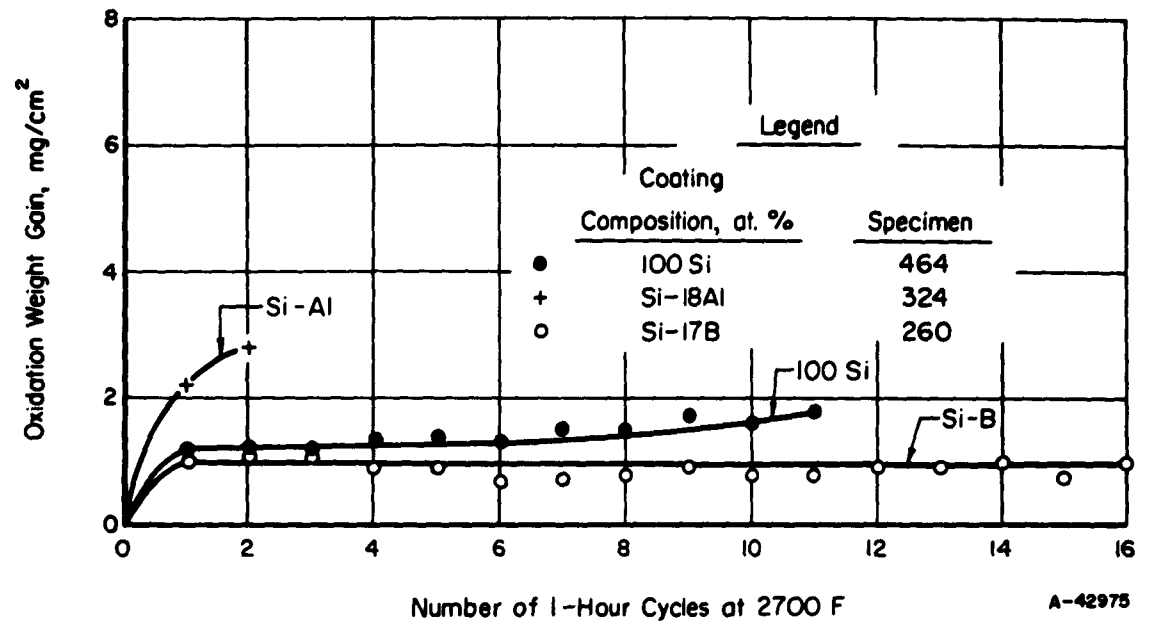


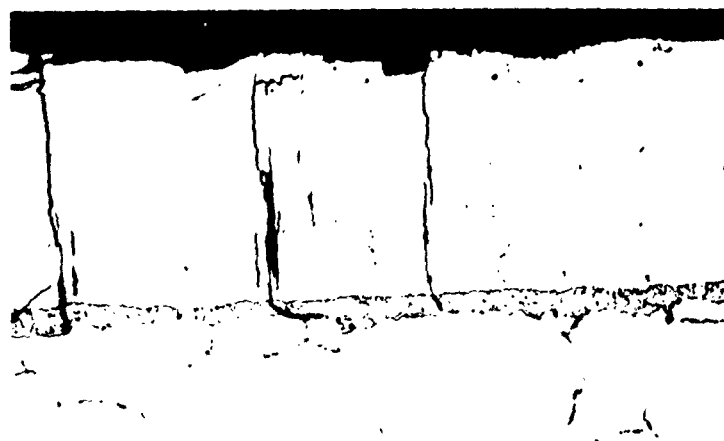
FIGURE 13. 2700 F CYCLIC OXIDATION WEIGHT GAINS OF MODIFIED SILICIDE COATINGS ON Ta-30Cb-7.5V



500X

N91133

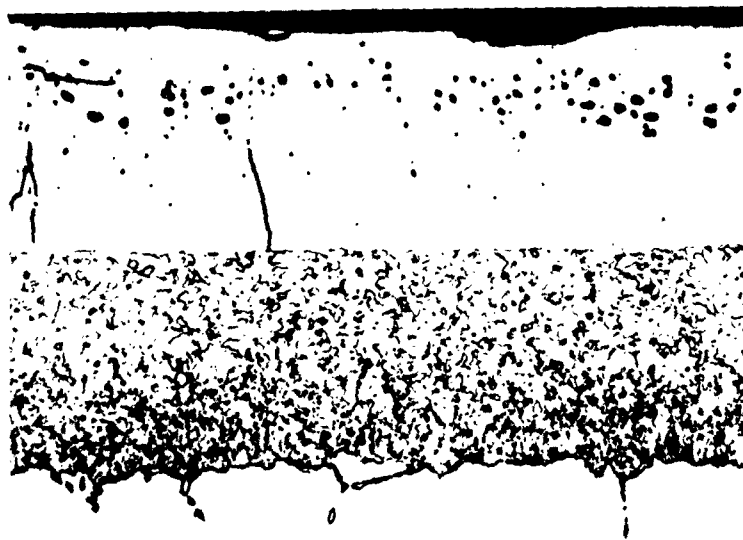
FIGURE 14. TWO-CYCLE Si-32 AT.% Al COATING ON Ta-30Cb-7.5V, AS APPLIED (SPECIMEN 222)



500X

N91145

a. Si-13 at.% B Coating (Specimen 258)



500X

N92953

b. Si-60 at.% B Coating (Specimen 455)

FIGURE 15. TWO-CYCLE Si-B COATINGS ON Ta-30Cb-7.5V, AS APPLIED

precipitation of a boron-containing phase is evident in the substrate. The oxidation-weight-change behavior of all of the Si-B coatings was outstanding, as shown by the flat curve, obtained for a Si-17 at. % B coating, in Figure 13. The initial oxidation weight gain was paralleled by the formation of a thin, clear glass on the surface, after which no change in appearance occurred until failure. Even after relatively long exposures at 2700 F, there was little or no consumption of the coating, either by oxidation or by diffusion into the substrate. As indicated in Table 7, one Si-57 at. % B-coated sample which survived 32 1-hour cycles at 2700 F subsequently survived an additional 17 cycles at 2900 F without failure. Even with this exposure history, the total weight gain was only 1 mg/cm², and the sample, illustrated in Figure 16, still showed no signs of oxidation.

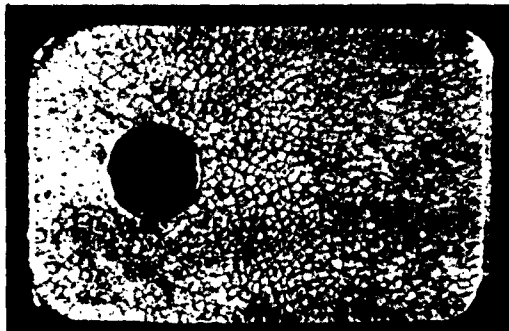
The manganese-modified silicide coatings on this alloy were evaluated at coating thicknesses slightly less than desired and considerably less than those which gave superior behavior in the prior year's work, i. e., average 2700 F cyclic life of 4.8 hours for an 8.9-mil-thick coating of Si-8 at. % Mn. The structures of these coatings on the Ta-30Cb-7.5V alloy were quite complex, as illustrated in Figure 17a. During oxidation at 2700 F, all of these Si-Mn coatings gave extremely fluid, glassy surface oxidation products which appeared to consume the underlying coating. (See Figure 17b.) This reactivity of the Si-Mn coatings on the Ta-30Cb-7.5V substrate apparently was the result of vanadium or columbium (from the substrate) in fluxing the Si-Mn coating. Thus, all of the oxidation products on these coatings were extremely fluid, showed strong reaction with the supporting boats, and failed in less than 1 hour.

A single attempt was made to evaluate a chromium-modified silicide coating on this alloy substrate, with the results shown in Table 7. As illustrated in Figure 18, these coatings were characterized by intergranular penetration of a chromium-rich phase into the substrate. During oxidation, the specimens formed a greenish oxide and were less glassy in appearance than the straight silicide and other modified silicide coatings on this alloy. None of the Si-Cr coatings survived a 1-hour exposure at 2700 F.

Coatings on Ta-8W-2Hf

Straight silicide and six modified silicide coatings were evaluated on this alloy. However, because of the delay in obtaining this alloy, none of these coatings were evaluated in as much detail as those for the Ta-10W and Ta-30Cb-7.5V substrates. Further, difficulties were encountered in obtaining coatings with good edge quality on the Ta-8W-2Hf substrate, especially with the straight silicide and Si-Mn coatings.

This trouble was manifested during the second-cycle application of silicon where it was found that edges of the specimens were extremely ragged, as shown in Figure 19, and that coatings contained cracks at the corners which penetrated almost completely but not quite through the coating. The severity of the edge condition varied with modifying addition, being most pronounced in the manganese-modified coating, moderate in the straight silicide, and slight or absent for the aluminum-, boron-, or vanadium-modified coatings on this substrate.



3X

FIGURE 16. S1-57 AT.% B-COATED Ta-30Cb-7, 5V SAMPLE AFTER AN ACCUMULATED EXPOSURE OF 32 and 17 1-HOUR CYCLES AT 2700 AND 2900 F, RESPECTIVELY



500X

N91143

a. Si-29 at.% Mn Coating on As Applied (Specimen 253)

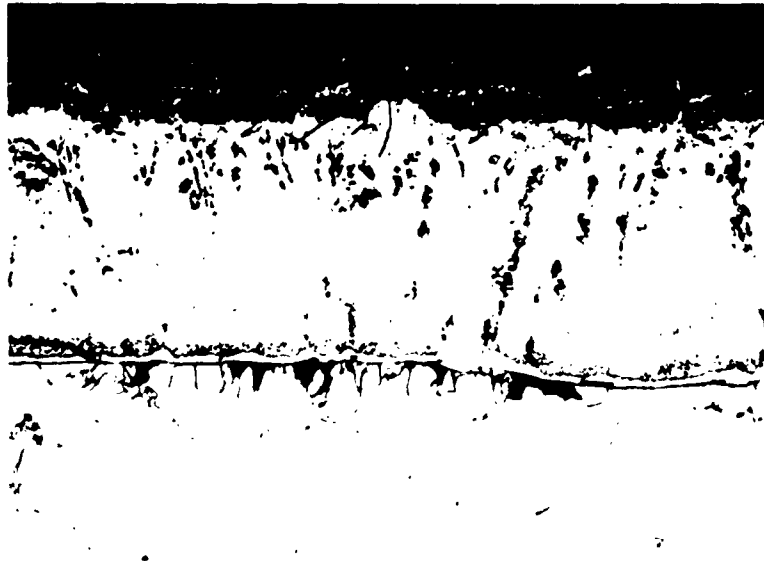


500X

N91422

b. Si-29 at.% Mn Coating Oxidized for One 1-Hour Cycle at 2700 F (Specimen 254)

FIGURE 17. TWO-CYCLE Si-Mn COATINGS ON Ta-30Cb-7.5V, AS APPLIED AND AFTER OXIDATION AT 2700 F



500X

N91833

FIGURE 18. TWO-CYCLE Si-9 AT.% Cr COATING ON Ta-30Cb-7.5V, AS APPLIED

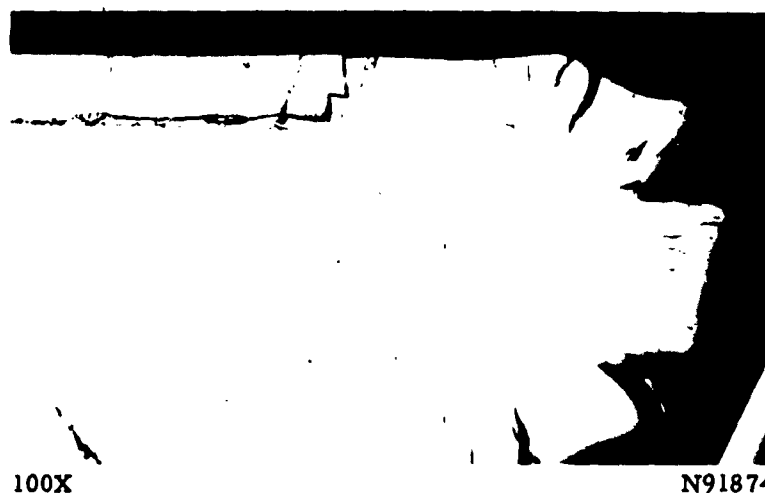


FIGURE 19. TWO-CYCLE, UNMODIFIED SILICIDE COATING ON Ta-8W-2Hf, AS APPLIED

The same type of defective edges in the as-coated condition were later found in thicker (6 to 7 mils) coatings of Si-Mn on the Ta-10W substrate. It was concluded that this coating defect was related to both deposition rate and the corner radius of the substrate. Thus, the formation of ragged edges was promoted in coatings which were deposited rapidly, at thicknesses of 4 mils or greater, and on the substrate with the smallest corner radius, i. e., the 20-mil-thick Ta-8W-2Hf.

The oxidation lives achieved with coatings on the Ta-8W-2Hf alloy are summarized in Table 8. The unmodified silicide exhibited structures and behavior similar to that for the straight silicide on the Ta-10W in that, during oxidation, both glassy and granular oxidation products formed simultaneously. A similar pattern of relatively rapid weight gain was found, as shown in Figure 20.

The aluminum-modified silicide on this alloy was evaluated at two levels of modifier content and at fair thickness (4 to 4-1/2 mils), but had shorter cyclic life than the straight silicide. As with the other alloy substrates, aluminum additions to the silicide resulted in increased glass formation accompanied by rapid weight gains during oxidation.

The boron-modified coating on this alloy exhibited the same nonuniform structure as observed on the Ta-10W alloy, accompanied by very short oxidation life, i. e., less than 1 hour at 2700 F (see Table 8).

The manganese-modified silicide coatings on the Ta-8W-2Hf had microstructures similar to those of the same coating on Ta-10W (Figure 11). As noted earlier, these coatings were unevenly deposited at the edges, giving the appearance of delamination at the edges. Even with the most careful handling, some flaking and chipping of the coating from the edges occurred. In spite of this, these were the only coatings on this alloy which gave longer lives at 2700 F than the unmodified silicide. Oxidation-weight-gain data were not obtained for these coatings because the characteristic glassy oxides of this system caused these specimens to stick to the supporting boats.

