HIGH TEMPERATURE OXIDATION RESISTANT COATINGS
FOR TANTALUM BASE ALLOYS

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FOREWORD

This second quarterly progress report was prepared by the GT&E Laboratories under USAF Contract No. AF 33(657)-7339. This contract was initiated under Project No. 2(8-7312), Task No. 73120. 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.

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ABSTRACT

Tin-aluminum base coatings applied by a cold spray-hot vacuum diffusion technique were studied further on Ta-10 W and Ta-10 Hf-5 W and work initiated on Ta-30 Cb-7 1/2 V. Refractory additions to the coatings were optimized for Ta-10 W and the use of aluminum-silicon in tin was found beneficial for Ta-30 Cb-7 1/2 V. Furnace and oxy-acetylene torch tests were performed at temperatures from 1100 to over 3000°F. Diffusion treatments in vacuum, hydrogen, and argon were compared for coatings on Ta-10 W. Oxide formation on Ta-10 W coatings at various temperatures was studied by x-ray diffraction. The oxidation behavior of various tin-aluminum alloys and of the intermetallic (Ta-30 Cb-7 1/2 V) Al_3 was also studied, together with interactions of three alloys with Al_2O_3 at elevated temperatures in vacuum.

1. INTRODUCTION

The first quarterly report covered the effect of tin-aluminum coatings with 15-50 w/o Al on the oxidation behavior of pure tantalum, Ta-10 W and Ta-10 Hf-5 W. Some work was also done to show the applicability of these coatings to columbium, molybdenum and tungsten. The optimum aluminum composition range was determined for each alloy by oxidation tests in the 2000-3000°F range. For the tantalum and Ta-10 W the Sn-25 Al composition appeared optimum. However, it was found necessary to add tantalum and aluminum to the coating to form TaAl₃ particles which minimized coating run-off during processing. Attempts were also made to produce a similarly ductile coating with beryllides. The use of silver as a diluent appeared to meet the requirements structurally.

In the second quarter a Ta-30 Cb-7 1/2 V alloy, under ASD scale-up development elsewhere, was phased in for coating evaluation and the work on Ta-10 Hf-5 W was curtailed to a large extent. The investigation has been continued on the commercial Ta-10 W alloy for comparison and as a basis for extended evaluation. The investigation of beryllide coatings has been held in abeyance.

2. OXIDATION TESTS

2.1 COATED ALLOYS

2.1.1 Furnace Tests

The effect of Sn-Al coating compositions was pursued further on the Ta-10 W alloy and the protectiveness of Sn-25 Al was checked on Ta-30 Cb-7 1/2 V. Coatings were applied by the spray-diffuse method in a duplex vacuum treatment at 1900°F for 1/2 hour. Results of furnace

tests are listed in Table I for 0.010"-thick Ta-10 W and 0.020"-thick Ta-30 Cb-7 1/2 V coupons. Coating weights are listed as an approximate indication of relative coating thickness. Weight gains were taken every hour, but are not all shown. At 2000°F the coatings on the Ta-10 W alloy resulted in rather flat weight-gain curves after the first one-hour increase. There appears to be no anomalous behavior at 2000°F with Ta and Al additions to the coating in proportions to form TaAl₃. With the Ta-30 Cb-7 1/2 V alloy there was net weight loss in the first hour at 2000°F with little change thereafter.

At 2800°F, as shown also in Fig. 1, coatings on the Ta-10 W gave positive slopes to the weight-gain-time curves, with the 20 TaAl₃ addition having the maximum slope. Except for the first hour, the other two coatings were relatively similar to each other in behavior. The Ta-30 Cb-7 1/2 V alloy coated with Sn-25 Al is not shown, but it behaved similarly initially and then its weight gain rate increased more rapidly in the last four hours.

Several samples of Ta-10 W had been coated with Sn-25 Al and then overlaid with a flame-sprayed Al₂O₃ layer. One sample had the excess tin-aluminum at one end removed before application of the Al₂O₃ and failed during the sixth hour of exposure at 2800°F. The Al₂O₃ was applied to see if it would enhance the maximum temperature erosion resistance of the coating without detriment to lower temperature properties.