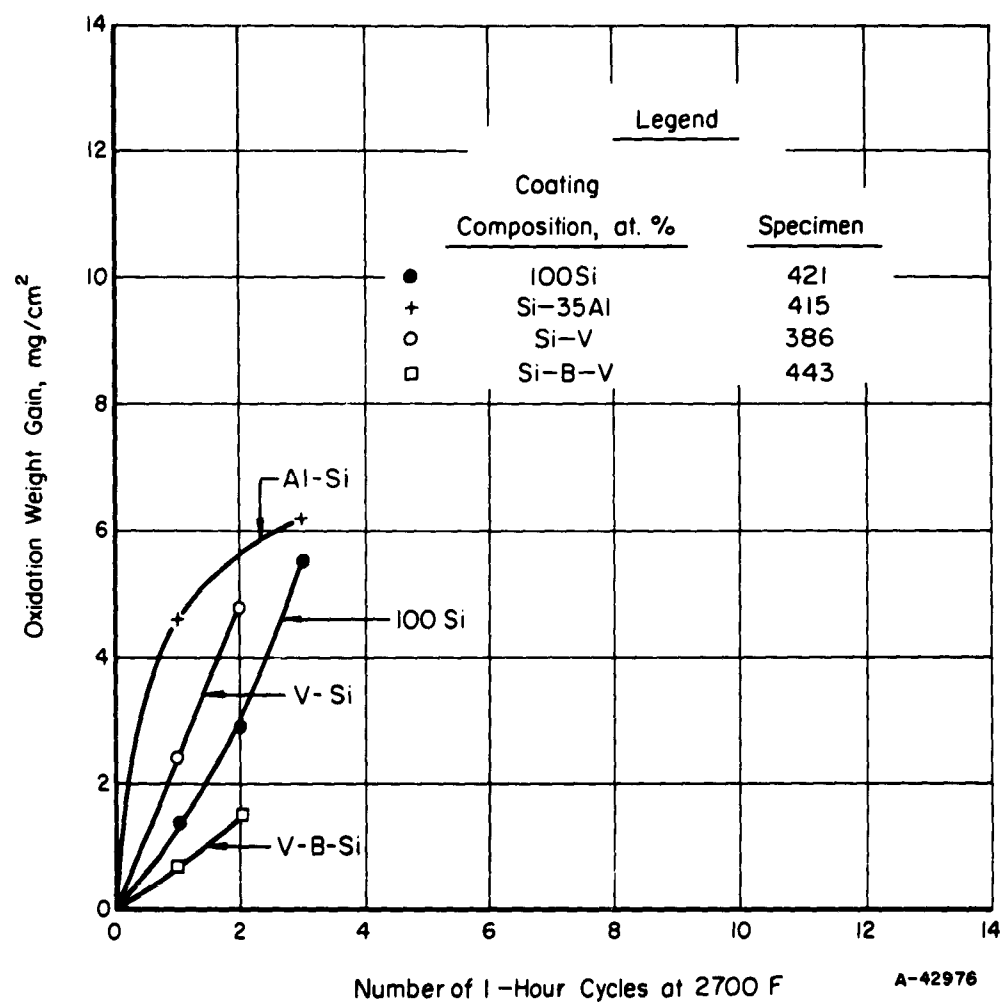


FIGURE 20. 2700 F CYCLIC OXIDATION WEIGHT GAINS OF MODIFIED SILICIDE COATINGS ON Ta-8W-2Hf

TABLE 8. 2700 F CYCLIC OXIDATION LIVES OF MODIFIED SILICIDE COATINGS ON Ta-8W-2Hf

Coating System	Calculated Modifier Content ^(a) , at.%, (Balance Si)	Coating Thickness ^(b) , mils/side	2700 F Cyclic Oxidation Life ^(c) , hours (Individual Specimens)
Si	0	4	2, 3
Si-Al	13	4	1, 2
	35	4-1/2	2, 2
Si-B	22 to 26	1 to 3	<1, <1
Si-Mn	12 ^(d)	2-1/2 to 5 ^(e)	<1, 1
	21 to 24 ^(d)	4 ^(e)	<1, 5
Si-V	±1 mg/cm ² ^(f)	4	<1, 2, 2, 2, 2
	-6 mg/cm ²	4	1, 1
	1, 2 mg/cm ²	4	1
Si-V-B	0, 1 mg/cm ² ^(f)	3-1/2	1, 1, 1, 2
Si-B (codeposited)	--	1 to 6	<1, <1, <1, <1

(a) Calculated from weight gains during coating.

(b) Measured metallographically or estimated from coating weight.

(c) Number of 1-hour cycles survived without failure.

(d) Rough estimates only due to weight losses from poor edges in as-coated condition.

(e) Coating thickness discounting edges and corners.

(f) Weight changes during first coating cycle.

The three sets of coating conditions used for vanadium deposition on Ta-8W-2Hf were the same as those which produced good oxidation-resistant coatings on the Ta-10W alloy. Examination of the structures of these Si-V coatings, after successive vanadizing and siliciding cycles, indicated that the Ta-8W-2Hf substrate was attacked to a lesser degree during the vanadizing cycle and that correspondingly less vanadium entered the substrate than for the Ta-10W alloy. Glass formation during oxidation was only slightly enhanced compared with the straight silicide, and granular oxides appeared simultaneously with the glass. It was concluded that the difference in alloy substrate had prevented the same degree of modification as was obtained in the Ta-10W alloy.

A single attempt was made to codeposit boron with vanadium on the Ta-8W-2Hf substrate. However, no evidence was obtained of any significant changes in coating behavior, structure, or improvement in oxidation performance over the Si-V coating on this substrate.

Similarly, one attempt at codeposition of silicon and boron in two cycles (with the aim of overcoming the difficulties encountered in alternate deposition) was unsuccessful. Here, positive weight gains and a thin but adherent coating were obtained in the first coating cycle. The second-cycle deposit was porous and discontinuous with evidence of oxidation in the form of lumps of glass mixed in the deposit. Oxidation lives were correspondingly short.

Advanced Screening

On the basis of the preliminary screening described above, the following coatings systems were selected for more extensive property evaluations on the substrates indicated:

<u>Substrate</u>	<u>Coating System</u>
Ta-10W	Si-V and Si-Mn
Ta-30Cb-7.5V	Si and Si-B

The test criteria of interest included (1) verification of prior 2700 F cyclic oxidation lives, (2) an evaluation of self-healing characteristics at 2700 F, (3) measurement of 1800 F cyclic oxidation resistance (to gage resistance of the coating system to accelerated failure), and (4) measurement of the effects of the coating processes on substrate bend ductility. Accordingly, additional samples of both the Ta-10W and Ta-30Cb-7.5V alloys were prepared and coated with the indicated silicide modifications.

Concurrent with this work, additional samples of the Ta-8W-2Hf alloy were coated with the straight silicide and Si-Mn coatings for more extensive characterization.

Sample Preparation

The deposition conditions used in applying these coatings were identical to those used in preparing the preliminary coatings, with one exception. This involved an adjustment of deposition conditions aimed at increasing the manganese content and coating thickness of the Si-Mn coating on Ta-10W to values above 25 at. % and 5 mils,

respectively. This led to several inconsistencies with this coating system which can be summarized as follows:

For unexplained reasons, the first attempt to deposit the target amount of 10 to 12 mg/cm² of manganese (using 2 grams of NaF and 5 hours at 1800 F as indicated in Table 15) gave only about half the expected amount. Consequently, a second manganizing cycle of 12 hours at 1800 F was applied which gave slightly greater amounts (13 to 14 mg/cm²) of manganese than were desired. The samples at this point appeared uniformly coated. In the subsequent siliconizing cycle, the silicon deposited at about twice the anticipated rate, a fact which was apparently associated with the relatively thick underlying layer of manganese. As a net result, all of these three-cycle, Si-Mn coated samples had defective edges similar to those obtained earlier in Si-Mn coatings on the Ta-8W-2Hf substrate. Metallographic examination of the three-cycle, Si-Mn-coated Ta-10W samples indicated that, although their total thickness (6 to 7 mils neglecting edges and corners) was in the desired range, the manganese content was less than desired (about 20 atom per cent rather than 30 or more).

As with Ta-10W, deposition conditions for obtaining the Si-Mn coatings on the Ta-8W-2Hf samples were adjusted to explore higher manganese levels and greater coating thicknesses. Table 17 summarizes the details of the processing modifications used. The results were consistent with the previous coating experiences on the Ta-8W-2Hf substrate. However, even though thicker coatings of higher estimated manganese content were obtained (i. e., 6 to 8-mil coatings of Si-30Mn versus 4-mil coatings of Si-24Mn), the resulting coatings again developed defective edges during siliconizing.

Test Results

The results of the advanced screening evaluations on these coated samples are summarized in Table 9.

2700 F Cyclic Tests. Generally, the additional 2700 F cyclic test results on the undefected samples agreed well with the preliminary screening test results. (See Tables 6, 7, and 8.) From this point of view, the 10-hour lives of the obviously-edge-defected samples of the Mn-Si-coated Ta-10W samples (in Table 9) were surprising.

Intentionally defecting these coatings by drilling a 40-mil-diameter hole through one side drastically shortened the 2700 F cyclic oxidation resistance of all coating systems excepting only those Ta-8W-2Hf samples coated with Si-30Mn which actually outlasted thin "undefected" companion samples.

The above results with the manganese-modified silicide coatings on Ta-10W and Ta-8W-2Hf were interpreted as strong evidence for superior self-healing characteristics of this coating system in comparison to the others.

2700 F Static Tests. As shown in Table 9, static oxidation lives of 87 to over 100 hours at 2700 F were achieved with the Si-V coating on Ta-10W, and the straight Si and Si-B coatings on Ta-30Cb-7.5V. All three coatings showed low weight gains with the Si-B coating on Ta-30Cb-7.5V being particularly outstanding as shown in Figure 21.

TABLE 9. RESULTS OF ADVANCED SCREENING TESTS OF MODIFIED SILICIDE COATINGS ON TANTALUM-BASE ALLOYS

Alloy Substrate	Coating Composition, at. %	Coating Thickness, mils./side	2700 F Cyclic Oxidation			1800 F Cyclic Oxidation Life, hours	Room-Temperature Bend Properties of Substrate After Coating
			Coating	Undefected Sample	Defected Sample(a)		
Ta-10W	Si-V	5		6 10	<1 <1	75-100 >100	>20T(b)
Ta-10W	Si-20Mn(c)	6-7(d)		10 10	<1 <1	1-3 1-3	0T
Ta-30Cb-7.5V	100Si	4-5		3	<1	>100	0T
				6	<1	>100	
		6		--	--	--	
Ta-30Cb-7.5V	Si-50B	4		3 11	<1 <1	>115 --	>20T
Ta-8W-2Hf	100Si	4-5		2 2	<1 <1	3-8 8-25	0T
Ta-8W-2Hf	Si-30Mn(c)	6-8(d)		5 1	>7 >7	3-8 3-8	0T

- (a) 0.040-inch-diameter hole drilled through one side of sample.
(b) Broke on 3/8-inch-radius bend die.
(c) Rough estimates only due to weight losses from poor edges in as-coated condition.
(d) Coating thickness discounting edges and corners.
(e) Time of failure uncertain; see text.

Each of these coating systems also showed marked glass formation. Of the three specimens of straight si-coated Ta-30Cb-7.5V tested, the life of the 6-mil-thick coating was approximately ten times that of the 4-mil-thick coatings.

Of the three remaining coating systems, all samples exhibited defective edges in the as-coated condition, as described earlier. Despite this, one each of the Si-Mn-coated Ta-10W and Ta-8W-2Hf samples survived 167 and 100 hours' exposure, respectively, at 2700 F. The weight-gain curves for these samples (see Figure 21) were paralinear, both showing high initial weight gains followed by a slower, but continuously increasing weight gain with increasing exposure time.

1800 F Cyclic Tests. The 1800 F cyclic test results listed in Table 9 confirmed earlier experiences which indicated the desirability of vanadium modifications in ameliorating accelerated failure at this temperature. Thus, the only coating systems to survive the 100-hour 1800 F cyclic exposures were those to which vanadium was added either independent of the substrate (i. e., as a Si-V coating to Ta-10W) or via the substrate (i. e., as coatings on the Ta-30Cb-7.5V substrate).

Total weight gains for the samples which survived the 100-hour exposure are given below:

<u>Alloy</u>	<u>Coating</u>	<u>Weight Gain, mg/cm²</u>
Ta-30Cb-7.5V	Si	8-12
Ta-30Cb-7.5V	Si-B	0.3-0.5
Ta-10W	Si-V	3

As in earlier tests at 1800 F, the straight silicide-coated Ta-30Cb-7.5V alloy continued to gain weight at a moderate rate over the 100-hour period. However, as shown by the above data, modification of this coating with the boron addition was almost completely effective in preventing any weight change. The weight gains for the Si-V-coated Ta-10W samples were intermediate to these other values and the curves generally paralleled those shown for the Ta-5V ($\pm 5\text{Mo}$ on 5W) alloys in Figure 3.

Bend Ductility. Room-temperature bend tests were conducted on each alloy substrate prior to coating as well as after. Before coating, each of the three alloys had excellent "OT" bend ductility values, i. e., could be bent over a radius of less than 1/64 inch without fracture. As indicated in Table 9, bend tests on the various as-coated samples showed Si-Mn coating of the Ta-10W and Ta-8W-2Hf alloys and straight silicide coating of the Ta-30Cb-7.5V and Ta-8W-2Hf alloys had no detrimental effect on substrate ductility. However, Si-B coating the Ta-30Cb-7.5V alloy and Si-V coating the Ta-10W alloy resulted in severe bend embrittlement of these substrates.

The bend embrittlement of the Ta-30Cb-7.5V alloy by the Si-B coating was attributed to the formation of an intergranular boron-rich phase in the alloy substrate during the coating process. Similarly, the embrittlement of the Ta-10W substrate by Si-V coating was the apparent result of the intergranular precipitate and/or crack network retained in this substrate after siliciding.

Because of the obvious desirability of incorporating vanadium as a silicide modifier, several additional experiments were performed in an attempt to overcome the bend embrittlement associated with this coating system. These are described and summarized as follows:

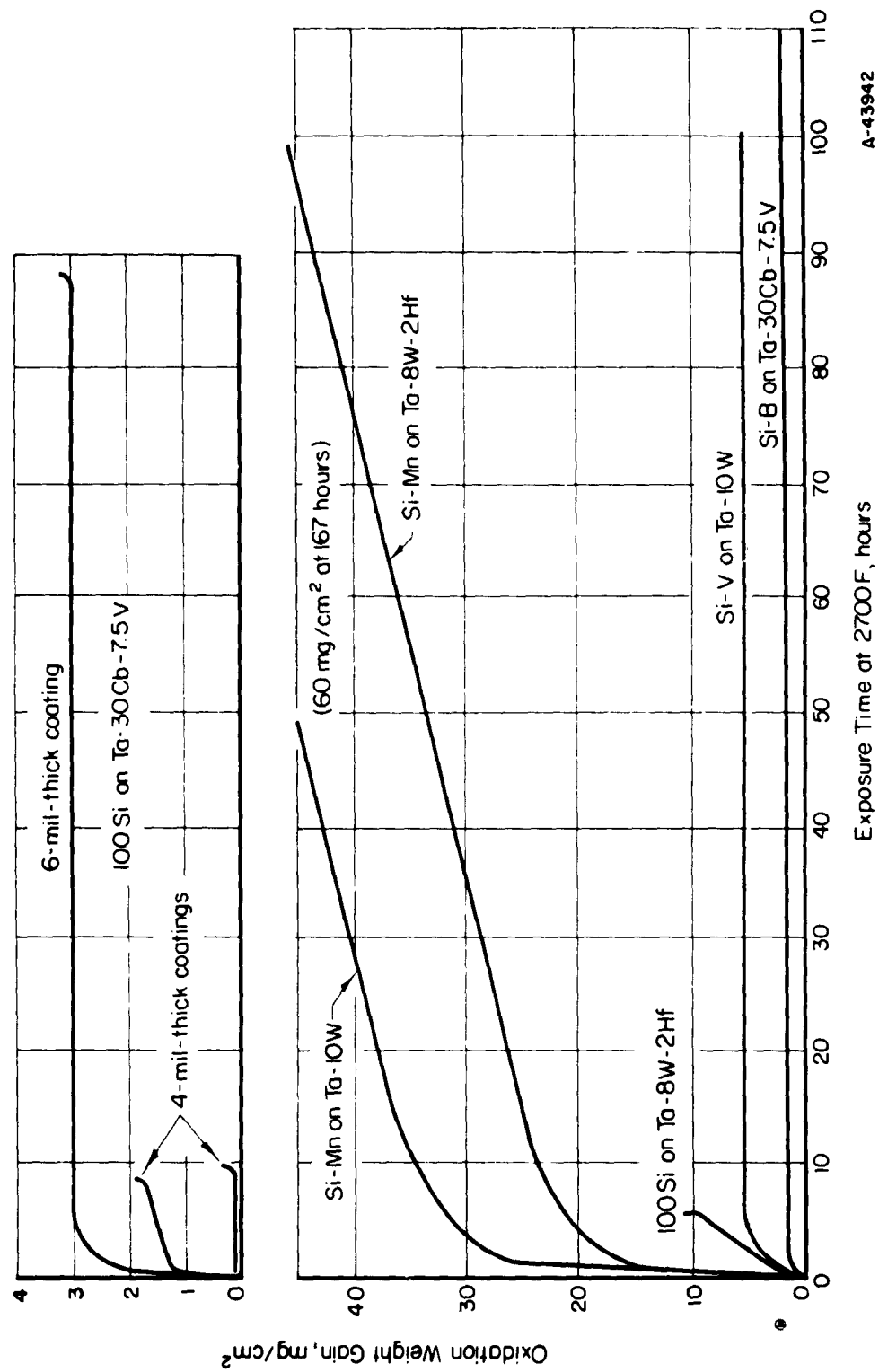


FIGURE 21. 2700 F STATIC OXIDATION WEIGHT GAINS OF MODIFIED SILICIDE COATINGS ON TANTALUM-BASE ALLOYS

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- (1) Bend tests on the Ta-10W substrate, after vanadizing with the "standard" NaF carrier, confirmed that the embrittlement was associated with the vanadizing cycle (see Table 10). Vanadizing coating cycles using alternative carriers were successful, on the basis of metallographic study, in eliminating the intergranular precipitate and attack associated with the NaF carrier. As shown in Table 10, the alternative carriers were also nonembrittling. However, after subsequent siliconizing, oxidation tests indicated that not enough vanadium was deposited by any of the alternative carriers to achieve any improvement in oxidation life.
- (2) Microprobe analyses were performed on the as-vanadized Ta-10W substrate (Figure 12a) and gave an unexpected indication that the fine, intergranular precipitate contained calcium. Subsequent microprobe analysis on the Si-V-coated sample which had survived 101 hours' exposure gave the results shown in Figure 22 and Table 11. These can be summarized as follows:
 - (a) The intergranular precipitate in the substrate matrix was positively identified as a tantalum-calcium phase with an indicated stoichiometry of TaCa₃.
 - (b) The major portion (i. e. , matrix) of the unoxidized silicide layer corresponded to (Ta, 10W) Si_{2.9}. A dispersed phase (not evident in Figure 22) in this layer adjacent to the matrix corresponded to (Ta, 10W)_{1.1}Si.
 - (c) Vanadium was present only as a minor constituent (maximum of 3 per cent) in the partially oxidized outer layer.

TABLE 10. EFFECT OF VARIATIONS OF HALIDE CARRIERS ON THE PROPERTIES OF Si-V COATINGS ON Ta-10W

Carrier(a)	Vanadizing Conditions		Weight Change, mg/cm ²	Substrate Bend Ductility(b)	2700 F Static Oxidation Life, hours(c)
	Time, hours	Temperature, F			
2 g NaF	4 or 8	2400	-5 to -9	>20T	>100
2 g NaI	4	2200	0.2	0T	2-1/3
2 g KI	4	2200	0.2	0T	2-1/3
2 g NH ₄ Cl	4	2200	0.2	0T	3-1/3
6 g NH ₄ Cl	4	2200	1.0	0T	--

(a) Balance of pack was 23.8 g V, 48 g Al₂O₃.

(b) After vanadizing cycle.

(c) After vanadizing and siliciding.

On the basis of the above evidence, it is postulated that, during the vanadizing cycle, NaF reacted with the calcium contained in the vanadium to form CaF₂. The CaF₂,

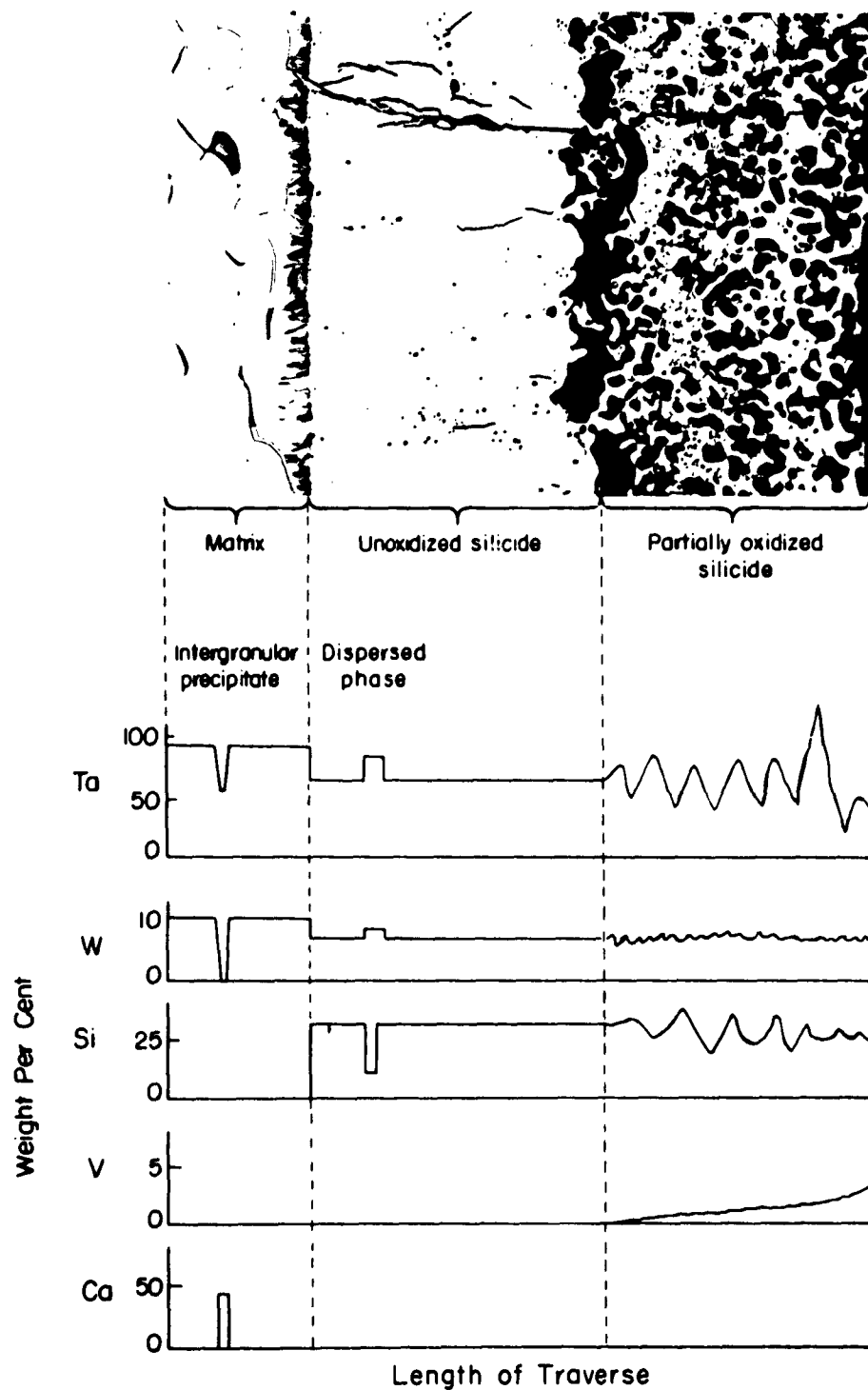


FIGURE 22. SCHEMATIC SUMMARY OF ELECTRON-BEAM MICROPROBE TRAVERSE ANALYSES OF Si-V-COATED Ta-10W
Specimen exposed 101 hours at 2700 F.

in turn, had a severe intergranular, corrosive attack on the substrate and, by exchange with the tantalum, transferred a sufficient amount of calcium to form the intergranular $TaCa_3$ phase. It was then concluded that calcium contamination of the vanadium was the major cause of bend embrittlement in the Ta-10W substrate after vanadizing.

TABLE 11. RESULTS OF MICROPROBE SPOT ANALYSES ON Si-V-COATED Ta-10W ALLOY AFTER 101 HOURS' EXPOSURE AT 2700 F

Phase Analyzed(a)	Analyses, At. %				
	Ta	W	Si	V	Ca
Substrate matrix	90(b)	10(b)	0	0	0
Intergranular precipitate	25	0	0	0	75
Dispersed silicide phase	50	5.2	44.9	0	0
Unoxidized silicide matrix	23.4	2.5	74.9	0	0
Partially oxidized silicide	Present	Present	Present	3 max(b)	0

(a) See Figure 22.

(b) Weight per cent.

Subsilicide Growth Rates

The thickness of the subsilicide layers formed on exposure of the various coated alloys for various times at 2700 F was determined metallographically. These data are given in Figure 23 which also contains data obtained in the previous year's work for unalloyed tantalum. Generally, for a given alloy substrate, modification of the silicide (e.g., Si $\pm$ V or Mn for Ta-10W) had no measurable effect on the growth rate of the subsilicide layer formed, at least at exposure times to 13 hours.

Analyses of the curves in Figure 23, using the relationship $w^2 = kt^*$, gave the following growth rate constants for the subsilicide layers:

Substrate	Rate Constant, mils ² /hr
Ta-10W	6.2×10^{-2}
Ta	11×10^{-2}
Ta-30Cb-7.5V	15×10^{-2}

The relative order of these values is that which would be expected on considering the differences in melting temperature of the substrates (Ta-10W, Ta, and Ta-30Cb-7.5V, decreasing in that order) relative to the melting point of silicon, the common diffusing species.

Advanced Evaluation

On the basis of the results of the advanced screening tests, the straight Si coating on Ta-30Cb-7.5V was chosen for more detailed characterization. This study included

*w = subsilicide layer thickness, mils

k = rate constant, mils²/hour

t = exposure time, hours.

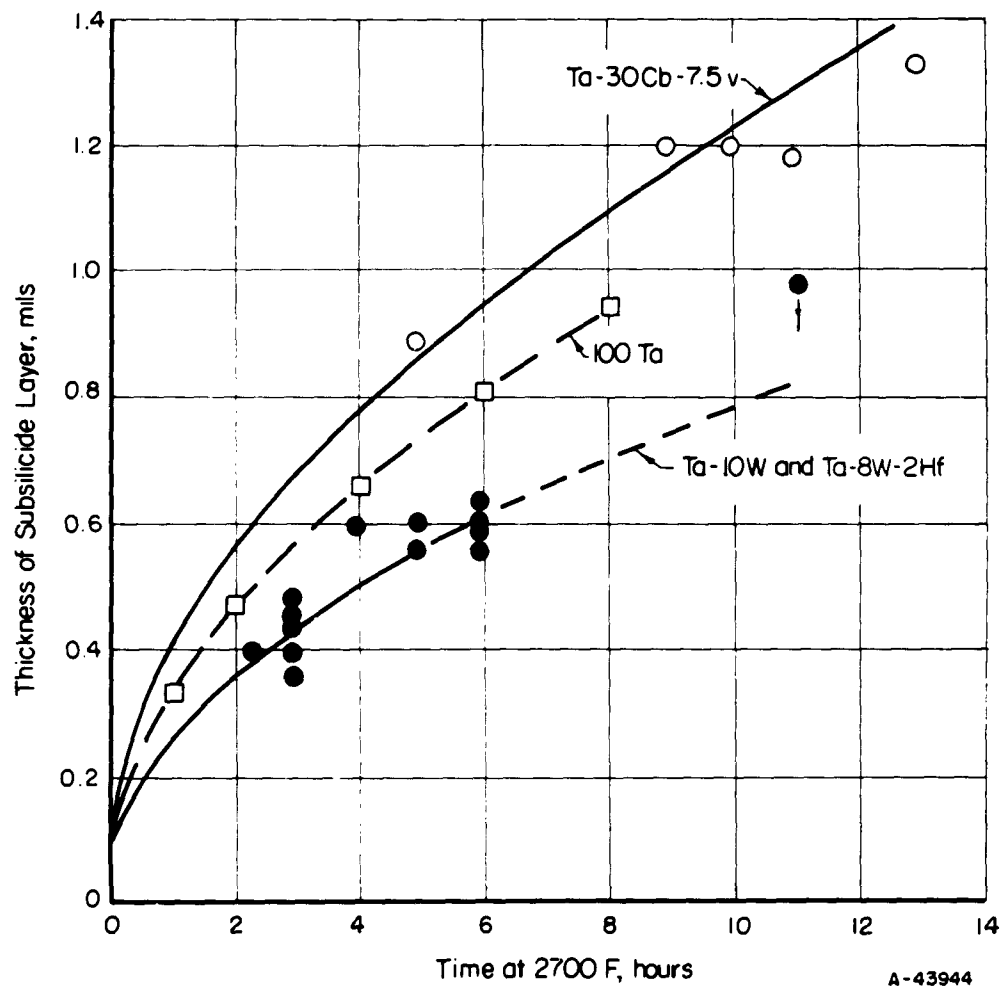


FIGURE 23. EFFECT OF SUBSTRATE COMPOSITION ON SUBSILICIDE GROWTH RATES AT 2700 F

furnace oxidation tests of defected and undefected specimens, oxyacetylene torch oxidation tests, and tensile tests of coated specimens.

All specimens were coated in two cycles of 4 and 12 hours each at 2200 F, using a pack composition of 16.5 weight per cent silicon, 3.5 weight per cent NaF, and the balance -100 + 140 mesh Al_2O_3 . Coating weights ranged from 20 to 30 mg/cm² corresponding to thicknesses of 4 to 6 mils. Specific data for each specimen are given in Table 18, Appendix I.

Cyclic Oxidation Tests

Furnace oxidation tests were run at temperatures of 1200 to 2900 F using 1/2 by 3/4-inch tab specimens. For tests at temperatures of 1200 to 2200 F, specimens were cycled at cumulative times of 1, 25, 50, 75, and 100 hours, giving five cycles in the 100 hours. At 2500 F, specimens were checked at 1, 3, 7, 11, 15, 19, 20, 22, and 24 hours, constituting eight cycles. At 2700 and 2900 F, cycles were 1 hour long. Deliberately defected specimens, with a 0.020-inch-diameter hole drilled in one side to expose the substrate, were tested at 1800 and 2700 F.

The cyclic oxidation lives obtained in these tests are summarized in Table 12, and weight-gain curves for representative specimens are shown in Figure 24.

TABLE 12. CYCLIC OXIDATION LIVES OF STRAIGHT SILICIDE COATED Ta-30Cb-7.5V ALLOY SPECIMENS

Exposure Temperature, F	Oxidation Lives of Individual Specimens, hours		Room-Temperature Bend Properties of Substance After Exposure
	Undefected	Defected ^(a)	
1200	>100, >100, >100	--	OT
1500	>100, >100, >100	--	OT
1800	>100, >100	<1, <1	OT(b)
2000	25-50, 50-75, 50-75	--	Embrittled
2200	>100, >100, >100	--	OT
2500	>24, >24, >24	--	OT
2700	2, 10, 12	<1, <1	--
2900	6, >17, >17	--	OT

(a) 0.020-inch-diameter hole drilled through coating on one side of the sample.

(b) Defected specimens were embrittled.

Oxidation at 1200 F was characterized by the appearance of blue tint on the surfaces of the specimens and no measureable weight change. At 1500 F patches of brownish oxide appeared on the surfaces and weight gains were relatively low, about 3 mg/cm² at 100 hours.

At 1800 F, the coatings exhibited very small shiny specks (interpreted as incipient glass formation) in a light brown, porous oxide, accompanied by moderately high weight

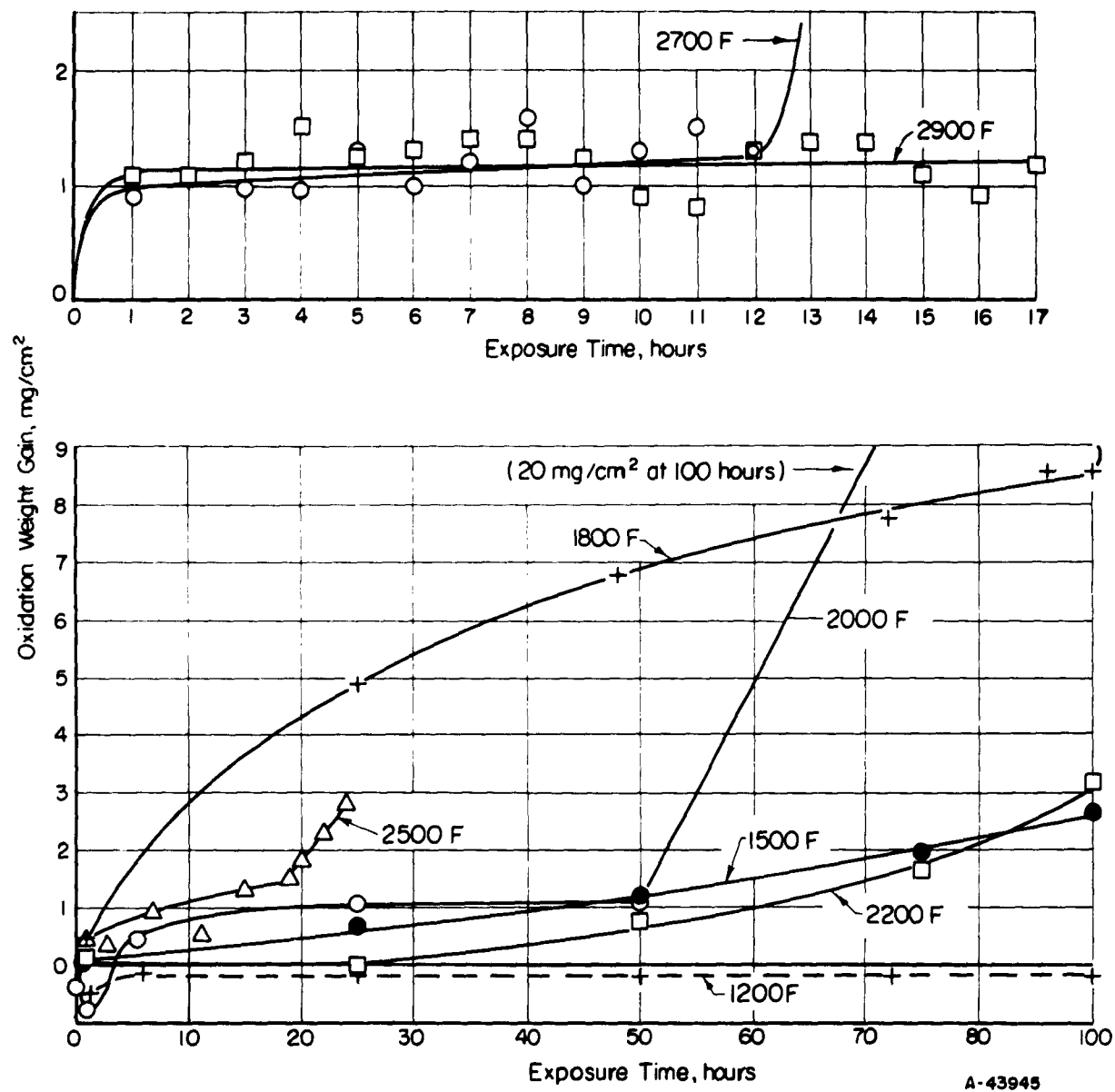


FIGURE 24. OXIDATION WEIGHT GAINS OF Si-COATED Ta-30Cb-7.5V ALLOY
AT 1200 TO 2900 F

gains (8 to 10 mg/cm²). As noted earlier, the measured weight gains at 1800 F correspond closely to the cubic relationship $m^3 = 6.7 t$.

At 2000 F, a porous white oxide was formed on initial exposure which contained small specks of glass. These were gradually hidden, with increasing exposure time, by increasing amounts of the white oxide. As shown in Figure 23, weight gains during accumulated exposures to 24 hours remained fairly low despite the presence of the porous oxide. However, after exposures of 25 to 75 hours, the weight-gain curves for all three of the samples tested rose rapidly in "breakaway" fashion. Subsequent bend tests showed that sufficient oxygen contamination of the substrate had occurred after 75 hours' exposure to render the coated samples brittle.

At 2200 F, incipient glass formation was again observed along with a porous oxide, but weight gains were low and life was >100 hours.

At 2500 F, glass formation was marked, with a uniform continuous film generated in the initial 1-hour cycle. However, after about 19 hours' exposure, specks of a porous oxide appeared at which point "breakaway" occurred in the weight-gain curve. However, all three samples exposed 24 hours at 2500 F retained their original excellent bend ductility.

At 2700 F glass formation increased relative to 2500 F, and failures occurred primarily by rapid oxidation at one or more coating defects, predominantly at specimen edges. At 2900 F a thick coating of glass formed that appeared almost perfectly clear and very fluid. The longer life at 2900 F, relative to 2700 F, was attributed to the increased fluidity of the glass at the higher temperature.

Metallographic measurement was made of the thickness of the subsilicide layer formed on exposure of each of these samples from 1200 to 2900 F. Those values from the 100-hour runs (given in Figure 25) indicated significantly greater rates of subsilicide growth at 1200 and 1500 F than at 1800 F. Accordingly, rate constants were calculated for each temperature assuming the relationship $w^2 = kt$. These are given in an Arrhenius plot in Figure 25 which shows that the k values from 1800 to 2900 F fall very close to a straight line. An activation energy of 54 kcal/mol was computed from the slope of this curve. While no data was available for silicon diffusion in tantalum, this value is close to the activation energy of 59 kcal/mol determined for the diffusion of silicon in columbium.* The increased rate of growth observed at 1200 and 1500 F indicates either a change in the mechanism of diffusion or the character of the subsilicide occurs at these temperatures.

Self-healing capability, or defect resistance, was evaluated by exposing deliberately defected coatings at 1800 and 2700 F. At both temperatures localized oxidation occurred only at the 0.02-inch-diameter hole. Oxidation proceeded less rapidly at 1800 F than at 2700 F, but oxide penetration into the substrate was observed metallographically in both cases.

*Arzhanyy, P. M., Volkova, R. M., and Prokoshkin, "An Investigation of the Structure and Phase Composition of a Silicon Diffusion Coating for Niobium", *Issledovaniya Po Zharoprochnym Splyavam*, Moskva, Vol 6, pp 201-205 (1960).

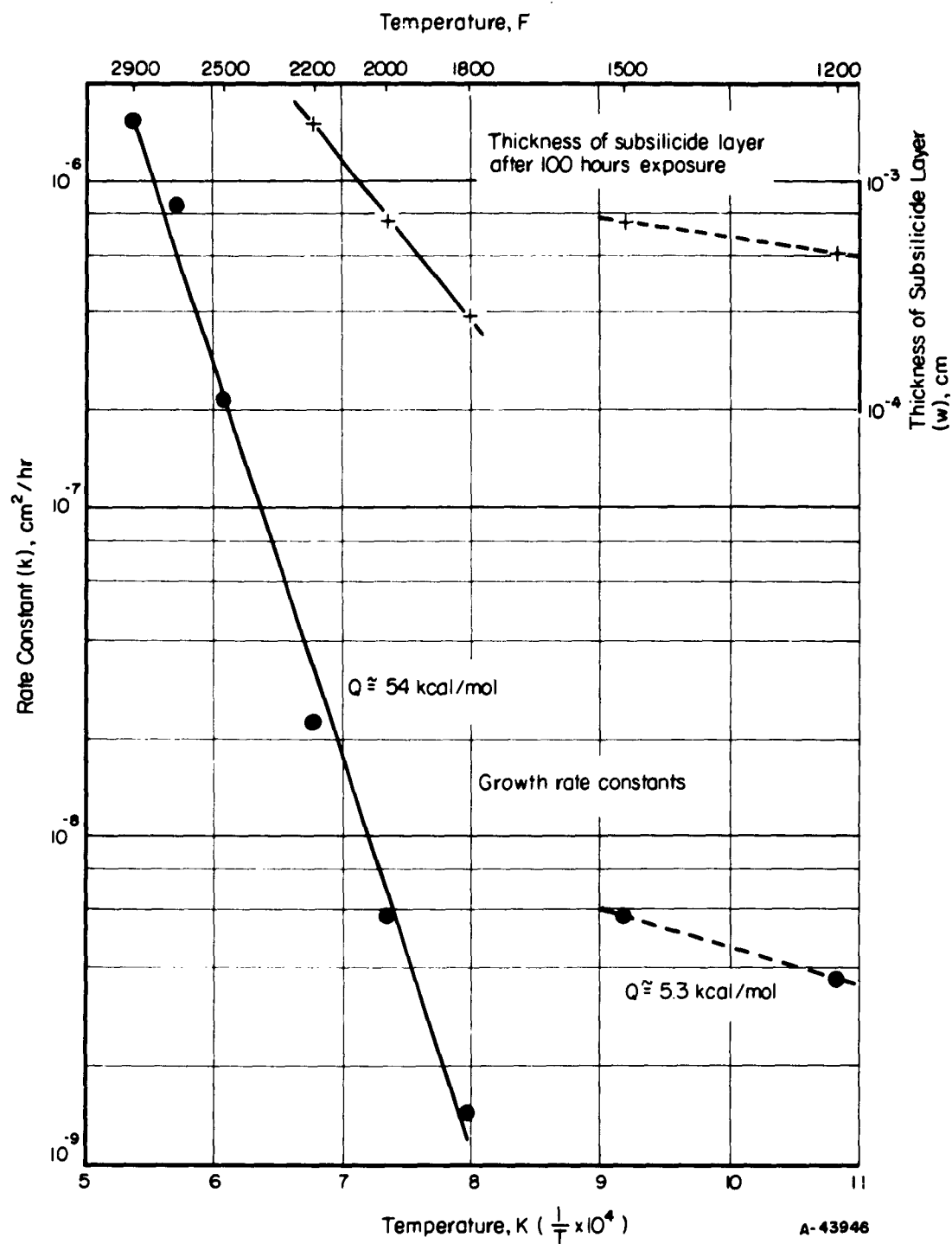


FIGURE 25. RELATIONSHIP OF RECIPROCAL TEMPERATURE TO THICKNESS AND GROWTH RATE OF SUBSILICIDE LAYER IN SILICIDE-COATED Ta-30Cb-7.5V ALLOY

Torch Tests

Cyclic torch tests were run to determine, qualitatively, whether silicide coatings were especially subject to erosion. Here, the coated 1/2 by 2-inch samples were clamped at one end and a torch flame was applied normal to the surface at a spot about 1/2 inch from the free end. The test specimen was thrust under the flame, held at temperature 1/2 hour and quenched in an air blast. Specimens were held at ± 60 F of the nominal test temperature in terms of the apparent optical temperature (no correction applied). Temperatures were read on the spot directly beneath the flame. Tests were continued for 10 half-hour cycles (i. e., 5 hours) or until failure. The results of these tests are summarized in Table 13, and the tested specimens shown in Figure 26.

TABLE 13. RESULTS OF CYCLIC OXYACETYLENE
TORCH OXIDATION TESTS

Test Temperature (a), F	Number of 1/2-Hour Cycles	Observation
3000	2	Failed at 3180 F
3000	4	Failed by cratering
2700	10	Did not fail
2500	10	Did not fail
1800	10	Did not fail

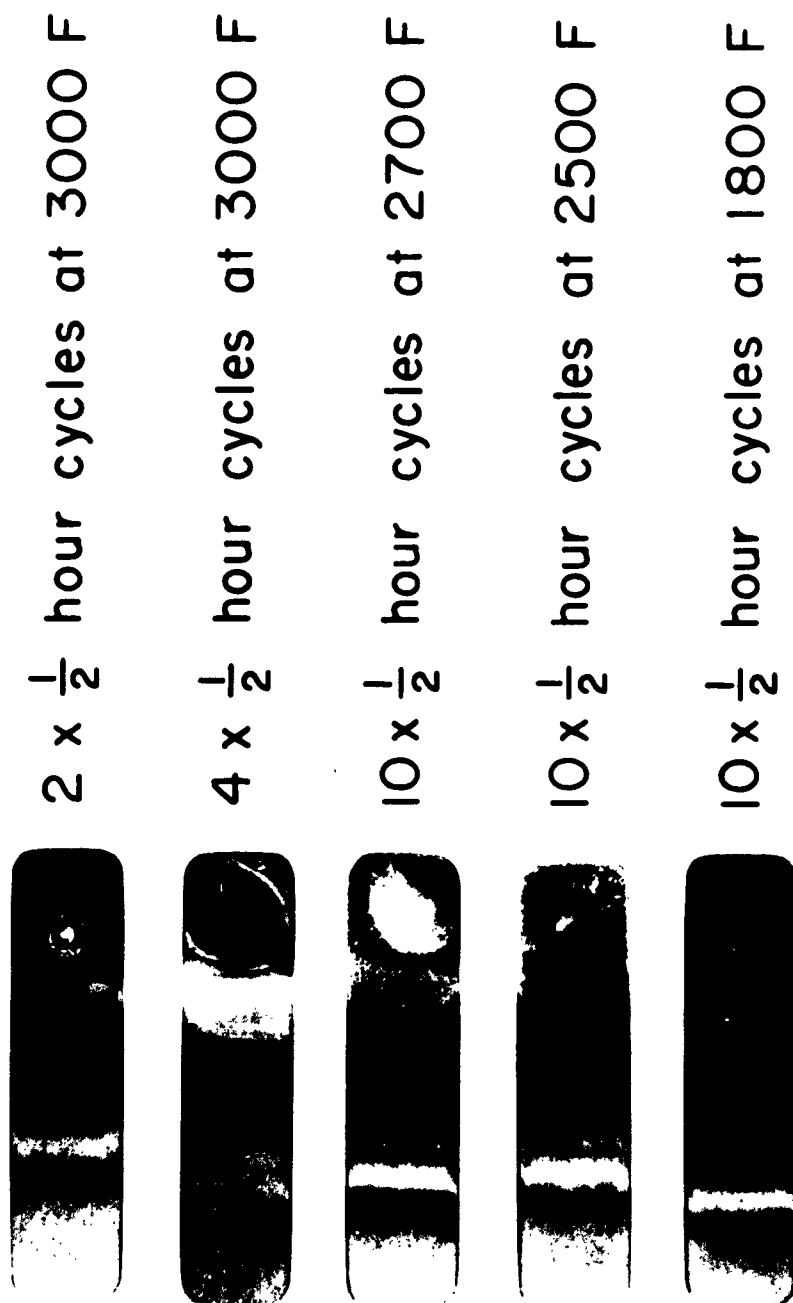
(a) Uncorrected, optically determined.