A platinum-rhodium wound furnace was used for the tests at 3000°F. Weight gains were taken every two hours. During the 5-6 hour period the Ta-Cb-V alloy coating failed, but the Ta-10 W samples survived 10 hours of exposure. Although the (Sn-15 Al) 10 TaAl₃ coating appeared to have optimum oxidation resistance, larger samples prepared

TABLE I

Furnace Test Results on Coated Ta-10 W and Ta-30 Cb-7 1/2 V Coupons

<u>Run no.</u>	<u>Alloy</u>	<u>Coating comp.</u>	<u>Coating weight mg/cm²</u>	<u>Test temp., °F</u>	<u>Test time, hrs.</u>	<u>Weight gain mg/cm²</u>	<u>Remarks</u>
U-17391-1	Ta-W	(Sn-25 Al) 10 TaAl ₃	72	2000	8	8.8	O. K.
U-17391-3	Ta-W	(Sn-25 Al) 20 TaAl ₃	89	2000	8	2.0	O. K.
U-17391-4	Ta-W	(Sn-15 Al) 10 TaAl ₃	80	2000	8	0.6	O. K.
U-17391-2	Ta-Cb-V	Sn-25 Al	95	2000	8	-7.9	O. K.
U-17365-1	Ta-W	(Sn-25 Al) 10 TaAl ₃	60	2800	8	6.6	O. K.
U-17365-2	Ta-W	(Sn-25 Al) 20 TaAl ₃	89	2800	8	12.6	O. K.
U-17365-3	Ta-W	(Sn-15 Al) 10 TaAl ₃	70	2800	8	4.7	O. K.
U-17365-4	Ta-W	Sn-30 Al	-	2800	8	5.8	O. K.
U-17384-1	Ta-Cb-V	Sn-25 Al	85	2800	8	6.8	O. K.
U-17384-2	Ta-W	Sn-25 (Al-5 Cr-5 Ti)	-	2800	7	8.6	Failed
U-17384-3	Ta-W	(Sn-25 Al)*-Al ₂ O ₃	-	2800	5	5.3	Failed
U-17384-4	Ta-W	(Sn-25 Al)*-Al ₂ O ₃	-	2800	8	7.0	O. K.
U-17387-1	Ta-W	(Sn-25 Al) 10 TaAl ₃	70	3000	10	7.3	O. K.
U-17387-2	Ta-W	(Sn-25 Al) 20 TaAl ₃	88	3000	10	12.0	O. K.
U-17387-3	Ta-W	(Sn-15 Al) 10 TaAl ₃	75	3000	10	8.1	O. K.
U-17387-4	Ta-Cb-V	Sn-25 Al	84	3000	4	3.9	Failed

* Excess Sn-Al removed from one end.

Fig. 1. Weight gain curves of coated Ta-10 W samples tested at 2800°F.

for flame tests were not coated as uniformly with the (Sn-15 Al) 10 TaAl₃ as with the (Sn-25 Al) 10 TaAl₃. Therefore the latter coating was selected as the basis for further investigation.

It was also found that, even with the TaAl₃ additions, some run-off occurred on longer samples if the coating was too thick. Therefore control was exercised during spraying to obtain various coating thicknesses for later comparison. It should be kept in mind that the unit coating weight is only useful in comparison for approximately the same coating composition. For example, where the tin content is appreciably lowered, a thicker coating is obtained for an equivalent weight of coating. It has been found metallographically that the (Sn-25 Al) 10 TaAl₃ coating in the range 25-60 mg/cm² is correspondingly 2 1/2 to 4 mils thick. The lower part of the range is considered "thin" and the upper part "thick." Samples of Ta-30 Cb-7 1/2 V with coating thicknesses in this range were prepared and tested at 2500, 2800 and 3000°F. The results are listed in Table II. A Ta-10 W sample was run for comparison at 2500°F.

At 2500°F samples of both alloys survived 8 hours and 8 cycles with low weight gains. However, one thin-coated sample of Ta-Cb-V failed but this was at the hole from which the suspension wire had been removed. Weight gains compared closely with Sn-25 Al coatings tested previously.

At 2800°F thin coatings survived 3 to 6 hours and thick coatings 7 to 8 hours. After 2 hours at 3000°F two samples appeared to be intact. However, the surfaces were quite rough and measured about 0.007" thicker overall.

It should be noted that failures detected in the early stages were located at an edge. At 2500°F the failure sites were dark in color and grew progressively to form a solid oxide. At 2800°F failures

TABLE II

Furnace Oxidation Tests on Ta-30 Cb-7 1/2 V and Ta-10 W
Alloy Samples Coated with (Sn-25 Al) 10 TaAl₃

<u>Run no.</u>	<u>Sample</u>	<u>Coating weight mg/cm²</u>	<u>Test temp., °F</u>	<u>Test time, hrs.</u>	<u>Weight gain mg/cm²</u>	<u>Remarks</u>
U-173-97	Ta-W-1	Thin*	2500	8	2.04	O. K.
	Ta-Cb-V-A	Thick*	2500	8	2.08	O. K.
	Ta-Cb-V-1	27.6	2500	2		Hole Failure
	Ta-Cb-V-2	27.6	2500	8	1.92	O. K.
U-160-3	Ta-Cb-V-5	24.2	2800	2	-	O. K.
	Ta-Cb-V-6	23.9	2800	3-8	-	Failed
	Ta-Cb-V-7	23.9	2800	3-8	-	Failed
	Ta-Cb-V-9	23.2	2800	3	-	Failed
	Ta-Cb-V-10	Thin*	2800	4	-	Failed
	Ta-Cb-V-11	21.5	2800	6-8	-	Failed
U-160-7	Ta-Cb-V-1	48.6	2800	7-8	-	Failed
	Ta-Cb-V-2	57.9	2800	8	-	Failed
U-160-3	Ta-Cb-V-3	28.1	3000	2	-	O. K.
	Ta-Cb-V-4	23.8	3000	2	-	O. K.