No signs of coating failure were found on the specimens tested at 1800, 2500, or 2700 F, although oxidation products characteristic of various temperatures were present in an annular pattern around the hottest point. Glass formation occurred during tests at 2500 and 2700 F. Although the glass tended to flake off during quenching in the air blast, it apparently reformed during each cycle.

Of two specimens tested at 3000 F, the first failed early in the third 1/2-hour cycle at which time an apparent temperature reading of 3180 F was obtained. It is not known whether the excessive temperature was due to a fluctuation in torch flame temperature or to an exothermic reaction. Whatever the cause, the failure took the form of a burnthrough which completely pierced the specimen (top sample in Figure 26).

The second specimen tested at 3000 F failed during the fourth 1/2-hour cycle. Here, failure was evidenced by the gradual build up of fluid oxidation products and the formation of a crater in the specimen.

These tests indicate that the straight silicide coating on the Ta-30Cb-7.5V alloy has good resistance to thermal shock and dynamic oxidizing gas atmosphere at temperatures to around 3000 F.



1X

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FIGURE 26. SILICIDE-COATED Ta-30Cb-7.5V ALLOY SPECIMENS AFTER TORCH TESTING AT 1800 TO 3000 F

Tensile Tests

Tensile tests were run on uncoated and silicide-coated Ta-30Cb-7.5V alloy samples prepared to the configuration shown in Figure 27. For the notched test samples, an 0.060-inch-diameter hole was drilled at the center of the reduced section. The hole reduced the cross-sectional area by 30 per cent and provided a theoretical stress concentration factor of 2.3. Prior to coating, all corners and edges were carefully rounded.

As noted earlier, all of the Ta-30Cb-7.5V alloy substrate samples were recrystallized by vacuum annealing for 1 hour at 2200 F prior to coating. Also, the two-cycle coating process used to apply the silicide coating to this alloy involved an accumulated exposure of 16 hours at 2200 F. To isolate the effects of the coating itself on this alloy's properties, approximately heat-treated control samples were included. The results of tensile tests at room temperature and 2200 F on the unnotched and notched tensile properties are given in Table 14.

The unnotched room-temperature test data show the 16-hour heat treatment at 2200 F lowers the yield and tensile strength slightly without significantly affecting tensile elongation. The coating per se had no detrimental effect on room-temperature properties. Moreover, the room-temperature properties of the substrate were retained after exposures of 1 hour at 2700 F in air as well as after a plastic strain of 1.5 per cent in air at 2200 F.

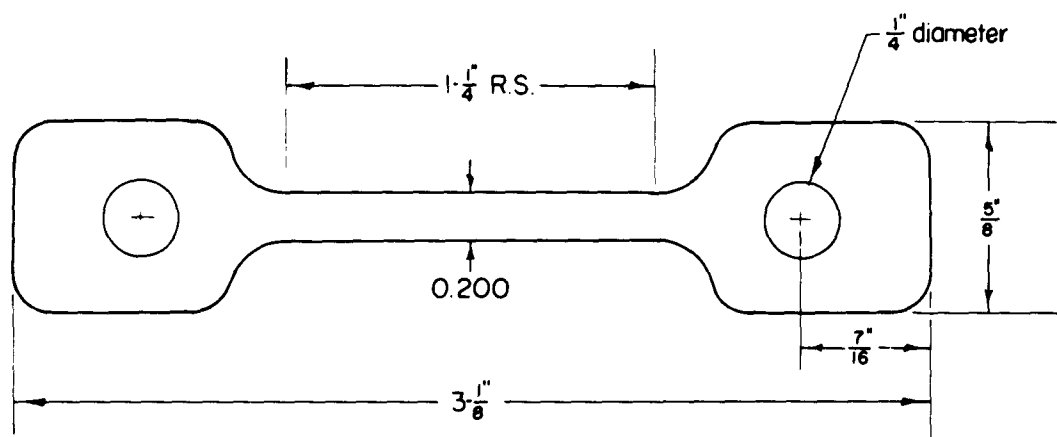
The notched tensile data also show that the application of the coating is not detrimental to substrate ductility. Comparison of notched to unnotched strength ratios for samples with identical processing treatments gives values close to unity. Thus, the coated system is not notch sensitive as coated or after exposure for 1 hour in air at 2700 F.

The 2200 F test data show that the 16-hour treatment at 2200 F does result in a slight increase in hot strength and a corresponding decrease in tensile elongation. The presence of the coating acts further to increase the 2200 F strength as well as to reduce tensile ductility.

DISCUSSION

The original intent of this program was to develop and optimize one silicide-base coating for each of three tantalum substrates, Ta-30Cb-7.5V, Ta-10W, and Ta-8W-2Hf. Because of unforeseen difficulties in coating application, it was not possible to meet this objective. This program did show, however, that silicide coatings are capable of providing effective protection to tantalum alloys in dynamic as well as static oxidation atmospheres at temperatures to 3000 F. Moreover, a sufficient amount of information and experience was obtained to lay the basis for the intelligent design of silicide coatings for future as well as current tantalum-base alloys.

One of the first important facts experimentally established was that alloy additions contained in a tantalum substrate transfer, by diffusion, to an otherwise unalloyed



A-43947

FIGURE 27. TENSILE TEST SPECIMEN (BEFORE COATING)

TABLE 14. TENSILE PROPERTIES OF SILICIDE-COATED Ta-30Cb-7.5V ALLOY

Specimen Geometry	Condition(a)	Test Tem- perature, F	0.2% Offset Yield Strength, ksi ^(b)	Ultimate Tensile Strength, ksi ^(b)	Elonga- tion in 1 Inch, per cent
Unnotched	Uncoated	RT	93.0	108.0	>20
			92.0	103.5	>23
			Average 92.0	106	>20
Unnotched	Uncoated; 16 hours at 2200 F in vacuum	RT	82.2	98.8	26
			85.0	101.8	25
			Average 83.6	100.3	26
Unnotched	Coated	RT	89.0	115.0	16
			82.4	95.7	10
			Average 85.7	105.4	13
Unnotched	Coated and exposed 1 hour at 2700 F in air	RT	85.8	105.0	20
			85.0	99.7	20
			Average 85.4	102.4	20
Unnotched	Coated and strained 1.5% in 1/4 hour at 2200 F in air	RT	91.6	105.3	26
			83.5	103.8	28
			Average 87.6	104.6	27
Notched ^(c)	Uncoated; 16 hours at 2200 F in vacuum	RT	--	104.0	2
			--	106.2	4
			Average --	105.1	3
Notched ^(c)	Coated	RT	--	107.0	4
			--	107.0	3
			Average --	107.0	4
Notched ^(c)	Coated and exposed 1 hour at 2700 F in air	RT	--	101.5	3
			--	103.6	4
			Average --	102.6	4
Unnotched	Uncoated	2200	30.5	37.0	75
			--	36.0	95
			Average 30.5	36.5	85
Unnotched	Uncoated; 16 hours at 2200 F in vacuum	2200	37.0	38.7	57
			39.5	40.6	55
			Average 38.3	39.6	56
Unnotched	Coated	2200	47.6	50.3	38

(a) All specimens annealed 1 hour at 2200 F in vacuum prior to the treatments listed; coating treatment consisted of two cycles of 4 and 12 hours each at 2200 F.

(b) Strengths based on area of substrate core only; data were corrected for substrate consumed during coating formation.

(c) Center hole notch with a stress concentration factor of 2.3.

silicide coating in about the same proportions as they occur in the substrate. Also, the performance of such coatings is significantly affected by the modifying metals introduced in this manner.

From the viewpoint of high strength at elevated temperatures, the most desirable alloy additions to tantalum include tungsten, molybdenum, vanadium, and hafnium. It is perhaps fortuitous that, of these additions, all excepting hafnium improve the oxidation resistance of tantalum-silicide coatings at 2500 F and above. Vanadium, however, is the only one of this group which also provides effective protection at low temperatures as well. Thus, where vanadium was absent from the coating system, oxidation failure at 1800 F occurred in less than 50 hours. Of the three substrates of major interest, it was not surprising, therefore, to find the best all-around performance of straight silicide coatings on the Ta-30Cb-7.5V alloy. Thus, application of this coating had no detrimental effects on the room-temperature properties of the alloy and the coating was protective for times to 100 hours at temperatures to 1800 F in static oxidation, and for times to 1 hour at 3000 F in dynamic oxidation.

At low temperatures, this coating system (Si on Ta-30Cb-7.5V) shows similar, but not identical, behavior to that observed in the previous years' work with straight silicide coatings on unalloyed tantalum. Here, the oxidation life was more than 100 hours at 1200 F and decreased with increasing temperatures to 1800 F. At 2200 F, the next highest temperature investigated, coating life was increased to over 100 hours. This improvement was the apparent result of a change in the surface reaction product from a crystalline, nonadherent SiO_2 layer to a partially amorphous, adherent, glassy SiO_2 layer.

The low-temperature performance of the straight silicide-coated Ta-30Cb-7.5V alloy is considerably improved over that for silicide-coated tantalum. Thus, the coated alloy has a life of at least 100 hours at temperatures from 1200 through 1800 F and also at 2200 F. At 2000 F, however, the effective coating life is reduced to between 25 and 50 hours.

As implied above, tungsten, molybdenum, and hafnium modifications of the silicide (via diffusion from the substrate) did not confer any improvement in 1800 F oxidation life. The available evidence also indicates that columbium contained in the Ta-30Cb-7.5V alloy may be detrimental to 1800 F life. Further, modification of the silicide coating with aluminum and manganese had no beneficial effects at 1800 F. It is then apparent that the improvement in the low-temperature performance of silicide coatings on tantalum is unique to systems containing vanadium, e.g., Si-V coatings on Ta-10W and Si coatings on various vanadium-containing substrates. This beneficial effect of vanadium is thus apparently the combined result of modifications in the sub-silicide and TaSi_2 layer as well as in the oxidation characteristics of these modified silicides.

It is pertinent to point out that no boron-modified silicides were evaluated on vanadium-free coating systems for 1800 F behavior. However, boron modification of the silicide on the Ta-30Cb-7.5V alloy did result in a further significant improvement in 1800 F performance, as judged by weight-change behavior.

As pointed out below, the oxides of boron and vanadium have appreciably lower melting points than any of the oxides of the other silicide modifiers investigated.

<u>Oxide</u>	<u>Melting Temperature, C</u>
B ₂ O ₃	577
V ₂ O ₅	660
MoO ₃	795
WO ₃	1470
SiO ₂	1713
MnO	1790
Ta ₂ O ₅	1890
Al ₂ O ₃	2020
HfO ₂	2790

Thus, the beneficial effects of these additions in improving low-temperature oxidation correlates well with their observed effects in promoting vitrification of the SiO₂-rich scale at low temperatures.

At 2200 F and above, most of the silicide modifiers investigated (including aluminum, boron, manganese, and vanadium) also promote the formation of a glassy, surface oxidation product. However, the degree of protection afforded by these modified silicides varied appreciably.

Thus, aluminum modifications did not improve the 2700 F life on any of the three substrates evaluated despite the increased glass-forming tendency of these coatings. Vanadium, as applied in a coating to the Ta-10W alloy and as introduced to the coating from the Ta-30Cb-7.5V substrate, was quite effective in providing a high degree of protection. Boron, as incorporated in the coating on the Ta-30Cb-7.5V alloy, provided the longest 2700 F and 2900 F cyclic oxidation lives found of all of the coating systems evaluated.

Manganese-modified silicides, as applied to the Ta-10W and Ta-8W-2Hf substrates, showed outstanding defect-healing capability at 2700 F. This effect appeared to be due to a favorably high degree of fluidity imparted to the glassy surface oxidation product. * This coating, however, was not as protective to Ta-10W against oxygen penetration as the vanadium-modified silicide. However, manganese modification of the silicide on the Ta-30Cb-7.5V substrate resulted in too high a degree of fluidity in the resulting oxidation products at 2700 F.

It is quite apparent from the foregoing, that in order to achieve optimum performance from silicide coatings on tantalum alloys, the ideal coating system should contain vanadium and boron. Where these are not incorporated in the substrate, these elements should be added in the coating process.

Unfortunately, in the present study, severe substrate embrittlement was encountered where vanadium and boron were added in the coating process. In the case of applying the Si-V coating to Ta-10W, it is believed that the embrittlement was actually caused by calcium contamination and was, in fact, unrelated to the effect of vanadium per se. The embrittling effect of boron, on the other hand, appears intrinsically due to the intergranular boron-rich phase observed in the substrate of all of the boron-silicide modifications evaluated. It appears feasible, however, that the embrittling effects of boron can be reduced in degree by adjusting the boron content to lower values than those which were evaluated in the present study.

* The MnO and SiO₂ binary equilibrium diagram is characterized by a low-melting eutectic reaction which occurs at approximately 2200 F.

CONCLUSIONS

The following conclusions are offered on the basis of this experimental work:

- (1) Alloying additions from tantalum-alloy substrates diffuse rapidly into otherwise unalloyed silicide coatings in about the same proportions as these occur in the substrate. The performance of such coatings can be significantly affected by modifications introduced in this manner.
- (2) Vanadium is the most beneficial modifier to silicide coatings on tantalum alloys. Thus, of a group of modifiers including boron, molybdenum, tungsten, hafnium, manganese, and aluminum, vanadium was the only one to significantly improve the protective life of silicide coatings at both low (1200 to 1800 F) and high (2500 to 2700 F) temperatures.
- (3) Boron additions, in combination with vanadium, give further significant improvements in the degree of protection at both high and low temperatures. However, at the boron levels investigated, substrate bend embrittlement occurred as the result of the presence of an intergranular boron-rich phase.
- (4) Additions of molybdenum and tungsten have a beneficial effect on the 2700 F life of silicide coatings while hafnium additions may be slightly detrimental.
- (5) Manganese additions to the silicide result in an increased fluidity of the surface oxidation products and show outstanding self-healing characteristics on the Ta-10W and Ta-8W-2Hf alloys at 2700 F. This coating is not as protective to Ta-10W as the Si-V coating. Moreover, as applied to the Ta-30Cb-7.5V alloy, Si-Mn coatings form an extremely fluid oxidation product which is nonprotective at 2700 F.
- (6) Aluminum modifications of the silicide on the three substrates of major interest showed no significant improvements in 2700 F oxidation life.
- (7) Of the three major substrates, straight silicide-coated Ta-30Cb-7.5V showed the best performance characteristics. These included:
 - (a) Application of the coating had no detrimental effect on the alloy's room-temperature properties.
 - (b) The coating capabilities included:
 1. Protection during 1-1/2 per cent plastic deformation in air at 2200 F
 2. Useful lives in cyclic oxidation testing through 2900 F
 3. Resistance to thermal shock and oxidation in torch tests to 3000 F.

- (8) Additional study on methods of obtaining high-integrity vanadium- and boron-modified silicide coatings on vanadium-free tantalum alloy is desirable.

* * * *

Data on which this report is based are contained in Battelle Laboratory Research Books Numbers 18960, 18961, 19316, 19345, 19369, and 19478.

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APPENDIX I

DEPOSITION CONDITIONS AND TEST RESULTS FOR SILICIDE COATINGS ON TANTALUM-BASE ALLOYS

The tables in this appendix give the details of coating deposition conditions and the test results for individual specimens used in applying silicide coatings on three major tantalum-base alloy substrates of interest in this program. The data are organized so that each of the three tables includes all the coatings on a single substrate, and the coatings are grouped, within each table, according to modifying addition.

TABLE 15. SILICIDE

Specimen	First Cycle					Second Cycle ^(b)		
	Pack		Time, hours	Temperature, F	Weight Change, mg/cm ²	Time, hours	Temperature, F	Weight Gain, mg/cm ²
	Composition ^(a) , g	Carrier						
	Coating Element							
<u>Si</u>								
52	10.3 Si	1 NaF	4	2200	10.6	12	2200	14.5
339	Ditto	Ditto	4	2200	11.9	12	2200	16.3
340	"	"	4	2200	12.0	12	2200	16.2
341	"	"	4	2200	12.1	12	2200	16.7
345	"	2 NaF	4	2200	10.1	12	2200	11.6
<u>Si-Al</u>								
220	12.6 Al	1 KI	3/4	2200	9.2	24	2200	22.4
221	Ditto	Ditto	3/4	2200	7.6	24	2200	22.4
225	"	"	1-1/2	2200	7.6	24	2200	20.6
226	"	"	1-1/2	2200	6.8	24	2200	19.8
227	"	"	1-1/2	2200	7.8	24	2200	20.8
231	"	"	13-3/4	2200	33.0	14	2200	4.1
232	"	"	13-3/4	2200	13.3	14	2200	11.3
233	"	"	13-3/4	2200	13.3	14	2200	13.2
321	6.0 Al	3.6 NaF	4	2000	2.3	4	2400	27.6
333	24.0 Al	3.6 NaF	4	2000	4.7	4	2400	23.7
<u>Si-B</u>								
255	9.3 B	1 NaF	3/4	1800	1.1	16	2200	10.1
256	Ditto	Ditto	3/4	1800	1.3	16	2200	10.3
257	"	"	3/4	1800	1.2	16	2200	10.8
261	"	"	1-3/4	1800	1.5	24	2200	6.9
262	"	"	1-3/4	1800	1.1	24	2200	7.2
263	"	"	1-3/4	1800	1.3	24	2200	6.0
267	"	"	4-3/4	1800	1.7	16	2200	5.0
268	"	"	4-3/4	1800	1.5	16	2200	4.9
269	"	"	4-3/4	1800	1.6	16	2200	5.3
357	"	2 NaF	4	2200	4.0	8	2400	5.3
390	"	Ditto	1	1800	1.0	4	2400	11.5
391	"	"	1	1800	0.9	4	2400	11.7
392	"	"	1	1800	0.9	4	2400	11.6
396	"	"	4	1800	1.3	4	2400	5.0
397	"	"	4	1800	1.7	4	2400	5.7
398	"	"	4	1800	1.7	4	2400	5.7
<u>Si-Mn</u>								
237	28.8 Mn	1 NaF	3-1/2	1800	0.8	6	2200	13.3
238	Ditto	Ditto	3-1/2	1800	0.8	6	2200	14.1
239	"	"	3-1/2	1800	0.9	6	2200	12.6
243	"	"	7-1/4	1800	3.4	6	2200	10.2
244	"	"	7-1/4	1800	3.4	6	2200	10.6
245	"	"	7-1/4	1800	3.5	6	2200	11.3
249	"	"	12	1800	6.1	6	2200	10.3
250	"	"	12	1800	6.5	6	2200	10.9
251	"	"	12	1800	6.5	6	2200	10.2

COATINGS ON Ta-10W

Total Coating			2700 F Cyclic Oxidation Life ^(e) , hours	2700 F Cyclic Oxidation Life of Defected Specimens ^(f) , hours	1800 F Cyclic Oxidation Life, hours	Room-Temperature Bend Properties of Substrate After Coating
Total Weight Gain, mg/cm ²	Coating Thickness ^(c) , mils/side	Calculated Coating Composition ^(d) , at. %				
<u>Si</u>						
25.1	5.5	100Si	--	--	--	--
28.3	--	100Si	3	--	--	--
28.2	--	100Si	4	--	--	--
28.8	--	100Si	4	--	--	--
21.7	--	100Si	2	--	--	--
<u>Si-Al</u>						
31.6	--	Si-30Al	3	--	--	--
30.0	--	Si-25Al	2	--	--	--
28.1	--	Si-32Al	3	--	--	--
26.6	4.3	Si-43Al	--	--	--	--
28.6	--	Si-28Al	3	--	--	--
37.2	--	Si-89Al	3	--	--	--
24.5	--	Si-54Al	3	--	--	--
26.5	5.6	Si-52Al	--	--	--	--
30.0	--	Si-8Al	4	--	--	--
28.4	--	Si-17Al	4	--	--	--
<u>Si-B</u>						
11.2	--	Si-22B	1	--	--	--
11.6	--	Si-24B	2	--	--	--
11.9	1.0-3.6	Si-22B	--	--	--	--
8.4	--	Si-36B	<1	--	--	--
8.2	--	Si-29B	<1	--	--	--
7.5	--	Si-35B	<1	--	--	--
6.7	--	Si-47B	<1	--	--	--
6.4	1.1	Si-45B	--	--	--	--
7.0	--	Si-44B	2	--	--	--
9.3	--	Si-65B	<1	--	--	--
12.5	--	Si-18B	1	--	--	--
12.6	--	Si-16B	2	--	--	--
12.5	--	Si-16B	1	--	--	--
6.3	--	Si-40B	1	--	--	--
7.3	--	Si-53B	<1	--	--	--
7.4	--	Si-53B	1	--	--	--
<u>Si-Mn</u>						
14.1	2.4	Si-3Mn	--	--	--	--
14.9	--	Si-3Mn	<1	--	--	--
13.4	--	Si-3Mn	2	--	--	--
13.6	--	Si-14Mn	2	--	--	--
14.0	1.8-2.3	Si-14Mn	--	--	--	--
14.8	--	Si-13Mn	2	--	--	--
16.5	--	Si-23Mn	<1	--	--	--
17.4	2.4	Si-23Mn	--	--	--	--
16.7	--	Si-25Mn	2	--	--	--

TABLE 15.

Specimen	First Cycle					Second Cycle ^(b)		
	Pack Composition ^(a) , g		Time, hours	Temperature, F	Weight Change, mg/cm ²	Time, hours	Temperature, F	Weight Gain mg/cm ²
	Coating Element	Carrier						
405	28.8 Mn	2 NaF	2	1800	5.2	10	2200	20.2
406	Ditto	Ditto	2	1800	5.4	10	2200	20.1
407	"	"	2	1800	5.3	10	2200	20.4
Second Manganese Cycle								
473 ^(g)	28.8 Mn	2 NaF	5	1800	4.8	12	1800	14.5
476 ^(g)	Ditto	Ditto	5	1800	5.8	12	1800	13.4
477 ^(g)	"	"	5	1800	5.7	12	1800	14.6
478 ^(g)	"	"	5	1800	5.7	12	1800	14.4
479 ^(g)	"	"	5	1800	4.2	12	1800	11.6
480 ^(g)	"	"	5	1800	3.7	12	1800	9.9
481 ^(g)	"	"	5	1800	4.4	12	1800	13.0
Third Cycle (Siliconizing)								
473						10	2200	49.4
476						10	2200	54.2
477						10	2200	50.3
478						10	2200	46.5
479						10	2200	37.0
480						10	2200	40.5
481						10	2200	45.3
Si-V								
363	23.8 V	2 NaF	4	2400	-5.5	(Used for metallography; showed		
364	Ditto	Ditto	4	2400	-5.1	12	2200	23.6
365	"	"	4	2400	-5.3	12	2200	24.1
372	"	"	8	2400	-6.9	12	2200	24.4
373	"	"	8	2400	-7.4	12	2200	24.6
374	"	"	8	2400	-7.3	12	2200	24.4
436	"	2 NaCl	6	1800	1.5	12	2200	19.9
437	"	Ditto	6	1800	1.4	12	2200	23.2
438	"	"	6	1800	1.4	12	2200	24.9
482 ^(l)	"	2 NaF	8	2400	-8.9	12	2200	29.3
483 ^(l)	"	Ditto	8	2400	-8.7	12	2200	29.1
485 ^(l)	"	"	8	2400	-5.5	12	2200	25.6
486 ^(l)	"	"	8	2400	-6.3	12	2200	26.7
487 ^(l)	"	"	8	2400	-8.3	12	2200	28.1
488 ^(l)	"	"	8	2400	-15.4	12	2200	19.2
489 ^(l)	"	"	8	2400	-15.1	12	2200	20.6
490 ^(l)	"	"	8	2400	-16.8	12	2200	20.4
Si-V-B								
366	3 B, 18 V	2 NaF	4	2400	-1.1	12	2200	22.0
367	Ditto	Ditto	4	2400	-1.6	12	2200	22.7
368	"	"	4	2400	-1.4	12	2200	22.6
382	"	2 NaF	8	2400	-0.2	12	2200	17.1
383	"	Ditto	8	2400	-0.2	12	2200	16.5

Footnotes appear on the following page.

(Continued)

Total Weight Gain, mg/cm ²	Total Coating		2700 F Cyclic Oxidation Life(e), hours	2700 F Cyclic Oxidation Life of Defected Specimens(f), hours	1800 F Cyclic Oxidation Life, hours	Room-Temperature Bend Properties of Substrate After Coating
	Coating Thickness(c), mils/side	Calculated Coating Composition(d), at. %				
25.4	--	Si-11Mn	--	--	--	--
25.5	--	Si-12Mn	3	--	--	--
25.7	--	Si-11Mn	5	--	--	--
<u>Total Manganese</u>						
19.3						
19.2						
20.3						
20.0						
15.7						
13.6						
17.4						
<u>Total Si-Mn Coating</u>						
68.7(h)			--	--	--	OT
73.4(h)			--	<1	--	--
70.6(h)			--	<1	--	--
66.5(h)	6-7(i)	Si-20Mn(h)	10	--	--	--
52.7(h)			10	--	--	--
54.1(h)			--	--	1-3	--
62.7(h)			--	--	1-3	--
<u>Si-V</u>						
roughened surface and 0.8-mil-thick coating)						
4.3		--	--	--	--	--
--		--	5	--	--	--
--		--	--	--	--	--
--		--	4	--	--	--
--		--	10	--	--	--
--		--	--	--	--	--
--		--	2	--	--	--
--		--	2	--	--	--
5.3		--	--	--	--	Broke on 3/8 in. radius die
--		--	--	--	--	Broke on 3/8 in. radius die
--		--	--	<1	--	--
--		--	--	<1	--	--
--		--	6	--	--	--
--		--	10	--	--	--
--		--	--	--	75-100	--
--		--	--	--	> 100	--
<u>Si-V-B</u>						
20.9	4.2	--	--	--	--	--
21.1	--	--	4	--	--	--
21.2	--	--	4	--	--	--
16.9	--	--	2	--	--	--
16.3	3.4	--	--	--	--	--

Footnotes for Table 15

- (a) Balance of pack was 48 g of Al_2O_3 .
- (b) Siliconizing pack contained 10.3 g of Si, 2 g of NaF, and 48 g of Al_2O_3 .
- (c) Measured metallographically.
- (d) Calculated on the basis of weight gains.
- (e) Number of 1-hour periods survived without failure.
- (f) Defect was a 0.04-inch-diameter hole drilled through the coating.
- (g) Specimens used in advanced screening evaluation.
- (h) Rough estimates only due to weight losses from poor edges.
- (i) Coating thickness discounting edges and corners.

TABLE 16. SILICIDE

Specimen	First Cycle				Second Cycle ^(b)			
	Pack Composition ^(a) , g		Time, hours	Temperature, F	Weight Change, mg/cm ²	Time, hours	Temperature, F	Weight Gain, mg/cm ²
	Coating Element	Carrier						
<u>Si</u>								
342	10.3 Si	1 NaF	4	2200	10.4	12	2200	14.3
343	Ditto	Ditto	4	2200	11.0	12	2200	13.8
344	"	"	4	2200	10.6	12	2200	13.8
348	"	2 NaF	4	2200	9.0	12	2200	10.6
530(g)	"	Ditto	4	2200	10.1	12	2200	13.5
531(g)	"	"	4	2200	9.7	12	2200	13.7
532(g)	"	"	4	2200	10.2	12	2200	13.9
533(g)	"	"	4	2200	8.6	12	2200	11.9
534(g)	"	"	4	2200	9.1	12	2200	11.4
535(g)	"	"	4	2200	9.6	12	2200	11.9
536(g)	"	"	4	2200	8.2	12	2200	11.3
464	"	"	14	2200	22.4	12	2200	8.0
465	"	"	14	2200	22.2	12	2200	8.3
466	"	"	14	2200	22.4	12	2200	8.0
<u>Si-Al</u>								
222	12.6 Al	1 KI	3/4	2200	9.3	24	2200	20.7
224	Ditto	Ditto	3/4	2200	12.8	24	2200	17.5
228	"	"	1-1/2	2200	9.1	24	2200	19.3
229	"	"	1-1/2	2200	11.1	24	2200	20.1
230	"	"	1-1/2	2200	12.9	24	2200	17.9
234	"	"	13-3/4	2200	14.2	14	2200	10.4
235	"	"	13-3/4	2200	14.2	14	2200	10.2
236	"	"	13-3/4	2200	15.7	14	2200	8.6
324	6.7 Al	"	4	2000	4.3	4	2400	20.1
337	23.8 Al	"	4	2000	5.1	4	2400	21.2
<u>Si-B</u>								
258	9.3 B	1 NaF	3/4	1800	0.9	24	2200	15.4
259	Ditto	Ditto	3/4	1800	1.0	24	2200	15.6
260	"	"	3/4	1800	1.3	24	2200	15.6
264	"	"	1-3/4	1800	2.4	24	2200	10.2
265	"	"	1-3/4	1800	2.0	24	2200	9.9
266	"	"	1-3/4	1800	2.2	24	2200	10.9
270	"	"	4-3/4	1800	2.1	16	2200	9.7
271	"	"	4-3/4	1800	1.9	16	2200	9.8
272	"	"	4-3/4	1800	2.0	16	2200	9.7
354	"	2 NaF	4	2200	7.0	4	2400	13.8
360	"	Ditto	4	2200	7.3	8	2400	14.9
455(g)	"	"	4	2200	7.7	8	2400	13.6
456(g)	"	"	4	2200	7.7	8	2400	14.1

COATINGS ON Ta-30Cb-7.5V

Total Coating			2700 F Cyclic Oxidation Life ^(e) , hours	2700 F Cyclic Oxidation Life of Defected Specimens ^(f) , hours	1800 F Cyclic Oxidation Life, hours	Room-Temperature Bend Properties of Substrate After Coating
Total Weight Gain, mg/cm ²	Coating Thickness ^(c) , mils/side	Calculated Coating Composition ^(d) , at. %				
<u>Si</u>						
24.7	--	100Si	6	--	--	--
24.8	--	100Si	10	--	--	--
24.5	--	100Si	9	--	--	--
19.6	--	100Si	4	--	--	--
23.6	--	100Si	--	--	>100	--
23.5	--	100Si	--	--	>100	--
24.0	--	100Si	6	--	--	--
20.5	--	100Si	--	<1	--	--
20.5	--	100Si	--	<1	--	--
21.5	--	100Si	3	--	--	--
19.5	--	100Si	--	--	--	OT
30.4	--	100Si	>11	--	--	--
30.5	--	100Si	>11	--	--	--
30.4	6	100Si	--	--	--	--
<u>Si-Al</u>						
30.0	4.5	Si-32Al	--	--	--	--
30.3	--	Si-43Al	3	--	--	--
28.4	--	Si-33Al	2	--	--	--
31.2	--	Si-37Al	4	--	--	--
30.8	--	Si-43Al	4	--	--	--
24.6	4.5	Si-58Al	--	--	--	--
24.4	--	Si-58Al	3	--	--	--
24.3	--	Si-65Al	3	--	--	--
24.3	--	Si-18Al	2	--	--	--
26.3	--	Si-20Al	2	--	--	--
<u>Si-B</u>						
16.3	3.0	Si-13B	--	--	--	--
16.7	--	Si-14B	17	--	--	--
16.9	--	Si-17B	16	--	--	--
12.6	--	Si-38B	<1	--	--	--
11.9	2.5	Si-35B	--	--	--	--
13.1	--	Si-35B	1	--	--	--
11.8	--	Si-36B	3	--	--	--
11.7	--	Si-33B	18	--	--	--
11.8	--	Si-35B	16	--	--	--
20.7	4.4	Si-58B	--	--	--	--
22.1	--	Si-57B	>20	--	--	--
21.3	--	Si-60B	--	--	--	Broke on 3/8-in. - radius die
21.8	--	Si-58B	--	--	--	Broke on 3/8-in. - radius die

TABLE 16.