* Exact weight not determined.

progressed quite rapidly with the formation of a molten dark oxide which reacted almost completely with anything in the vicinity and permeated the Al_2O_3 boats used for testing.

Samples tested for 8 hours at 2800°F and 2 hours at 3000°F could be bent over a 2T radius to a 90-degree angle. Metallographic examination of these samples showed that the 2800°F sample had tensile cracks in the intermetallic compound layer of the coating which did not extend into the base metal substrate. In the 3000°F sample the cracks penetrated to a considerable depth into the substrate. Microhardness tests of the substrate after oxidation exposure indicated little hardening at distances more than several ten-thousandths of an inch from the coating-substrate interface. Results for as-coated and two-hour oxidation tests are plotted in Fig. 2.

In low-temperature furnace tests at 1100 and 1400°F , duplicate samples of both alloys were in excellent condition after 260 hours, thus there does not appear to be a low-temperature anomaly with these coating-alloy combinations within any reasonable time interval.

Since the (Sn-25 Al) 10 TaAl_3 coating appeared to give only borderline 8-hour protection to Ta-30 Cb-7 1/2 V at the thick end of the coating range, work was directed toward investigating the effect of coating composition further. The results of oxidation tests are tabulated in Table III. Higher or lower aluminum additions were not particularly advantageous. However, a prealloyed Al-11 w/o Si powder was used instead of pure aluminum in order to check the effect of silicon also. The addition of 50% of this powder appeared to give the best protection. Since a wide range of coating thicknesses was effective at 2800°F , thickness did not appear to be solely responsible. Tests at temperatures as low as 1100°F for long times indicated there was no low-temperature

Fig. 2. Microhardness traverses taken on as-coated and oxidized samples of Ta-30 Cb-7 1/2 V coated with (Sn-25 Al) 10 TaAl₃.

TABLE III

Furnace Oxidation Tests of Coated Ta-30 Cb-7 1/2 V Coupons. All Coatings Modified by Addition of 10% TaAl₃.
(Al-Si) is Al-11 w/o Si Alloy Powder.

<u>Run no.</u>	<u>Coating comp. w/o (bal. Sn)</u>	<u>Coating weight, Mg/cm²</u>	<u>Test Temp., °F</u>	<u>Test Time, (hrs.)</u>	<u>Weight gain, Mg/cm²</u>	<u>Remarks</u>
U-160-15-1	15 Al	43.5	2800	4	-	Failed
U-160-15-2	15 Al	51.7	2800	4	-	Failed
U-160-15-6	50 Al	29.7	2800	5	-	Failed
U-160-15-7	50 Al	29.2	2800	2	-	Failed
U-160-35-8	50 Al	34.6	2800	7	5.4	Failed
	50 Al	34.7	2800	7	4.5	Failed
U-160-16-1	15 (Al-Si)	45.7	2800	3	-	Failed
U-160-16-2	15 (Al-Si)	46.1	2800	4	-	Failed
U-160-16-6	25 (Al-Si)	36.8	2800	5	-	Failed
U-160-16-7	25 (Al-Si)	40.3	2800	4	-	Failed
U-160-17-1	50 (Al-Si)	24.5	2800	8	3.8	O. K.
U-160-17-2	50 (Al-Si)	29.0	2800	8	3.9	O. K.
U-160-35-6	50 (Al-Si)	47.5	2800	8	4.7	O. K.
U-160-35-9	50 (Al-Si)	61.5	2800	8	5.0	O. K.
U-160-19-7	56 Al-8 Si*	39.7	2800	8	4.1	O. K.
U-160-19-4	70 Al-10 Si*	24.5	2800	3	-	Failed
U-160-23-1	50 (Al-Si)	34.8	2500	8	2.1	O. K.
U-160-23-2A	50 (Al-Si)	38.2	2500	8	2.0	O. K.
U-160-23-8	56 Al-8 Si*	37.1	2500	8	2.5	O. K.
U-160-28-3	50 (Al-Si)	26.4	1400	99	0.5	O. K.
U-160-28-4	50 (Al-Si)	29.4	1100	144	0.2	O. K.

* Elemental silicon used.

anomaly. Higher aluminum compositions with silicon did not appear to give any better protection at 2800°F. Therefore the 50 w/o (Al-Si) coating appeared to be optimum.

Metallographic examination of Sn-50 (Al-Si) 10 TaAl₃ coated Ta-30 Cb-7 1/2 V samples showed the average coating thickness to be linearly proportional to the unit coating weight in the range 25-47 mg/cm². The corresponding average coating thickness was 3 to 6 mils. Examples of the structures of the extremes are shown in Fig. 3. It was found that at the high end of the range the coating was considerably less uniform, with a general thickening at the bottom of the sample. Where thin spots occurred they were almost always at edges of the sample and were usually mostly thinner in the tin-aluminum overlay.

The structures of samples tested at various temperatures are shown in Fig. 4. The major significant features are: (1) the presence of a new phase in the 2500°F sample, (2) the very small amount of tin-aluminum left, and (3) the growth of a thin additional layer at the substrate interface. Neither Sn-25 Al nor Sn-50 Al coatings on Ta-10 W have had these structural features after testing.

The effect of aluminum-silicon coating additions was checked further on Ta-10 W and Ta-10 Hf-5 W coupons. Results of oxidation tests are listed in Table IV. The ternary alloy had short lives at 2500 and 2800°F. Aluminum-silicon at the 25% level gave good protection to Ta-10 W, but increasing the composition to 50% shortened the protective life.

2.1.2 Flame Tests

In order to determine maximum temperature capabilities and some measure of erosion resistance, coated samples were tested in an

Plate 25200 500X

Sample 25286-1 U-16034-1

(a)

Plate 25202 500X

Sample 25286-3 U-16034-5

(b)

Fig. 3. Sn-50 (Al-Si) 10 TaAl₃ coatings on Ta-30 Cb-7 1/2V samples
(polarized light)

(a) Average coating thickness 0.003"

(b) Average coating thickness 0.006"

Mt. 25264-2 500X
U-160-22-4
(a)

Mt. 25264-3 500X
U-160-22-3
(b)

Mt. 25264-5 500X
U-160-22-5
(c)

Mt. 25264-4 500X
U-16014-1
(d)

Fig. 4. Ta-30 Cb-7 1/2 V samples coated with Sn-50(Al-Si)10 TaAl₃ after oxidation tests: (a) 2500°F - 2 hrs., (b) 2800°F - 2 hrs., (c) 3000°F - 2 hrs., (d) 2800°F - 8 hrs.

TABLE IV

Furnace Oxidation Tests of Coated Ta-10 W and Ta-10 Hf-5 W Coupons.
All Coatings Modified by Addition of 10% TaAl₃. (Al-Si) is Al-11 w/o
Si Alloy Powder.

<u>Run no.</u>	<u>Alloy</u>	<u>Coating comp. w/o (bal. Sn)</u>	<u>Coating weight mg/cm²</u>	<u>Test temp., °F</u>	<u>Test time, hrs.</u>	<u>Weight gain, mg/cm²</u>	<u>Remarks</u>
U-160-30-1	Ta-W	25 (Al-Si)	44.6	2800	8	5.2	O. K.
U-160-30-6	Ta-W	50 (Al-Si)	33.5	2800	5	5.0	Failed
U-160-37-1	Ta-Hf-W	50 (Al-Si)	33.5	2800	2	12.8	Failed
U-160-37-4	Ta-Hf-W	50 (Al-Si)	41.2	2800	2	-8.4	Failed
U-160-38-2	Ta-Hf-W	50 (Al-Si)	39.6	2500	1	-	Failed
U-160-38-3	Ta-Hf-W	50 (Al-Si)	39.5	2500	1	-	Failed
U-160-19-1	Ta-10 W	25 Al*	55.3	2800	8	7.1	O. K.
U-160-23-2	Ta-10 W	25 Al*	62.3	2500	8	3.5	O. K.

* Coating diffusion treatment at 30 microns pressure.

oxy-acetylene torch flame. The samples were 1/2" wide x 2" long, and the flame was concentrated about 1/2" from one end. Control was attained by moving the torch toward or away from the sample and monitoring the temperature continually by means of an optical pyrometer. No correction was made for emissivity. Results are tabulated in Table V.

It was felt that a flame- or plasma-sprayed overlay of Al_2O_3 would improve the erosion behavior of the Sn-25 Al coating on Ta-10 W. However, the thin Al_2O_3 sprays gave a nonuniform emissivity to the overall coating and made it difficult to select a good average approximation of the temperature. Therefore erratic test results were obtained, and it is not possible to say whether the Al_2O_3 gave any improvement. In fact, the plasma-sprayed sample had the excess tin-aluminum at one end removed before the Al_2O_3 overlay was made, and it appeared to fail at a lower temperature than did the others. This indicated that the sub-coating was more important.

The best results were obtained with the two Sn-25 Al coated Ta-10 W samples which did not have the excess tin-aluminum at one end (run-off) removed. One sample was tested for a total of two hours at 3375°F (optical) with eight 15-minute thermal cycles without failure.