Specimen	First Cycle				Weight Change, mg/cm ²	Second Cycle ^(b)		
	Pack Composition ^(a) , g		Time, hours	Temperature, F		Time, hours	Temperature, F	Weight Gain, mg/cm ²
	Coating Element	Carrier						
<u>Si-B (continued)</u>								
458(g)	9.3 B	2 NaF	4	2200	6.2	8	2400	13.3
459(g)	Ditto	Ditto	4	2200	6.6	8	2400	13.7
460(g)	"	"	4	2200	6.7	8	2400	12.6
461(g)	"	"	4	2200	5.7	8	2400	11.7
462(g)	"	"	4	2200	5.6	8	2400	12.6
463(g)	"	"	4	2200	5.4	8	2400	12.0
<u>Si-Mn</u>								
240	28.8 Mn	1 NaF	3-1/2	1800	2.5	6	2200	12.0
241	Ditto	Ditto	3-1/2	1800	2.4	6	2200	13.3
242	"	"	3-1/2	1800	2.7	6	2200	11.5
246	"	"	7-1/4	1800	5.9	6	2200	12.5
247	"	"	7-1/4	1800	6.0	6	2200	13.8
248	"	"	7-1/4	1800	6.0	6	2200	12.9
252	"	"	12	1800	7.7	6	2200	9.1
253	"	"	12	1800	7.5	6	2200	9.6
254	"	"	12	1800	7.4	6	2200	9.4
408	"	2 NaF	2	1800	5.2	10	2200	16.1
409	"	Ditto	2	1800	5.1	10	2200	16.6
410	"	"	2	1800	5.2	10	2200	16.6
<u>Si-Cr</u>								
369	27.1 Cr	2 KI	4	2400	1.8	16	2200	17.9
370	Ditto	Ditto	4	2400	1.8	16	2200	17.0
371	"	"	4	2400	1.9	16	2200	17.1

(a) Balance of pack was 48 g of Al₂O₃.(b) Siliconizing pack contained 10.3 g of Si, 2 g of NaF, and 48 g of Al₂O₃.

(c) Measured metallographically.

(d) Calculated on the basis of weight gains.

(e) Number of 1-hour periods survived without failure.

(f) Defect was a 0.04-inch-diameter hole drilled through the coating.

(g) Specimens used in advanced screening evaluation.

(Continued)

Total Weight Gain, ₂ mg/cm	Total Coating		2700 F Cyclic Oxidation Life ^(e) , hours	2700 F Cyclic Oxidation Life of Defected Specimens ^(f) , hours	1800 F Cyclic Oxidation Life, hours	Room-Temperature Bend Properties of Substrate After Coating
	Coating Thickness ^(c) , mils/side	Calculated Coating Composition ^(d) , at. %				
<u>Si-B (continued)</u>						
19.6	--	Si-55B	--	<1	--	--
20.3	--	Si-55B	--	<1	--	--
19.3	--	Si-55B	11	--	--	--
17.5	--	Si-55B	3	--	--	--
18.2	--	Si-55B	--	--	>100	--
17.4	--	Si-55B	--	--	>100	--
<u>Si-Mn</u>						
14.4	1.6-2.2	Si-9Mn	--	--	--	--
15.7	--	Si-8Mn	<1	--	--	--
14.2	--	Si-13Mn	<1	--	--	--
18.3	2.7	Si-19Mn	--	--	--	--
19.8	--	Si-18Mn	<1	--	--	--
18.9	--	Si-19Mn	<1	--	--	--
16.8	--	Si-31Mn	<1	--	--	--
17.1	2.3	Si-29Mn	--	--	--	--
16.8	--	Si-29Mn	<1	--	--	--
21.3	3.0	Si-14Mn	--	--	--	--
21.8	--	Si-13Mn	<1	--	--	--
21.8	--	Si-14Mn	<1	--	--	--
<u>Si-Cr</u>						
19.7	--	Si-9Cr	<1	--	--	--
18.8	3	Si-9Cr	--	--	--	--
19.0	--	Si-9Cr	<1	--	--	--

TABLE 17. SILICIDE

Specimen	First Cycle				Second Cycle ^(b)			
	Pack Composition ^(a) , g		Time, hours	Temper- ature, F	Weight Change, mg/cm ²	Time, hours	Temper- ature, F	Weight Gain, mg/cm ²
	Coating Element	Carrier						
<u>Si(g)</u>								
420	10.3 Si	2 NaF	4	2200	10.8	12	2200	11.7
421	Ditto	Ditto	4	2200	10.6	12	2200	11.8
422	"	"	4	2200	11.5	12	2200	11.8
491 ^(h)	"	"	4	2200	12.8	12	2200	17.1
494 ^(h)	"	"	4	2200	14.1	12	2200	12.6
495 ^(h)	"	"	4	2200	14.0	12	2200	13.0
496 ^(h)	"	"	4	2200	14.7	12	2200	12.8
497 ^(h)	"	"	4	2200	11.5	12	2200	10.4
498 ^(h)	"	"	4	2200	11.8	12	2200	10.4
499 ^(h)	"	"	4	2200	11.9	12	2200	10.6
<u>Si-Al</u>								
414	12.6 Al	2 KI	4	2000	8.0	14	2200	15.6
415	Ditto	Ditto	4	2000	7.9	14	2200	15.9
416	"	"	4	2000	7.9	14	2200	15.8
417	"	"	3	1800	2.7	16	2200	17.8
418	"	"	3	1800	2.5	16	2200	18.5
419	"	"	3	1800	3.0	16	2200	17.9
<u>Si-B</u>								
393	9.3 B	2 NaF	1	1800	1.1	4	2400	9.7
394	Ditto	Ditto	1	1800	1.2	4	2400	9.3
395	"	"	1	1800	1.3	4	2400	9.4
445	0.9 B, 20.8 Si	"	4	2200	5.1	12	2200	19.8
446	Ditto	"	4	2200	4.8	12	2200	22.2
447	"	"	4	2200	4.4	12	2200	19.9
448	"	"	4	2200	2.1	12	2200	12.8
449	"	"	4	2200	2.0	12	2200	30.4
<u>Si-Mn^(j)</u>								
411	28.8 Mn	2 NaF	2	1800	3.8	10	2200	13.6
412	Ditto	Ditto	2	1800	3.8	10	2200	13.0
413	"	"	2	1800	3.5	10	2200	13.2
403	"	"	4	1800	5.6	12	2200	10.7
404	"	"	4	1800	5.7	12	2200	9.2
500 ^(h)	"	"	8	1800	15.6	12	2200	20 ^(k)
503 ^(h)	"	"	8	1800	15.6	12	2200	
504 ^(h)	"	"	8	1800	16.1	12	2200	
505 ^(h)	"	"	8	1800	15.1	12	2200	
506 ^(h)	"	"	8	1800	12.7	12	2200	
507 ^(h)	"	"	8	1800	12.4	12	2200	
508 ^(h)	"	"	8	1800	13.3	12	2200	

COATINGS ON Ta-8W-2Hf

Total Coating		Calculated Coating Composition (d)	2700 F Cyclic Oxidation Life (e), hours	2700 F Cyclic Oxidation Life of Defected Specimens (f), hours	1800 F Cyclic Oxidation Life, hours	Room-Temperature Bend Properties of Substrate After Coating
Total Weight Gain, mg/cm ²	Coating Thickness (c), mils/side					
<u>Si(g)</u>						
22.5	4.1	100Si	--	--	--	--
22.4	--	100Si	3	--	--	--
23.3	--	100Si	2	--	--	--
29.8	5.2	100Si	--	--	--	0 T
26.7	--	100Si	--	<1	--	--
27.0	--	100Si	--	<1	--	--
27.5	--	100Si	2	--	--	--
22.0	--	100Si	2	--	--	--
22.2	--	100Si	--	--	3-8	--
22.6	--	100Si	--	--	8-25	--
<u>Si-Al</u>						
23.6	4.6	Si-35Al	--	--	--	--
23.8	--	Si-35Al	2	--	--	--
23.7	--	Si-35Al	2	--	--	--
20.5	4.0	Si-13Al	--	--	--	--
20.9	--	Si-13Al	2	--	--	--
21.0	--	Si-13Al	1	--	--	--
<u>Si-B</u>						
10.8	--	Si-22B	<1	--	--	--
10.5	1-3	Si-25B	--	--	--	--
10.7	--	Si-26B	<1	--	--	--
25.0 ⁽ⁱ⁾	1-6	--	--	--	--	--
27.0 ⁽ⁱ⁾	--	--	<1	--	--	--
24.3 ⁽ⁱ⁾	--	--	<1	--	--	--
14.9 ⁽ⁱ⁾	--	--	<1	--	--	--
32.4 ⁽ⁱ⁾	--	--	<1	--	--	--
<u>Si-Mn(j)</u>						
17.4	--	Si-12Mn	--	--	--	--
16.8	--	Si-13Mn	1	--	--	--
16.7	--	Si-12Mn	<1	--	--	--
16.3	--	Si-21Mn	<1	--	--	--
14.9	--	Si-24Mn	5	--	--	--
30 ^(k)	6-8 ^(l)	Si-30Mn ^(k)	--	--	--	0 T
			--	>7	--	--
			--	>7	--	--
			5	--	--	--
			1	--	--	--
			--	--	3-8	--
			--	--	3-8	--

TABLE 17.

Specimen	First Cycle				Second Cycle ^(b)			
	Pack Composition ^(a) , g		Time, hours	Temperature, F	Weight Change, mg/cm ²	Time, hours	Temperature, F	Weight Gain, mg/cm ²
	Coating Element	Carrier						
<u>Si-V</u>								
384	21.7 V	2 NaF	4	2400	0.3	12	2200	19.8
385	Ditto	Ditto	4	2400	-0.1	12	2200	19.7
386	"	"	4	2400	-0.9	12	2200	20.2
376	"	"	8	2400	-6.6	12	2200	22.3
377	"	"	8	2400	-7.1	12	2200	22.2
427	"	2 NaCl	4	2200	0.5	12	2200	21.6
428	"	Ditto	4	2200	0.6	12	2200	22.2
429	"	"	4	2200	0.6	12	2200	22.5
439	"	"	6	1800	1.3	12	2200	18.6
<u>Si-V-B</u>								
430	3 B, 18 V	2 NaCl	4	2200	0.1	12	2200	19.5
431	Ditto	Ditto	4	2200	0.1	12	2200	19.5
432	"	"	4	2200	0.2	12	2200	19.3
442	"	"	6	1800	0		(Used for metallography;	
443	"	"	6	1800	0.1	12	2200	14.8
444	"	"	6	1800	0.1	12	2200	14.9

(a) Balance of pack was 48 g of Al₂O₃.

(b) Siliconizing pack contained 10.3 g of Si, 2 g of NaF, and 48 g of Al₂O₃.

(c) Measured metallographically.

(d) Calculated on the basis of weight gains.

(e) Number of 1-hour cycles survived without failure.

(f) Defect was a 0.04-inch-diameter hole drilled through the coating.

(g) Edges were cracked.

(h) Specimens used in advanced screening evaluation.

(i) The same codeposition pack was used for the second cycle; second-cycle coating was discontinuous and partially oxidized.

(j) All specimens showed cracked and flaking edges.

(k) Rough estimates only due to weight losses from poor edges.

(l) Coating thickness discounting edges and corners.

(Continued)

Total Coating			2700 F Cyclic Oxidation Life(e), hours	2700 F Cyclic Oxidation Life of Defected Specimens(f), hours	1800 F Cyclic Oxidation Life, hours	Room-Temperature Bend Properties of Substrate After Coating
Total Weight Gain, mg/cm ²	Coating Thickness(c), mils/side	Calculated Coating Composition(d), at. %				
Si-V						
20.1	--	--	2	--	--	--
19.6	--	--	2	--	--	--
19.3	--	--	2	--	--	--
15.7	--	--	1	--	--	--
15.1	--	--	1	--	--	--
22.1	4.2	--	--	--	--	--
22.8	--	--	<1	--	--	--
23.1	--	--	2	--	--	--
19.9	--	--	1	--	--	--
Si-V-B						
19.5	--	--	1	--	--	--
19.7	--	--	1	--	--	--
19.6	3.6	--	--	--	--	--
0.1-mil-thick first-cycle coating)			--	--	--	--
14.9	--	--	2	--	--	--
14.9	--	--	1	--	--	--

APPENDIX II

OBSERVATIONS ON THE APPLICATION OF MODIFIED SILICIDE COATINGS TO TANTALUM ALLOY BY THE PACK-CEMENTATION METHOD

As stated in the body of this report, in evaluating the silicide coatings on this program, a coating thickness of 3 to 5 mils per side was arbitrarily fixed as a target value. These thicknesses correspond to total coating weight gains of 17 to 28 mg/cm².

Initially, it was assumed that the deposition rate for each metal to be deposited would be parabolic as was the case for silicon on unalloyed tantalum in the first year's work. Deposition temperature was the main variable used to control coating thickness with deposition time being used as a secondary variable.

Experience with straight silicide coating on the Ta-10W, Ta-30Cb-7.5V, and Ta-8W-2Hf alloys indicated that the deposition rate for silicon directly on to these substrates was parabolic and did not vary appreciably from one alloy to the others. However, experiences showed the deposition rates for other metals not only varied for the individual metals but also from one substrate to another. Inasmuch as this program was primarily concerned with coating performance, it was not possible to optimize or even systematically study the coating variables for each of the numerous coating systems investigated. However, certain observations were made from the coating experiences obtained. These are summarized in the paragraphs which follow to serve as a guide in the further development of coatings of this type.