From the other results it appears that the maximum optical temperature attainable is approximately 3450°F. This probably corresponds to the temperature at which the Al_2O_3 film melts. The Ta-10 W alloy appeared protected to some degree to temperatures almost up to 3400°F for at least several minutes. At temperatures up to 3350°F protection for one hour appears reasonable. Although the Sn-25 Al coating appears to give the most protection, it is known that removal of the excess tin-aluminum from one end is detrimental. The TaAl_3 additions minimize the formation of the excess lump and provide a thicker coating

TABLE V

Oxy-Acetylene Torch Tests on 0.04" x 1/2" x 2" Ta-10 W and 0.020" x 1/2" x 2" Ta-30 Cb-7 1/2 V
Samples, with Most Thermally Cycled Every 15 Minutes

Run no.	Alloy	Coating comp.	Coating weight Mg/cm ²	Temp., °F	Time, min.	No. of cycles	Remarks
U-17366-1	Ta-W	(Sn-25 Al) FS Al ₂ O ₃	-	3000	60	4 S	O. K.
U-17367-1	Ta-W	(Sn-25 Al) FS Al ₂ O ₃	-	3160-3270	30	2 S	O. K.
U-17370-1	Ta-W	(Sn-25 Al) FS Al ₂ O ₃	-	3000-3160	4	-	Failed
U-17371-1	Ta-W	(Sn-25 Al) PS Al ₂ O ₃	-	2870-2900	-	-	Failed
U-17372-1	Ta-W	(Sn-25 Al) 10 TaAl ₃	-	3200-3340	60	4 S	O. K.
U-17380-F2	Ta-W	(Sn-25 Al) 10 TaAl ₃	111	3270	60	4 S	O. K.
U-17392-F3	Ta-W	(Sn-25 Al) 10 TaAl ₃	88	3360-3400	54	4 S	Failed
U-17379-F1	Ta-W	(Sn-25 Al) 20 TaAl ₃	101	3170-3270	60	4 S	O. K.
U-17393-F2	Ta-W	(Sn-25 Al) 20 TaAl ₃	95	3350-3380	32	2 S	Failed
U-17381-F1	Ta-W	(Sn-15 Al) 10 TaAl ₃	89	3100-3270	60	4 S	O. K.
U-17386-F2	Ta-W	(Sn-15 Al) 10 TaAl ₃	103	3450	-	-	Melted
U-17386-F11	Ta-W	Sn-25 Al	23*	3450	-	-	Melted
U-17378-F9	Ta-W	Sn-25 Al	90	3000-3320	60	4 S	O. K.
U-17388-F10	Ta-W	Sn-25 Al	87	3375	120	8 S	O. K.
U-17385-F1	Ta-Cb-V	Sn-25 Al	69	3000	4	4 F	Failed
U-17385-F2	Ta-Cb-V	Sn-25 Al	84	3000	30	-	O. K.
U-160-2-1	Ta-Cb-V	(Sn-25 Al) 10 TaAl ₃	Thick	2550-3200 3300 max.	6 -	- -	O. K. Failed
U-160-2-2	Ta-Cb-V	(Sn-25 Al) 10 TaAl ₃	Thick	2400-3150 3270 max.	6 -	- -	O. K. Failed
U-160-27-F1	Ta-Cb-V	(Sn-50 Al-Si) 10 TaAl ₃	30.9	2980	-	-	Failed
U-160-27-F2	Ta-Cb-V	(Sn-50 Al-Si) 10 TaAl ₃	33.6	2965	75	-	Failed
U-160-27-F3**	Ta-Cb-V	(Sn-50 Al-Si) 10 TaAl ₃	34.7	3000	50	-	Failed

* Excess Sn-Al removed from one end

** Preoxidized 2800°F for one hour

S - Slow
F - Fast

FS - Flame Sprayed
PS - Plasma Sprayed

over the entire sample, thus reflecting a more practical means of protection extending to larger and longer samples.

The Sn-25 Al coating is not as protective to the Ta-Cb-V alloy as to Ta-W at 3000°F. However, the fast cycling which was attempted on the Ta-Cb-V may have given higher instantaneous temperatures during testing. The TaAl₃ modified Sn-25 Al coating on the Ta-Cb-V appeared to have a maximum temperature capability for a few minutes at about 3200°F optical. For the modified Sn-50 (Al-Si) coating the maximum temperature is closer to 3000°F.

Additional samples of both alloys with the (Sn-25 Al) 10 TaAl₃ coating were given more rigorous thermal cycling. The test regimen is one minute at 2500°F and 1/2 minute at black heat performed by moving the sample into and out of the oxy-acetylene flame. This test is somewhat arbitrary, but has been designed after tests performed at the P&W jet engine test facilities for coated samples. Previous tests on Sn-25 Al coated Ta-10 W samples at this Laboratory withstood 400 cycles; these samples did not have the excess tin-aluminum removed from the end.

The present test results are listed in Table VI. Samples with thick coatings were used with the slight excess at the end removed. These samples had excellent thermal cycling resistance, equivalent to Sn-25 Al coating without the excess removed, and survived 400 cycles without failure. The Ta-10 W sample was subsequently heated to 2700°F for one hour without failure. Similar tests have not been run on Sn-(50 Al-Si) 10 TaAl₃ coated samples.

2.2 SPECIAL DIFFUSION TREATMENTS

The usual diffusion treatment involves heating the spray-coated samples to 1900°F for 1/2 hour under a vacuum pressure of one micron

TABLE VI

Oxy-Acetylene Torch Tests on Ta-10 W and Ta-30 Cb-7 1/2 V
Samples Coated with (Sn-25 Al) 10 TaAl₃. Samples
Thermally Cycled Once Every Minute.

<u>Run No.</u>	<u>Sample</u>	<u>Coating Weight*</u>	<u>Test Temp., °F</u>	<u>Time, hrs.</u>	<u>Cycles</u>	<u>Remarks</u>
U-173-95	Ta-W-1	Thick	2500	6.6	400	O.K.
			2700	1	-	O.K. (fur- nace test)
U-173-100	Ta-Cb-V	Thick	2500	6.6	400	O.K.

* Exact weight not determined.

or less. Therefore some attention was given to using cruder atmospheres for the diffusion treatments. All samples were spray-coated with (Sn-25 Al) 10 TaAl₃. Good results were obtained with Ta-10 W coupons treated in a vacuum system at 30 microns pressure. With this particular system only a mechanical back-up vacuum pump was used. Samples oxidation tested at 2500 and 2800°F are listed in Table IV. Coatings were protective for 8 hours.

Additional Ta-10 W samples were treated in hydrogen. However, although these were intact on removal from the hot zone, they disintegrated on cooling.

On tungsten and molybdenum samples the coatings wet satisfactorily in hydrogen on the first treatment, but were quite spotty after the second coat. Similar spotty second coats were obtained on Ta-10 W samples treated in argon. In all cases it appears that a thin oxide film forms when the first coat is heated for the second diffusion treatment, and this causes incomplete wetting. This was confirmed by coating Ta-10 W samples by resistance heating in a small simple container which could be thoroughly purged of residual air. The resultant second coats were excellent in appearance.

In connection with the above treatments in argon, a curious phenomenon was observed. When coated samples were resistance heated in the purged argon to approximately 2340°F directly after coating at 1900°F, the samples began to smoke. If heated to temperatures higher than 2340°F they smoked more copiously. The resultant surface was quite clean and had a bright metallic luster. On subsequent exposure to air the sample could be heated to 3000°F for 5 minutes without failure, without smoking, and without visibly tarnishing the surface. Metallographic examination of such a sample revealed only that: (1) the surface

intermetallic was no longer $TaAl_3$ but a lower aluminide, as is usually the case, (2) there was an excess tin-aluminum phase with no unusual dispersion, and (3) there was no oxide film, or it was too thin to be resolved at 750X. Previous resistance heated samples oxidized at 3000°F for 5 minutes grew a protective Al_2O_3 film approximately 0.3 mil thick. At present no explanation has been formulated which explains all aspects of this curious behavior.

2.3 Sn-Al ALLOYS

Attempts were made to obtain a better idea of the oxidation protection of tin-aluminum alloys as coatings by studying their behavior as bulk material for comparison. Various compositions up to 50 w/o Al were prepared. Coupons approximately 1/8 to 1/4" thick x 1/2" wide x 3/4" long were cut from cast ingots and oxidation tested. Rough approximations of weight gains were obtained, since the oxidation temperatures were far above the melting points of the alloys and the coupons change shape slightly. However, where protection occurred the oxide film held the sample together and certain trends were observable. At 2500°F after one hour exposure voluminous nonprotective oxides were obtained on pure tin, Sn-1 Al and Sn-2 Al. Alloys with 5, 10, 25 and 50 w/o Al appeared protected for 8 hours with weight gains increasing with aluminum content. There was a considerable jump in weight gain in going from 10 Al to 25 Al. A similar relationship was noted at 2800°F.

Therefore it appears that it is only necessary to have approximately 5% aluminum in the tin to grow a protective scale at 2500 and 2800°F. This figure correlates with previous calculations as to the aluminum content of the tin-aluminum phase in the as-diffused coated samples of Ta-10 W.