These comments are confined to experiences in preparing silicide coatings on the Ta-10W, Ta-30Cb-7.5V, and Ta-8W-2Hf substrates in which the modifying elements were aluminum, boron, and manganese. In each instance, the modifying element was applied to the substrate in the first cycle with silicon being added in the second cycle. Experiences in preparing Si-V coatings on the Ta-10W and Ta-8W-2Hf and in codeposition of various coatings have been adequately summarized in the text.

Al-Si COATINGS

Al on Alloys

Aluminum deposited satisfactorily at a parabolic rate on each of the three alloy substrates. However, the deposition rate was sensitive to both the amount of aluminum contained in the pack mixture (Figure 28) and to substrate composition (Figures 28 and 29).

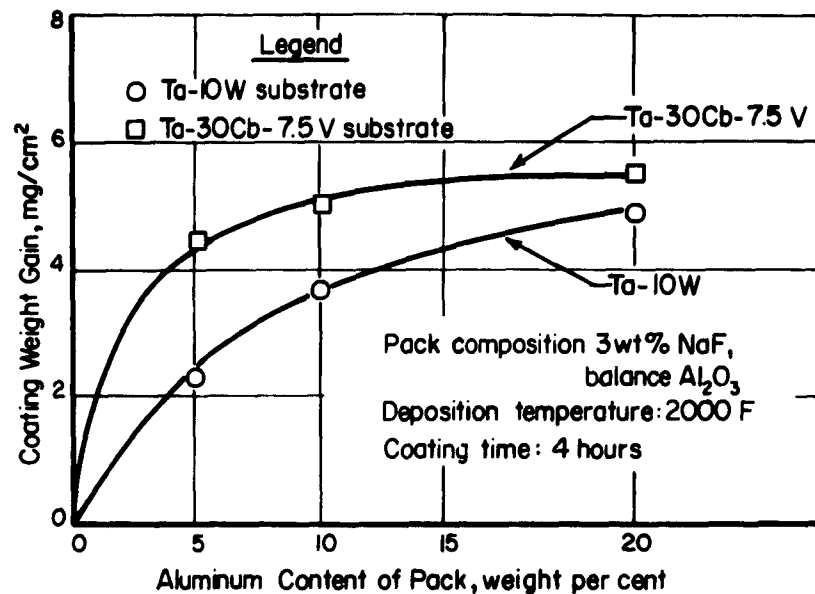


FIGURE 28. THE EFFECT OF PACK COMPOSITION ON THE DEPOSITION OF ALUMINUM ON Ta-BASE ALLOYS

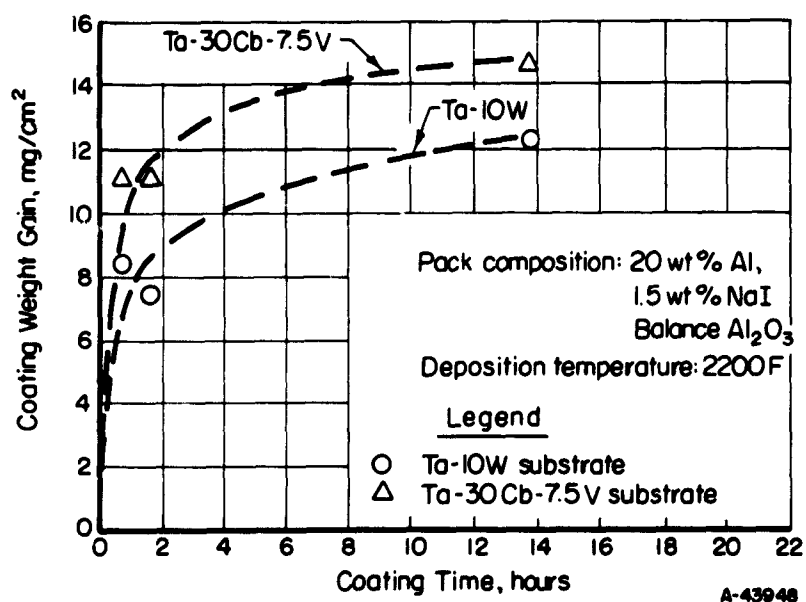


FIGURE 29. COATING WEIGHT GAIN VERSUS TIME FOR THE DEPOSITION OF ALUMINUM ON Ta-BASE ALLOYS

Si Over Al

The deposition rate of silicon over aluminum appeared linear and sensitive to the composition of the underlying substrate as shown in Figure 30.

B-Si COATINGS

B on Alloys

Boron deposition followed a parabolic rate which, at 1800 F, was essentially the same for each of the alloy substrates (Figure 31). However, limited experiences at 2200 F indicate that, at this temperature, boron deposits more rapidly on Ta-30Cb-7.5V than on Ta-10W.

Si Over B

For all three substrates, the rate of siliconizing was reduced appreciably by the presence of the boron layer. Deposition of silicon over boron showed no systematic behavior, and no coatings of reasonable thickness (3 mils or more) or integrity were obtained on Ta-10W and Ta-8W-2Hf.

Mn-Si COATINGS

Mn on Alloys

Manganese deposition appeared to be linear but was sensitive to a number of variables including substrate composition, the amount of carrier, and type of manganese (Figure 32). With regard to the manganese, both lots were of the same type (electrolytic grade) but from different shipments.

Si Over Mn

Deposition rates for silicon over manganese appeared to be linear and independent of substrate composition (Figure 33).

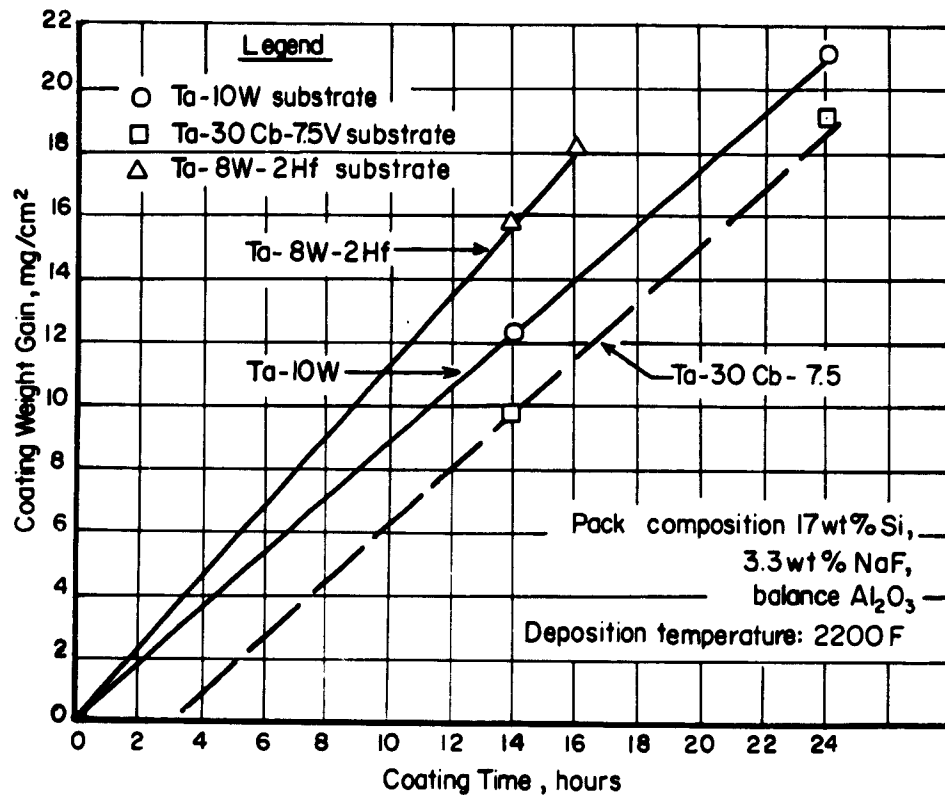


FIGURE 30. COATING WEIGHT GAIN VERSUS TIME FOR THE DEPOSITION OF SILICON OVER ALUMINUM ON Ta-BASE ALLOYS

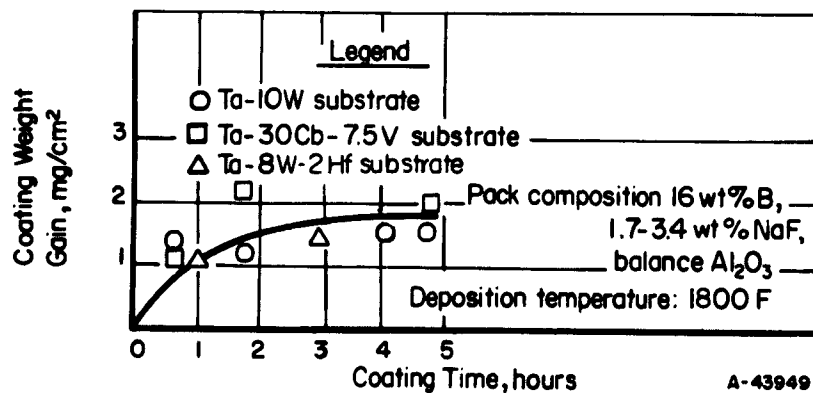


FIGURE 31. COATING WEIGHT GAIN VERSUS TIME FOR THE DEPOSITION OF BORON ON Ta-BASE ALLOYS

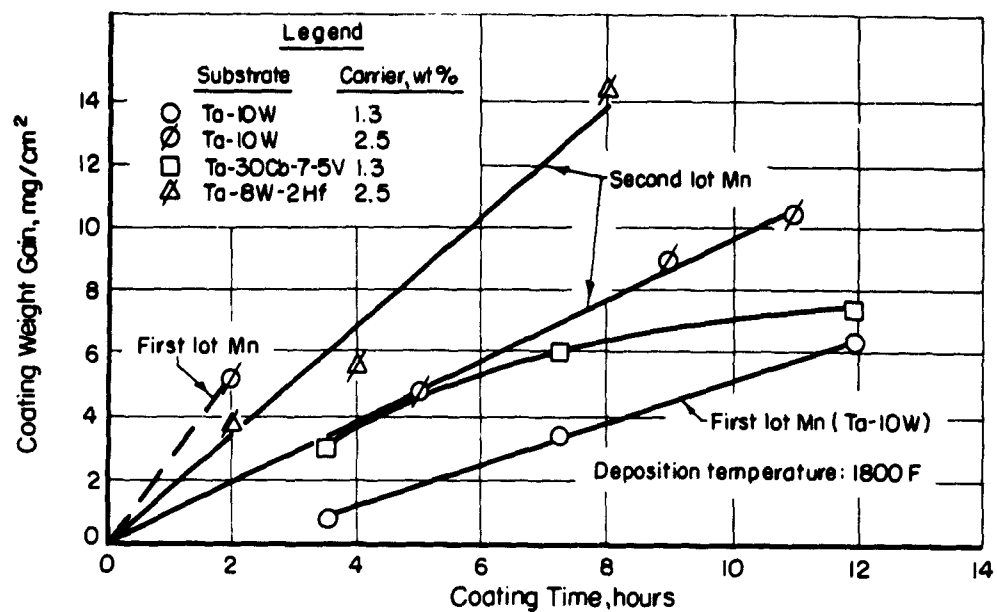


FIGURE 32. COATING WEIGHT GAIN VERSUS TIME FOR THE DEPOSITION OF MANGANESE ON Ta-BASE ALLOYS

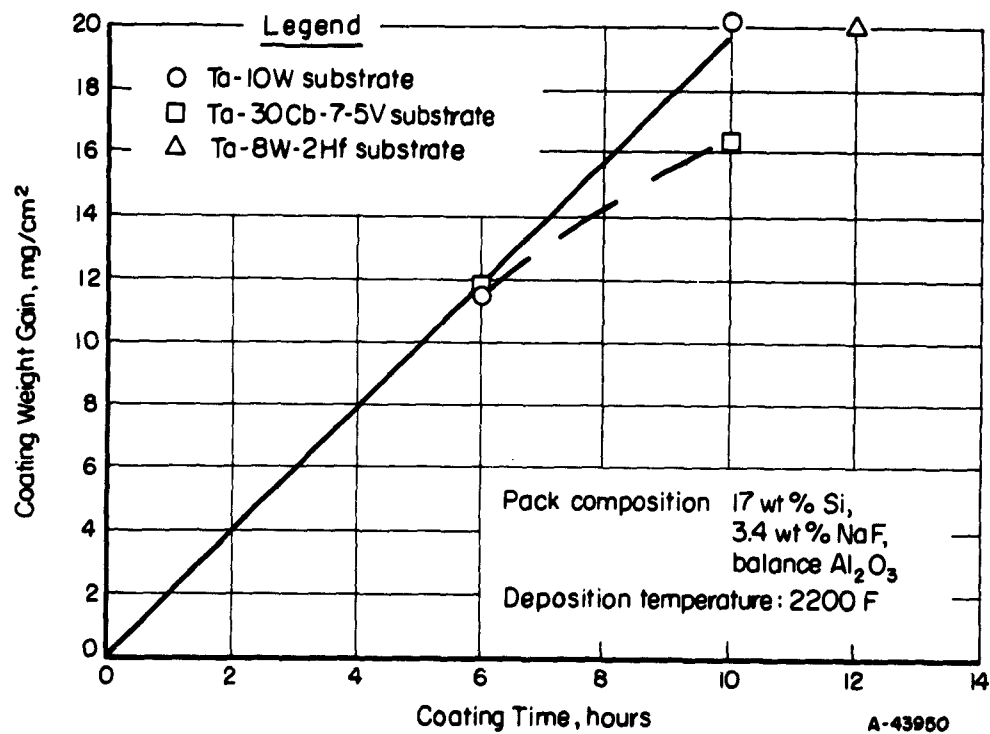


FIGURE 33. COATING WEIGHT GAIN VERSUS TIME FOR THE DEPOSITION OF SILICON OVER MANGANESE ON Ta-BASE ALLOYS

COMPARISONS BETWEEN Al, B, AND Mn

Generally, manganese deposited more rapidly than aluminum or boron. Also, the deposition rates for each of these metals tended to vary with substrate composition, the rates being highest for Ta-30Cb-7.5V, intermediate for Ta-8W-2Hf, and lowest for Ta-10W. Siliciding rates were greatest over manganese, less over aluminum, and very low over boron.

Aeronautical Systems Division, Dir. Materials & Processes,
Metals & Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt No. ASD-TDR-63-232. COATINGS FOR TANTALUM-
BASE ALLOYS. FINAL report, Apr 63, 80 p. incl illus.,
tables.

Unclassified Report

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additions in the silicide coating. Of the modifiers studied,
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(over)

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cations of the silicide with boron and vanadium show further
improvements in static oxidation performance at tempera-
tures from at least 1800 through 2900 F.

(over)

I. Tantalum-Coatings
2. Silicide Coatings
3. Heat-Resistant Alloys
I. AFSC Proj 7312, Task 731201
II. Contract No. AF 33(657)-
7909

III. Battelle Memorial Institute,
Columbus, Ohio
IV. Hallowell, J. B.,
Maykuth, D. J., and
Ogden, H. R.
V. Avail fr OTS
VI. In ASTIA collection

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