2.4 INTERMETALLIC COMPOUNDS

It was felt that the large percentages of columbium and vanadium in the Ta-30 Cb-7 1/2 V alloy (Ta-39.7 a/o Cb-18 a/o V) might lower considerably the melting point of the trialuminide formed on such an alloy compared to TaAl₃. Therefore 12-gram arc-melted buttons were prepared of (Ta-30 Cb-7 1/2 V) Al₃ for investigation. Since TaAl₃, CbAl₃ and VAl₃ are isomorphous, no difficulty was expected in obtaining a solid solution. The melts are listed in Table VII. For intermetallic compounds their hardness values are quite low (DPH 330-400). Samples from melt No. 1 were oxidation tested at 2800°F for 8 hours and at 3000°F for 2 hours. Metallographic structures of the as-cast and of the tested samples are shown in Fig. 5. The microstructures indicate the alloy to be slightly off stoichiometry. This is understandable if the weight loss in melting is assumed to be all aluminum. Oxidation resistance, as evidenced by appearance and oxide thickness was quite good at 2800 and 3000°F. The 3000°F sample after testing had a slightly shrunken appearance, as though melting occurred. Metallographically, the sample appeared somewhat porous and internally oxidized in spots. This appeared to be indicative that some volatile instability occurred at 3000°F.

TABLE VII

Arc-Melted Buttons of (Ta-30 Cb-7 1/2 V) Al₃

Melt No.	Charge, Grams		Melting Loss, Grams	Average Hardness DPH (10 kg)
	Weight, Alloy	Weight, Aluminum		
1	7.2	4.8	0.2	395
2	7.2	4.8	0.05	387
2-A	7.2	4.9	0.06	330
3	7.2	5.05	0.10	355

Mt. 25287

100X

(a)

Mt. 25297

100X

(b)

Mt. 25304

200X

(c)

Fig. 5. (Ta-30 Cb-7 1/2 V) Al₃ Melt #1. (a) as arc-melted, (b) after 8 hours oxidation at 2800°F, (c) after 2 hours oxidation at 3000°F.

Tests were performed at lower temperatures on samples taken from Melts 2 and 2-A. It was interesting to note that oxidation behavior was excellent at 2200 and 2500°F for 8 hours. However, anomalous behavior, as evidenced by powdering, occurred at 1100, 1400 and 1800°F. This commenced after 3 hours at 1400°F, 6 hours at 1800°F and 7 hours at 1100°F. Therefore, unmodified aluminide coatings might be expected to behave similarly on the Ta-Cb-V alloy in equivalent times. Naturally tin-aluminum base coatings do not evidence low-temperature anomaly.

This behavior was checked further on trialuminide arc-melt No. 3 to which additional excess aluminum over stoichiometry was added. Oxidation results were excellent at all temperatures as shown in Table VIII.

TABLE VIII

Weight Gain of (Ta-30 Cb-7 1/2 V) Al₃ Arc-Melted
Buttons Oxidized at Various Temperatures

Temp., °F	Melts 2 and 2-A		Melt 3	
	Time, hrs.	Wt. Gain, Mg/cm ²	Time, hrs.	Wt. Gain, Mg/cm ²
1100	8	2.5 P	8	0.3
1400	7	CP	8	0.6
1800	3	41.0 P	8	1.7
2200	8	2.0	8	10.5*
2500	8	32.0	8	2.4

* Segregation in sample

P Powdering

CP Complete Powder

3. X-RAY STUDIES

X-ray diffraction studies were made on the surfaces of Ta-10 W samples coated with Sn-25 Al and tested at various temperatures. The results are shown in Table IX. It is interesting to note that, after low oxidation temperature exposure, the Al_2O_3 film is not fully formed, is exceedingly thin, or is amorphous. With higher temperature the Al_2O_3 film becomes more well defined. The presence of SnO_2 after 2000°F exposure is also interesting since it apparently does not exist after higher temperature oxidation. It should be noted that past examinations had been carried out on samples tested at 2500°F or higher. Several additional samples have been prepared for elevated temperature x-ray diffraction examination in a hot camera.

TABLE IX

X-ray Diffraction Analyses of Ta-10 W Sample Surfaces Coated
With Sn-25 Al and Oxidized at Various Temperatures

<u>Run No.</u>	<u>Sample</u>	<u>Temp., °F</u>	<u>Time, hrs.</u>	<u>Phases Present</u>
U-173-32	4	1100	2	Oriented Beta Tin Some Al_2O_3 Probably TaAl_3 Possibly Ta or Al
U-173-32	5	1400	2	Beta Tin Possibly Al_2O_3 , TaAl_3 , Ta, Al
U-173-42	H-1	2000	8	Alpha Al_2O_3 SnO_2 Beta Tin
U-173-42	H-2	2500	6	Alpha Al_2O_3
U-173-43	H-3	2800	4	Alpha Al_2O_3

4. Al_2O_3 -ALLOY REACTIONS

One of the boundary conditions governing maximum temperature capability could conceivably be the reduction of Al_2O_3 or a reaction to form a new compound oxide at some higher temperature. This could occur when the concentration of tantalum or its alloying elements in the alloys under consideration reach some critical concentration in contact with the Al_2O_3 protective film. In order to check these possibilities, samples of Ta-10 W, Ta-10 Hf-5 W and Ta-30 Cb-7 1/2 V were flame-sprayed with Al_2O_3 and fired in a tungsten-heater furnace under a 0.1 micron or lower pressure.

To check temperature and atmosphere effects, uncoated samples were treated in the same batch. The samples were heated to 3100 or 3300°F for 1/2 hour and then examined metallographically for evidence of reaction. Results are listed in Table X. The Ta-Hf-W alloy was most reactive, the entire cross section becoming completely contaminated with but little residual surface oxide left at 3100 and 3300°F. Representative photomicrographs are shown in Fig. 6. The Ta-10 W alloy showed no reaction at 3100°F but at 3300°F was starting to react, apparently beginning at the grain boundaries. In contrast the Ta-Cb-V alloy showed little or no reaction at either temperature.

It should be noted that the as-flame-sprayed samples, particularly the Ta-10 W alloy, showed some slight evidence of oxidation beneath the Al_2O_3 coating. This may have been the result of heating during the flame-spraying process. It is possible that the later reactions with the Ta-10 W alloy began as the result of oxide-oxide reactions rather than metal-oxide reactions. However, the absence of a reaction in the Ta-Cb-V alloy indicates that this possibility may be relatively insignificant.

TABLE X

Reactions Between Tantalum Alloys and Flame-Sprayed
Al₂O₃ After Vacuum Heat Treatment

<u>Alloy</u>	<u>Condition</u>	<u>Heat Treat., Temp., °F</u>	<u>Reaction</u>
Ta-10 W	As-sprayed	-	Thin Oxide Beneath Al ₂ O ₃
		3100	None
		3300	Reaction Plus Grain Boundary Attack
Ta-10 Hf-5 W	As-sprayed	-	None
		3100	Complete Reaction
		3300	Complete Reaction
TA-30 Cb-7 1/2 V	As-sprayed	-	Possibly Thin Oxide Beneath Al ₂ O ₃
		3100	None
		3300	None

Mt. 25168-3

(a)

500X

Mt. 25168-1

(b)

500X

Mt. 25168-2

(c)

500X

Fig. 6. Ta-10 Hf-5 W samples flame-sprayed with Al_2O_3 .
(a) as-coated, (b) coated sample after 1/2 hour in vacuum at 3300°F,
(c) non-coated sample after 1/2 hour in vacuum at 3300°F.

Another series of samples was checked for reactions by placing the uncoated samples in contact with a slab of recrystallized Al_2O_3 . After 1/2 hour at 3300°F in vacuum, metallographic examination showed the Ta-Hf-W alloy had reacted completely. Neither of the other two alloys was appreciably affected.

5. DISCUSSION

At present it appears that the optimum coating compositions for practical purpose are (Sn-25 Al) 10 TaAl_3 for Ta-10 W and Sn-50 (Al-Si) 10 TaAl_3 for Ta-30 Cb-7 1/2 V. Maximum temperature capability for short times is approximately 3400 and 3000°F respectively. However, thermal cycling is quite important at these temperatures and can materially shorten the protective life. Diffusion at 2800°F does not appreciably affect the excellent ductility of the Ta-Cb-V alloy. X-ray diffraction data and the oxidation behavior of Sn-Al alloys have shed further light on the behavior of these coatings. However, it is expected that electron-probe analyses will be much more informative; samples for this purpose have been prepared and submitted for analysis.

Although the (Ta-Cb-V) Al_3 intermetallic can have a low-temperature "pest," it appears that a slight excess of aluminum over stoichiometry in the melt modifies this behavior. Since the Sn-(Al-Si) coatings do not exhibit this phenomenon, the coating protection is probably related to the continuous presence of an excess tin-aluminum phase which maintains Al hyper-stoichiometry. This compound does not appear to melt at 3000°F or to grow thick oxide films, but does begin to be unstable. It is quite probable that the presence of tin and silicon in coatings where this trialuminide is formed tend to complicate the instability by causing incipient melting. When the coated sample is preoxidized

at a lower temperature, interdiffusion with the substrate results in the formation of a lower aluminide with resultant higher melting point and stability. This may account for the improved behavior noted at 3000°F in the torch tests on a preoxidized sample.

Since the Ta-Cb-V alloy does not appear to react with Al_2O_3 at temperatures up to 3300°F, it may be possible to utilize this oxide as a barrier in some way. However, it may be more fruitful to experiment with preoxidation treatments further.

6. FUTURE WORK

Electron probe analyses will be obtained on coated samples of Ta, Ta-10 W and Ta-30 Cb-7 1/2 V. The behavior of coatings under a thermal gradient and in vacuum will also be studied. Additional coating techniques will be attempted and a statistical evaluation of optimum coatings will be started.

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